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Lecture Notes on

Thermal Physics

for undergraduate students.

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Example isn't another way to teach, it is the only way to teach.

Albert Einstein

Preface

These notes are, almost, a verbatim reproduction of my lectures on thermal physics, to the undergraduate students of the Chennai Mathematical Institute, Chennai during August-November, 2017. Prior to this I have taught thermodynamics and statistical mechanics in o the University of Hyderabad, Hyderabad from 2006-2015, o the Rajeev Gandhi University for Knowledge Technology (RGUKT) (Video lectures) 2010, o the School of Basic Sciences, Indian Institute of Technology Bhubaneswa during January - April 2017 and o Chennai Mathematical Institute, in the years 2004 and 2005. While preparing this document, I have extensively drawn from the notes, assignment sheets, tutorial papers, and question papers generated and distributed to the students of these courses.

Each chapter can be taught in some three to five hours. The material in the entire document can be covered comfortably in one semester - forty to forty five hours or so, including one problem - solving session every other week.

A major problem of teaching thermal physics is not about what to teach; it is about what not to teach. *Thermal Physics* encompasses, the entire thermodynamics, and a good part of statistical mechanics. While making this statement, I am fully aware that strictly thermodynamics does not need any model or any assumptions about atoms and molecules - that make up matter. Thermodynamics does not require any help from statistical mechanics; nor does it require help from any other disciplines.

Thermodynamics is a stand-alone subject, self-contained with a coherent structure and inner consistency and with concepts that are well defined and well-knit.

One can teach traditional thermodynamics following, for example the book of Weinreich¹ or Callen² without involving statistical mechanics, stochastic-cum-kinetic heat or atomic matter. But then in such an approach, a beginner shall most likely, face huge difficulties. Defining internal energy in terms of adiabatic work is a bit odd, to say the least. So is describing heat as difference between adiabatic and actual work; entropy would remain enigmatic when defined in the context of converting an inexact differential to an exact one; a beginner is likely get more puzzled than wise if thermodynamic is taught this way³.

¹ Weinreich, *Fundamental Thermodynamics*, Addison-Wesley (1968)

² H B Callen, *Thermodynamics*, John wiley (1960)

³ It calls for a certain maturity, a deep knowledge, and a love for historical and traditional approach, to appreciate, and enjoy thermodynamics in its pure form.

Thermodynamics peppered with a bit of statistical mechanics, kinetic heat and atomic matter, is a different ball-game altogether. The subject would become knowable, and easily at that; the subject would become transparent and even a bit more interesting.

I would take the attitude that the notion of internal energy becomes transparent when it is taught invoking atoms, their properties and their interactions; entropy is best described and its tendency to increase, is best understood by invoking its statistical moorings. All said and done, isn't that a macroscopic system chooses that value of its macroscopic property, which is overwhelmingly most probable - the one that has maximum entropy ?

Hence bringing in a little bit of statistical mechanics right at the beginning of teaching thermodynamics would be very helpful. But then we should be careful to keep it to a bare minimum, lest statistical mechanics should push thermodynamics to its appendix-pages. I think I have maintained this balance in these lecture notes.

I have chosen to publish what I taught as lecture notes rather than a book. A book would demand a reasonably complete discussion of various issues and call for some serious efforts toward tying-up of all loose ends. Such problems are not there for lecture notes. You simply write up what you teach, and the way you teach; nothing more; and nothing less.

Leave it to the readers to complete the narrative you have initiated in the lecture notes; and they can do it by consulting other books and articles. To facilitate such an enterprise I have listed several books and articles, at the end of the first chapter. The list, I must admit, is, by no means, exhaustive. I have picked up for listing, the books I have studied and the ones that caught my fancy.

A reasonably good number of worked examples, and a set of practice problems, are included in separate sections. These are drawn mostly from other books. Where ever I remember, I have cited the sources.

The emphasis is on conceptual issues and on learning thermal physics by examples. I have made extensive use of toy-problems for illustrating important concepts.

I hope these lecture notes on *Thermal Physics* make one more useful addition to your bookshelf. If you find any mistakes, or find any portions that lack clarity, and if you have suggestions to improve the readability, please tell me⁴. I shall make use of your comments and suggestions while preparing subsequent edition(s) : I am hoping that there would be a demand for, atleast, one more edition !

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1. LECTURE 1

OPENING REMARKS

1.1 Nature of Heat

Thermodynamics deals with heat and work - two processes by which a system transacts energy with its surroundings or with another system. By touching we can tell a hot body from a hotter body; we can tell a biting cold metal knob from the warm comfort of a wooden door⁵ on a winter morning. When a hot body comes into contact with a cold body, we often observe, it is the hot body which cools down and the cold body which warms up. Energy flows, naturally and spontaneously, from hot to cold and not and never the other way around⁶. *Heat*⁷ is a process by which energy flows. Once the two bodies become equally warm, the flow stops. Thermal equilibrium obtains. Thus, an empirical notion of thermal equilibrium should have been known to man a long time ago.

1.2 Nature of Work

Coming to the notion of work, we observe that when an object moves against an opposing force, work is done. When you pull water up, from a well, against gravity, you do work. If you want to push a car against the opposing friction, you must do

⁵ Incidentally, the door knob, the wooden door, and the cold surrounding atmosphere have been in contact with each other for so long they should have come into thermal equilibrium. That means their temperatures should be the same. But then when you touch the metal knob, you feel the sharp chill; and not so when you touch the wooden door. Why ? I am leaving it to you to figure out the answer.

⁶ at least we have not seen it yet!

⁷ What is heat ? I don't think we know it as yet, completely. We mistook heat for a substance of combustion and called it phlogiston in the seventeenth century; much later we mistook it for an invisible fluid and called it calorie . Now we recognize, within the scope of thermodynamics, that heat, like work, is a process by which energy is transacted. I like the analogy of J. S. Dugdale, *Entropy and its Physical Meaning*, Taylor and Francis (1996)p.21 : Heat and work are like cheques and drafts you use to transact (deposit or draw) money in your bank-account. Money is like energy. It is absurd to ask how much of cheques are there in your account; it is equally absurd to ask how much of heat is there in an object. What resides in your account is money; what resides in an object is energy. Only at the time of transaction we need to specify whether the transaction occurs by heat or by work.

However, in statistical mechanics, we continuously endeavour to draw the elusive microscopic picture of heat and try to discover where and how it is buried in the phase space trajectories of some 10^{23} or more particles; we can not compute these trajectories; not just because they are obscenely large in number; but also because they are inherently unpredictable due to sensitive dependence on initial conditions. It is in this arena of phase space where dynamical trajectories repel / attract each other, we need to look for a meaning of heat. More on theses interesting issues later if time permits.

work. When you stretch a rubber band against the opposing entropic tension you do work. When a fat man climbs up the stairs against gravity, he does work; he does more work than what a not-so-fat man does. Of course in a free fall, you do no work - you are not opposing gravity - though you will get hurt, for sure, when you hit the ground!

Sir Isaac Newton (1643 - 1727) told us how to compute work : the dot product of force and displacement. In thermodynamics we compute work employing pressure and change of volume : Force divided by area is pressure; therefore pressure times volume-change is work. Pressure is something we became familiar⁸ with, long time ago.

$-P dV = \bar{d}W$ is the work done⁹ in an infinitesimal expansion by dV at constant pressure P . Do not read $\bar{d}W$ as ‘ change of work ’, since W is not a property of the system. To put it mathematically, $\bar{d}W$ is not an exact differential. To remind us of this I have decorated d with a bar. $\bar{d}W$ should be taken as small work, done in an infinitesimal change of volume dV . Volume V is a property of the system; dV is an exact differential.

1.2.1 Sign Convention for Work Done

The minus sign in the expression $\bar{d}W = -PdV$, is there by convention. When a system does work, its energy decreases; hence work done by the system is taken as negative. When you do work on a system its energy increases. Hence work done on a system is taken as positive. Physicists and chemists employ this convention. Engineers don’t; they take work done by the system as positive. Keep this in mind while reading books on thermodynamics written for engineers or by engineers; *e.g.* the beautiful little book of H. C. Van Ness¹⁰ based on his lectures to the engineering students of Rensselaer polytechnic institute in the spring term of 1968.

1.2.2 Other Kinds of Work

What we have considered above is the pressure - volume work, relevant for a system of compressible fluid. In general, any process by which energy is transacted between the system and its surroundings, other than heat, is called work.

⁸ Galileo Galilei (1560-1642) knew of atmospheric pressure and knew that it can stand thirty four feet of water. A few years later, his student Evangelista Torricelli (1608 - 1647) correctly surmised that mercury, fourteen times heavier, would rise in the tube only upto thirty inches. He demonstrated it experimentally. Blaise Pascal (1623 - 1662) was quick to point out that Torricelli’s reasoning would imply that the air pressure at the top of mountain should be less. This was verified experimentally in the year 1648. Daniel Gabriel Fahrenheit (1686 - 1736) invented mercury thermometer and the temperature scale named after him. Andres Celcius (1701 - 1744) invented the centigrade scale of temperature. Robert Boyle (1627 -1691) conducted numerous experiments and showed that the product of pressure and volume of a given amount of air remains constant if the temperature is kept constant. Boyle modelled air as a collection of tiny springs that resisted compression (which explains air pressure); the springs expand and the air occupies fully the available volume.

⁹ The formula $\bar{d}W = -PdV$ holds good only for a quasi static reversible process. What is a quasi static reversible process ? I shall answer this important question later.

¹⁰ H. C. Van Ness, *Understanding Thermodynamics*, Dover (1969)

Adjusting the tension in a metallic wire in a musical instrument like Veena or violin for purpose of tuning, is something we often observe. When you stretch the string by an infinitesimal length of $d\mathbf{l}$, reversibly, against the opposing linear tension \mathcal{F} , the work done equals $\mathcal{F} d\mathbf{l}$. When $d\mathbf{l}$ is positive, work is done on the system; hence the expression for work is consistent with our sign convention.

The surface tension, σ , in a thin film (like that in a soap bubble or in a membrane) opposes any attempt to increase its area. If the surface is stretched by an infinitesimal area $d\mathbf{A}$, by a reversible process, the work done is $\sigma d\mathbf{A}$.

Similarly we can talk of magnetic work done on a paramagnet or diamagnet, given by $\mathbf{B} d\mathbf{M}$, where \mathbf{B} is the applied magnetic field and \mathbf{M} , the magnetization.

When you stretch a rubber band, you do work against an opposing force which is of entropic origin. We shall see more of thermodynamics of rubber elasticity later, see Lecture Notes - 6.

In a dielectric material the work done is given by $\mathcal{E} d\mathcal{P}$, where \mathcal{E} is the applied electric field, and \mathcal{P} is the dipole moment.

1.3 Equality of Temperature \Rightarrow Thermal Equilibrium

We saw of thermal equilibrium that is established when two systems are brought into thermal contact with each other. When in thermal equilibrium, energy does not flow by heat. Is it possible to tell of thermal equilibrium without bringing the two systems into thermal contact with each other? The answer is "yes". This brings us to the most important concept in thermodynamics, namely temperature.

Measure the temperatures of the two systems. If they are the same, we can say the systems shall be in thermal equilibrium if we were to bring them into thermal contact with each other. The emergence of an empirical notion of temperature is a giant step in the development of thermodynamics : Equality of temperature implies thermal equilibrium¹¹. Though temperature is one of the early concepts to enter into thermodynamics, it remains the most difficult to define and to comprehend. A simple and correct definition : *temperature is what a thermometer measures !*

We also talk of mechanical equilibrium signalled by equality of pressure and diffusional equilibrium established by equality of chemical potential.

¹¹ **Thermal Equilibrium : Equivalence Relation** Thermal equilibrium is a binary relation defined on a set of thermal objects. The object \mathbf{A} is in thermal equilibrium with \mathbf{B} . Let us express it symbolically : $\mathbf{A} \mathcal{R} \mathbf{B}$. First we notice that this relation is reflexive : $\mathbf{A} \mathcal{R} \mathbf{A}$. In other words \mathbf{A} is in thermal equilibrium with itself. Then we notice that the relation is symmetric : $\mathbf{A} \mathcal{R} \mathbf{B} \Rightarrow \mathbf{B} \mathcal{R} \mathbf{A}$. The statement that \mathbf{A} is in thermal equilibrium with \mathbf{B} implies that \mathbf{B} is in thermal equilibrium with \mathbf{A} . Then comes the third important empirical observation : the relation is transitive. $\mathbf{A} \mathcal{R} \mathbf{B}$ and $\mathbf{B} \mathcal{R} \mathbf{C}$ imply $\mathbf{A} \mathcal{R} \mathbf{C}$. If \mathbf{A} is thermal equilibrium with \mathbf{B} , and \mathbf{B} is in thermal equilibrium with \mathbf{C} , then \mathbf{A} is in thermal equilibrium with \mathbf{C} . If a binary relation is reflexive, symmetric and transitive, we call it an equivalence relation. We can segregate all thermal objects of a set into mutually exclusive and exhaustive sub sets called equivalence classes. All elements of an equivalence class share a common property. We name that shared property as temperature. Thus, each equivalence class is characterized by a distinct empirical temperature.

1.4 Extensive and Intensive Thermodynamic Properties

Temperature, pressure, and chemical potential are intensive thermodynamic properties. We also have extensive thermodynamic variables like energy, volume, entropy *etc.* In general for a given system, we can write a thermodynamic property as a function of several other thermodynamic properties.

1.4.1 Fundamental Equation

For example, considering an isolated system, we can express the internal energy U as a function of entropy S , volume V and number of molecules N : $U \equiv U(S, V, N)$. Such relations, exclusively amongst the extensive properties of a system, are called *fundamental equations*. The adjective 'fundamental' is there for a good reason : a fundamental relation contains complete information about a thermodynamic system.

1.4.2 Equations of State

We also have equations of state that expresses an intensive property as a function of extensive properties. The most familiar equation of state is that for an ideal gas, and it reads as

$$P(U, V) = \frac{2}{3} \frac{U}{V}.$$

In a more familiar form¹² it reads as

$$PV = Nk_B T,$$

where N is the number of molecules, and $k_B = 1.38066 \times 10^{-23} \text{ J K}^{-1}$, the Boltzmann constant or

$$PV = nRT,$$

where n denotes the number of moles and $R = 8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$, is the universal gas constant. This is also known as ideal gas law¹³. A single equation of

¹² $PV = (2/3)U$; $U = 3Nk_B T/2 \Rightarrow PV = Nk_B T = nRT$

¹³ **Bernoulli and the Ideal Gas Law :** I must tell you of a beautiful derivation of the ideal gas law by Daniel Bernoulli (1700-1782). It goes as follows. Bernoulli speculated air to be made of spherical molecules; they are like billiard balls; these billiard ball molecules are all the time in motion, colliding with each other and with the walls of the container. When a billiard ball bounces off the wall, it transmits a certain momentum. Bernoulli imagined it as pressure. It makes sense.

First consider air contained in a cube of side one meter. There is a certain amount of pressure felt by the wall. Now imagine the cube length to be doubled with out changing the speeds of the molecule. In modern language this assumption is the same as keeping the temperature constant. The momentum transferred per collision remains the same. However since each billiard ball molecule has to travel twice the distance between two successive collisions with the wall, the force on the wall should be smaller by a factor of two.

Also pressure is force per unit area. The area of the side of the cube is four times more now. Hence the pressure should be less by a further factor of four. Taking into account both these factors, we find the pressure should be eight times less. But then, the volume of cube is eight times more. Bernoulli concluded that the product of pressure and volume must be a constant when there is no change in the molecular speeds - a brilliant argument indeed, based on simple scaling ideas.

state does not contain all information about the system. We need several equations of state to complete the thermodynamic picture.

Let us say x, y, z are extensive variables and η, μ, ν are intensive variables of a system. Let $x \equiv x(y, z, \eta, \mu)$. We say the property x is extensive if it is a first order homogeneous function¹⁴ of its extensive variables :

$$x(\lambda y, \lambda z, \eta, \mu) = \lambda x(y, z, \eta, \mu)$$

for any real number $\lambda > 0$. Let $\mu \equiv \mu(x, y, \eta, \nu)$. We say μ is intensive if it is zero-th order homogeneous function of its extensive variables :

$$\mu(\lambda x, \lambda y, \eta, \nu) = \mu(x, y, \eta, \nu).$$

What I am saying is simple. If you have two bottles of water each of volume V liters, entropy S units (joules/kelvin), energy U joules, temperature T kelvin, and density ρ kilogram per cubic meter, and if you empty the bottles on to a vessel, then the vessel shall contain $2V$ liters of water (Volume is extensive), having $2S$ units of entropy (entropy is extensive), $2U$ joules of energy (energy is extensive) at T kelvin (temperature is intensive) and density ρ kilogram per cubic meter (density is intensive). An extensive property adds up; an intensive property¹⁵ doesn't.

1.5 Then Came Sadi Carnot

Systematic development of thermodynamics as a distinct discipline of inquiry started when heat engines - that extract work from heat - came into existence during industrial revolution that started in the second half of eighteenth century. Lazare Nicolas Marguerite Count Carnot a French military engineer, was worried that the French steam engines were invariably less efficient than the English ones. It hurt his pride. He called his student son Sadi Carnot and asked him to investigate.

The very fact that work could come out of heat in a steam engine, came as a big surprise to Nicolas Léonard Sadi Carnot (1796 - 1832). It is work which dissipates into heat by friction, in nature : when you apply the breaks, the car stops because of friction; also because of friction, the break line heats up. However, the heat generated shall never assemble back and move the car. For Sadi Carnot, what the heat engine does is something unusual and very unnatural.

¹⁴ In general if $f(\lambda x, \lambda y, \lambda z) = \lambda^n f(x, y, z)$ we say that f is n -th order homogeneous function of its variables x, y , and, z .

¹⁵ a property which is the ratio of two extensive properties is automatically intensive. For example, consider density of a substance; it is the ratio of the extensive properties , mass and volume, of the substance. Density hence, is an intensive property. Molar specific heat is the ratio of (extensive) energy (required to raise the temperature by one degree kelvin) and number of moles (an extensive quantity) of the substance; molar specific heat is an intensive property. Think of other examples. We have temperature, pressure, and chemical potential which are intrinsically intensive.

1.5.1 Birth of Thermodynamics

Carnot¹⁶ imagined an heat engine to be a simple mill wheel. Water from a height falls on the mill wheel and it rotates. Similarly when q calories of heat falls from temperature T_1 to a lower temperature T_2 it produces movement. If it were to fall to absolute zero, then the whole of heat would have been converted to work. But since it falls to $T_2 > 0$, only the fraction $(T_1 - T_2)/(T_1 - 0)$ of q calories gets converted to work. Hence the efficiency of a heat engine can, at best, be

$$\eta = \frac{q}{w} = 1 - \frac{T_2}{T_1}.$$

Sadi Carnot concluded that just having a source of heat ‘ is not sufficient to give birth to the impelling power. It is necessary that there should be cold; without it heat is useless. ’We need both - the hot boiler, the heat source and the cold radiator, the heat sink - to extract work from heat. Carnot announced his findings in the year **1824**, and was born the subject of thermodynamics.

1.6 End Remarks

Nobody took notice of Carnot’s work for over twenty years. The most beautiful law of theoretical physics - the Second Law of thermodynamics, had arrived and there was no one to welcome it ! It was Benoit Paul Émile Clapeyron (1799 - 1864) who gave a mathematical scaffolding¹⁷ to Carnot’s work and brought it to the attention of Rudolf Julius Emanuel Clausius (1822 - 1888) and Lord Kelvin né William Thomson (1824 - 1907). Clausius felt that Carnot’s finding was correct and intuition told him that it is of great fundamental significance. Initially he called it Carnot’s principle and later elevated to the status of a law - the second law of thermodynamics.

Clausius however rejected Carnot’s derivation; justifiably so; for, Carnot’s derivation was based on caloric theory; and caloric theory has been overthrown¹⁸

¹⁶ Nicolaus Léonard Sadi Carnot, *Reflexions sur la puissance motrice du feu et sur les machines propres à développer cette puissance*, Paris (1824); English translation : Sadi Carnot, *Reflections on the motive power of fire and on machines fitted to develop that power*, in J Kestin (Editor) *The Second Law of Thermodynamics*, Dowden, Hutchinson and Stroudsburg, PA (1976)p.16

¹⁷ It was Clapeyron who gave the Carnot cycle, that we all are familiar with since our school days, consisting of an isothermal expansion followed by an adiabatic expansion, isothermal compression and an adiabatic compression.

¹⁸ Count Rumford, né Benjamin Thompson (1753 - 1814), Julius von Mayer (1814 - 1878) and James Prescott Joule (1818 - 1889) discovered that heat is equivalent to work; like work, heat is a way by which thermodynamic systems transact energy amongst themselves or with their surroundings. The change in internal energy of a system can be exactly accounted for, by the energy transacted by heat and work :

$$dU = \delta Q + \delta W.$$

This is known as the first law of thermodynamics. Thermodynamics has grown in a topsyturvy fashion. The Second law came first, when Sadi Carnot announced that a heat engine can not convert heat completely to work, whereas work can be completely converted into heat. There is an asymmetry

in the intervening years since the death of Sadi Carnot. When he was becoming familiar with Carnot's work, Clausius knew that heat, like work, was a process by which energy is transacted. To derive Carnot's principle Clausius discovered in the year 1865 a new thermodynamic property called entropy. I shall tell you of these exciting developments in the next lecture. For a beautiful, and an insightful account of the work of Sadi and Rudolf Clausius, see the book¹⁹ written by Michael Guillen.

Before I proceed further, let me give you a list of books and articles which you will find useful in your study of thermodynamics. I have listed several books. Each author has his own narrative to make, his very special idiosyncrasies, and his own pet stories to tell. My learning of thermodynamics has been influenced by several of the books and articles listed here and it will reflect in my lectures. But then, whenever I remember, I shall tell you what material I have picked up and from where.

I recommend you glance through the books and pick up one or two that suits your way of learning, for further serious study. It should also be quite fine if you simply listen to what I say in the class, think it over later, ask questions and hold discussions amongst yourselves and with me during and outside class hours, read the notes that I shall give you from time to time, and work out the problems I give in the class and in the assignment sheets.

1.7 Books

- **H C Van Ness**, *Understanding Thermodynamics*, Dover (1969). This is an awesome book; easy to read and very insightful. In particular, I enjoyed reading the first chapter on the first law of thermodynamics, the second on reversibility, and the fifth and sixth on the Second law. My only complaint is that Van Ness employs British Thermal Units. Another minor point : Van Ness takes work done by the system as positive and that done on the system as negative. Engineers always do this. Physicists and chemists employ the opposite convention. For them the sign coincides with the sign of change of internal energy caused by the work process. If the transaction leaves the system with higher energy, work done is positive; if it results in lowering of energy, work done is negative.
- **H B Callen**, *Thermodynamics*, John Wiley (1960). Callen sets the standard for how a text book should be. This book has influenced generations of teachers and students alike, all over the world. The book avoids all the pitfalls in

in nature. Twenty years later came the first law of thermodynamics which talks of conservation of energy. Then came the third law which talks of equilibrium system at absolute zero. It was discovered by Walther Nernst (1864-1941) in the first quarter of twentieth century. The zeroth law which talks about thermal equilibrium, came much later and the christening was done by R H Fowler (1899 - 1944) when he was discussing the 1935 text of Meghnad Saha (1893 - 1956) and B N Srivastava. We shall see, in detail, about these four laws of thermodynamics.

¹⁹ Michael Guillen, *An Unprofitable Experience : Rudolf Clausius and the Second Law of Thermodynamics*, in *Five Equations that Changed the World*, Hyperion (1995)p.165

the historical development of thermodynamics by introducing a postulational formulation.

- **H B Callen**, *Thermodynamics and an Introduction to thermostatistics*, Second Edition, Wiley, India (2005). Another classic from H B Callen. He has introduced statistical mechanics without undermining the beauty and the coherent structure of thermodynamics. In fact, the statistical mechanics he presents, enhances the beauty of thermodynamics.

The simple toy problem with a red die (the closed system) and two white dice (the heat reservoir), and restricting the sum to a fixed number (conservation of total energy) motivates beautifully the canonical ensemble formalism.

The pre-gas model introduced for explaining grand canonical ensemble of fermions and bosons is simply superb. I also enjoyed the discussions on the subtle mechanism underlying Bose condensation. I can go on listing several such gems scattered in Callen's narrative. The book is full of beautiful insights. A relatively inexpensive, Wiley-student edition of the book is available in the Indian market. Buy your copy now !

- **Gabriel Weinreich**, *Fundamental Thermodynamics*, Addison Wesley (1968). Weinreich is eminently original; has a distinctive style. Perhaps you will feel uneasy when you read this book for the first time. But very soon, you will get used to Weinreich's idiosyncracies; and you would love this book. This book is out of print. However a copy is available with Prof H S Mani, Chennai Mathematical Institute, Chennai.
- **N D Hari Dass**, *Principles of Thermodynamics*, CRC Press, Taylor and Francis (2014). A beautiful book on thermodynamics; perhaps the most recent one to arrive at the market place.

Hari Dass is a great story teller. He has the magic to convert prosaic things into exciting objects. If you are a beginner and plan to learn thermodynamics, I will recommend this book to you. There is pedagogy; titbits of history scattered all through; and, no dearth of rigour. You will learn thermodynamics correctly.

To a teacher or an expert, I shall recommend this book whole-heartedly. I am sure he will find something new, something interesting, and something surprising, in every chapter. He will get useful hints and substantial material which he can make use of while teaching the subject.

The only complaint I have is, the book gives a feeling of finality : the last word on thermodynamics has been said. I think we are still struggling to know what heat is. Thermodynamics tells us that heat is a process by which energy is transacted amongst macroscopic bodies. This helps; for, then, we shall not mistake heat for a substance that resides in a system or a property of the system²⁰. But then this statement of heat as an instrument for energy transfer, does not say anything about what exactly it is. Perhaps heat is something hidden, somewhere in the 10^{24} or so of trajectories; you can not compute these trajectories

²⁰ Our fore-fathers mistook heat for Phlogiston, residing in the flames or a Caloric fluid residing in thermal objects.

: not just because the numbers are obscenely large; but because their dynamics is inherently unpredictable due to sensitive dependence on initial conditions. It is perhaps here we have to look for a meaning of heat. I would like to hear of these in the words of Hari Dass, perhaps in the next edition of his book !

- **Evelyn Guha**, *Basic Thermodynamics*, Narosa (2000). Guha makes an extremely simple and beautiful exposition of traditional thermodynamics. The book contains an excellent set of worked-out examples and a large collection of well-chiselled problems. In particular I liked the chapter on the consequences of the Second law. I was also delighted to see a simple and beautiful exposition of the Carathéodary formulation based on the existence of adiabatically inaccessible states in the neighbourhood of every equilibrium thermodynamic state.
- **C B P Finn**, *Thermal Physics*, Nelson Thornes (2001). Beautiful; concise; develops thermodynamics from first principles. Finn brings out the elegance and the raw power of thermodynamics.
- **Max Planck**, *Treatise on Thermodynamics*, Third revised edition, Dover; first published in the year 1897. Translated from the seventh German edition (1922). A carefully scripted master piece; emphasizes chemical equilibrium. I do not think any body can explain irreversibility as clearly as Max Planck does. If you think the third law of thermodynamics is irrelevant, then read the last chapter; you will change your mind.
- **E Fermi**, *Thermodynamics*, Dover (1936). A great book from a great master; concise; the first four chapters (on thermodynamic systems, first law, the Second law, and entropy) are simply superb. I also enjoyed the parts covering Clapeyron and van der Waal equations.
- **J S Dugdale**, *Entropy and its physical meaning*, Taylor and Francis (1998). An amazing book. Dugdale de-mystifies entropy. This book is not just about entropy alone, as the name would suggest. It teaches you thermodynamics and statistical mechanics. A book that cleverly avoids unnecessary rigour. The analogy Dugdale gives for explaining internal energy, and the chapter on entropy in irreversible changes are beautiful. I shall make abundant use of this book in my lectures.
- **David Goodstein**, *States of Matter*, Dover (2002). A delightful and entertaining text. You are reminded of Feynman's writing when you read this book. The discussion on dimensional analysis is excellent. This book is a must in your bookshelf.
- **F Rief**, *Fundamentals of statistical and thermal physics*, McGraw-Hill (1965). One of the best text books on statistical thermodynamics. Felix Rief develops thermal physics entirely in the vocabulary of statistical mechanics. As a result after reading this book, you will get an uneasy feeling that the subject of thermodynamics has been relegated to the status of an uninteresting appendix to statistical mechanics.

My recommendation : read this book for learning statistical - thermodynamics; then read Callen, or Van Ness or Fermi for learning thermodynamics. Then you will certainly fall in love with both statistical mechanics and thermodynamics separately!

- **Joon Chang Lee**, *Thermal physics - Entropy and Free Energies*, World Scientific (2002). Joon Chang Lee presents statistical thermodynamics in an unorthodox and distinctly original style. In particular I like the discussions on Landau free energy. The presentation is so simple and so beautiful that you do not notice that the book is written in an awful English; almost at all places, the language is flawed. But then you hear very clearly what Joon Chang Lee wants to tell you; and what you hear is beautiful. You get a strange feeling that perhaps flawed English communicates better than chaste, grammatically correct and poetic English !
- **James P Sethna**, *Entropy, Order Parameters, and Complexity*, Clarendon Press, Oxford (2008) James Sethna covers an astonishingly wide range of modern applications; a book, useful not only to physicists, but also to biologists, engineers, and sociologists. I find exercises and footnotes very interesting, often more interesting than the main text! The exercises can be converted into exciting projects.
- **C Kittel**, and **H Krömer**, *Thermal physics*, W H Freeman (1980). A good book; somewhat terse. I liked the parts dealing with entropy, and Boltzmann weight; contains a good collection of examples.
- **Daniel V Schröder**, *An Introduction to Thermal Physics*, Pearson (2000). Schröder has excellent writing skills. The book reads well. Contains plenty of examples. Somewhat idiosyncratic.
- **M W Zamansky**, and **R H Dittman**, *Heat and Thermodynamics, an intermediate textbook*, Sixth edition, McGraw-Hill (1981). A good and dependable book for a first course in thermodynamics.
- **R Shanthini**, *Thermodynamics for the Beginners*, Science Education Unit, University of Peredeniya (2009). Student-friendly. Shanthini has anticipated several questions that would arise in the mind of an oriental student when he or she learns thermodynamics for the first time. The book has a good collection of worked out examples. A bit heavy on heat engines.
- **Dilip Kondepudi** and **Ilya Prigogine**, *Modern Thermodynamics : From heat engines to Dissipative Structures*, John Wiley (1998). Classical, statistical, and non equilibrium thermodynamics are woven into a single fabric. This book tells us learning thermodynamics can be fun. Contains lots of interesting tit-bits on history. Deserves a better cover design; the present one looks cheap.

1.8 Extra Reading : Books

- **Nicolaus Sadi Carnot**, *Reflexions sur la puissance motrice du feu et sur les machines propres á développer cette puissance*, Paris (1824); for English translation see **Sadi carnot**, *Reflections on the motive power of fire and on machines fitted to develop that power*, in **J Kestin** (Ed.) *The second law of thermodynamics*, Dowden, Hutchinson and Ross, Stroudsburg, PA (1976)p.16
- **J Kestin** (Ed.), *The second law of thermodynamics*, Dowden, Hutchinson and Ross (1976)
- **P Atkin**, *The Second Law*, W H Freeman and Co. (1984)
- **G Venkataraman**, *A hot story*, Universities Press (1992)
- **Michael Guillen**, *An unprofitable experience : Rudolf Clausius and the second law of thermodynamics* p.165, in *Five Equations that Changed the World*, Hyperion (1995)
- **P Atkins**, *Four Laws that drive the Universe*, Oxford university Press (2007).
- **Christopher J T Lewis**, *Heat and Thermodynamics : A Historical Perspective*, First Indian Edition, Pentagon Press (2009)
- **S G Brush**, *Kinetic theory* Vol. 1 : *The nature of gases and of heat*, Pergamon (1965) Vol. 2 : *Irreversible Processes*, Pergamon (1966)
- **S G Brush**, *The kind of motion we call heat*, Book 1 : *Physics and the Atomists* Book 2 : *Statistical Physics and Irreversible Processes*, North Holland Pub. (1976)
- **I Prigogine**, *From Being to Becoming*, Freeman, San Francisci (1980)
- **K P N Murthy**, *Excursions in thermodynamics and statistical mechanics*, Universities Press (2009)

1.9 Extra Reading : Papers

- **K K Darrow**, *The concept of entropy*, American Journal of Physics **12**, 183 (1944).
- **M C Mackay**, *The dynamical origin of increasing entropy*, Rev. Mod. Phys. **61**, 981 (1989).
- **T Rothman**, *The evolution of entropy*, pp.75-108, in *Science á la mode : physical fashions and fictions* Princeton University Press (1989)
- **Ralph Baierlein**, *Entropy and the second law : A pedagogical alternative*, American Journal of Physics **62**, 15 (1994)
- **G. Cook**, and **R H Dickerson**, *Understanding the chemical potential*, American Journal of Physics **63**, 738 (1995).
- **K. P. N. Murthy**, *Ludwig Boltzmann, Transport Equation and the Second Law*, arXiv: cond-mat/0601566 (1996)
- **Daniel F Styer**, *Insight into entropy*, American Journal of Physics **68**, 1090 (2000)

- **T P Suresh, Lisha Damodaran, and K M Udayanandan**, *Gibbs' Paradox : Mixing and Non-Mixing Potentials*, Physics Education **32**(3), Article No. 4 (2016).
- **B J Cherayil**, *Entropy and the direction of natural change*, Resonance **6**, 82 (2001)
- **J K Bhattacharya**, *à la Boltzmann*, Resonance **6**, 19 (2001)
- **J Srinivasan**, *Sadi and the second law of thermodynamics*, Resonance **6** 42 (2001)
- **D C Shoepf**, *A statistical development of entropy for introductory physics course*, American Journal of Physics **70**, 128 (2002).
- **K P N Murthy**, *Josiah Willard Gibbs and his Ensembles* Resonance **12**, 12 (2012).

2. LECTURES 2 - 5

U AND S IN STATISTICAL MECHANICS AND THERMODYNAMICS

2.1 Opening Remarks

We have acquired some nodding acquaintance with terms like internal energy, U and entropy, S in the previous lectures. We already know that U and S are extensive properties of a macroscopic system. It is time, we get to know more of these two important properties.

In thermodynamics the nature of internal energy and that of entropy are sort of shrouded in a bit of a mystery. Of course I must say these quantities are defined, in thermodynamics, unambiguously and rigorously; but they remain abstract. Let us take internal energy. Thermodynamics does not help us visualize this quantity : What is it ? Is it kinetic ? Is it potential ? Where does it reside inside the material ? and how ? The story is the same with entropy : What is the nature of entropy ? Can I understand this property of a macroscopic system like I ‘ understand ’ other properties *e.g.* volume, pressure, density, temperature, *etc.* ? why should entropy always increase in a spontaneous process ? How do I form a mental picture of entropy ?

Hence, first, I shall tell you of these quantities very briefly, in the language of statistical mechanics. Hopefully, this will help you get a feel for internal energy and entropy, and to some extent comprehend what they are and why they behave the way they do. Then I shall tell, how these properties are defined in thermodynamics²¹.

2.2 Internal Energy : Statistical Mechanics

Matter is made up of atoms and molecules. When two molecules are far apart they move about independently; they do not interact with each other. When they come close, they start attracting each other. The attraction can come about for example due to dipole-dipole interaction : when the centre of mass of the cloud of electrons and that of the positively charged core nucleus of a neutral atom, do not coincide, then a dipole emerges. Two dipoles attract each other.

²¹ to be precise, in thermodynamics, we shall define change in internal energy, ΔU and change in entropy, ΔS , and not absolute energy or absolute entropy.

When you try to push the two molecules closer, they start repelling each other. We know for example, the distance between the centres of two hard spheres can not be smaller than the sum of their radii. We call it hard core repulsion. But atoms are more like soft balls; electron clouds around each nucleus can overlap to some extent, when squeezed; their centres can come a bit closer than the sum of their radii, but not too close : the repulsion increases rather steeply.

2.2.1 Lennard-Jones 6-12 Potential

A good model for describing such interactions described above, between two atoms, is given by Lennard-Jones potential, also known as **6 – 12** potential. It is given by

$$\mathcal{V}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (2.1)$$

The potential is depicted in the Fig. (2.2.1), below.

The symbol r denotes the distance between two molecules. For plotting the graph, we have taken $\sigma = 0.1$ and $\epsilon = -3.5$. $\mathcal{V}(r = \sigma) = 0$. The depth of the potential well is ϵ . The potential is minimum at $r = r^* = 2^{1/6}\sigma$. When the atoms are separated by a distance of r^* there is no force between them. The atoms attract each other when their separated by distance more than r^* . If they come closer than r^* , they start repelling each other.

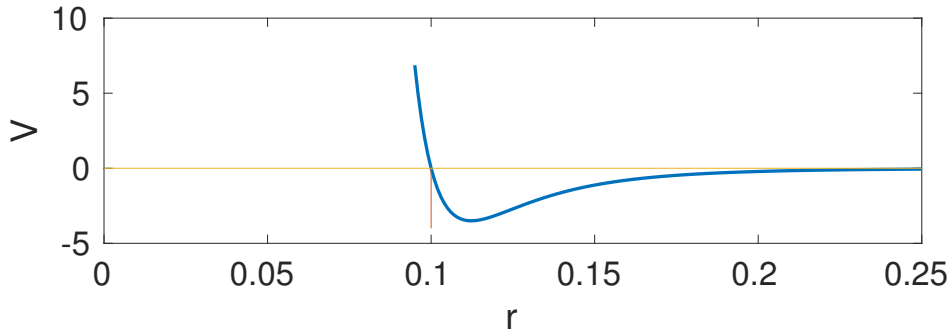


Fig. 2.1. Lennard-Jones potential

Consider all possible distinct pairs of atoms which are sufficiently close to each other; each pair carries some tiny potential energy. Since there are a large number of such pairs in a substance, the potential energy adds up to a substantial value.

The atoms are also moving all the time in gases and liquids and vibrating around their mean positions in a crystalline solid. There is kinetic energy $\sum_{i=1}^3 \mathbf{p}_i^2 / 2m$ associated with each atom of mass m and momentum $(\mathbf{p}_1, \mathbf{p}_2, \mathbf{p}_3)$. These tiny contribution to potential energy and kinetic energy from some 10^{23} or so of atoms, add up to a substantial number which we call internal energy.

2.3 Internal Energy : Thermodynamics

That the physicists and chemists of the yesteryears could at all come up with a property like internal energy, is amazing. They did not know of atoms and molecules that make up the object and the kinetic energy and interaction energy they carry. Hence there was no way they could know how and where does the internal energy arise and how and where does it reside inside an object.

Of course, they had their own compelling reasons to come up with the notion of internal energy. The compulsion came from the work of Rumford, Mayer and Joule. The trio had de-throned the caloric theory and had unambiguously established that heat is equivalent to work. From careful experiments with a vessel of water (isolated by adiabatic walls), paddle wheel (to stir the water), and falling weights (to measure the work done), see figure below, Joule had obtained the mechanical equivalence of heat : **1 calorie = 4.18 joules**.

If we want to take this mechanical equivalence of heat to its logical end, then we must define heat, completely in terms of work. How do we do this ? We know that in an adiabatic process²² no energy is transacted by heat. Consider a system going from one thermodynamic state to the another. If it does this adiabatically a certain amount of work is done. If it does this by an arbitrary process then also, a certain amount of work gets done. The difference between these two work values is heat. Thus **heat is adiabatic work done minus actual work done**. We have done the job. We have expressed heat completely in terms of work. Stated differently we have adiabatic work equals actual work plus heat. Take two points on the thermodynamic phase diagram. Take the system from one point to the other by an arbitrary process. Measure the work done (in units of joule) employing falling weights. Let it be W_1 . Measure the heat exchanged (in units of calories) by noting the temperature change and employing the standard calorimetric methods. Express the heat exchanged in units of joule, employing the calorie to joule conversion factor. Call it Q_1 .

Now consider another path between the same two points and calculate the work, W_2 and heat, Q_2 . In general $Q_1 \neq Q_2$ and $W_1 \neq W_2$; But their sum was found to be invariably the same : $Q_1 + W_1 = Q_2 + W_2$. What ever may be the path, the heat and work measured add up to the same quantity, provided the starting point and the end point of all the paths are the same. Heat plus work is found to be independent of the path. Hence the sum can be expressed as a difference between the values of a thermodynamic property at these two points. This observation provides a neat justification for calling the adiabatic work done in a process, as change in some property of the system. We name this property as internal energy of the system and denote it by the symbol U .

Accordingly, take an arbitrary point on a thermodynamic phase diagram. Call it O . Define a function/property U and assign to it an arbitrary value at the

²² a process that happens in a system which is isolated from the surroundings by a non conducting wall. Stuff kept inside a thermos flask is a good example of an isolated system.

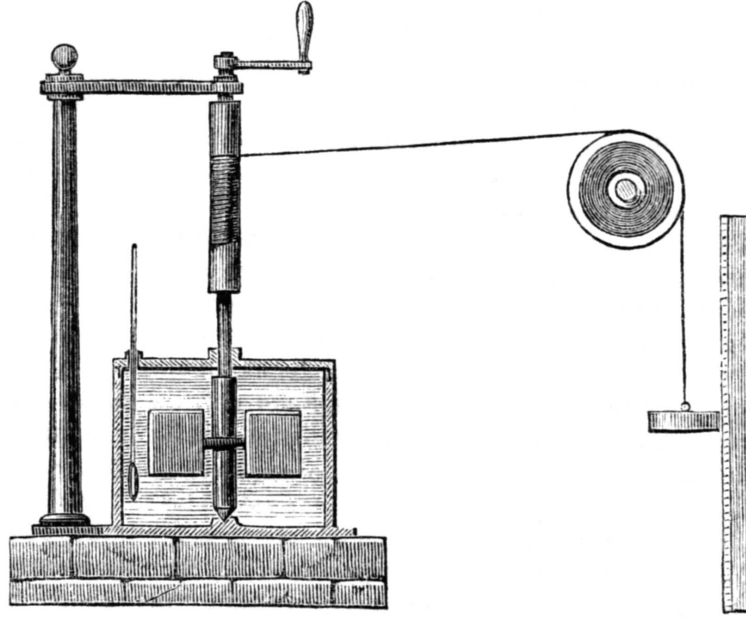


Fig. 2.2. Engraving of James Joule's apparatus for measuring the mechanical equivalence of heat, in which potential energy from the falling weight on the right is converted into heat through stirring of water on the left. Source Harper's New Monthly Magazine, No. 231, August, 1869.

chosen reference point O . Then consider a point A on the phase diagram and an adiabatic process that takes the system from O to A . Measure²³ the work done. Define

$$U(A) = U(O) + W_{O \rightarrow A}^{(A)}. \quad (2.2)$$

In the above $W_{O \rightarrow A}^{(A)}$ is the work done in the process that takes the system from O to A adiabatically. Carry out this exercise for all the points on the thermodynamic phase plane.

Let us say there exists a point B on the phase diagram which is not accessible adiabatically from O . In that case it is assured the system could go in the reverse, *i.e.* from B to O , adiabatically. Then, employing falling weights, make a measurement of the work done in an adiabatic process from B to O . We can write $U(O) = U(B) + W_{B \rightarrow O}^{(A)}$ or

$$U(B) = U(O) - W_{B \rightarrow O}^{(A)}. \quad (2.3)$$

Thus, you can define U at all points on the phase diagram.

Consider now two points A and B such that you can go from A to B adiabatically. Let $W_{A \rightarrow B}^{(A)}$ denote the work done. Consider an arbitrary thermodynamic

²³ Work done is measured as follows. Link the process to a falling weight. Determine by what height the weight falls during the process. That gives you the work done. Joule actually carried out experiments with falling weights and measured the work equivalence of heat quite accurately.

process that takes the system from A to B . Let $W_{A \rightarrow B}$ be the work done. We have $W_{A \rightarrow B}^{(A)} - W_{A \rightarrow B} = Q$.

In terms of the function U we have $U(B) - U(A) = W + Q$. The function or the property denoted by the symbol U is given the name Internal Energy. The reason for calling it energy is obvious : we have learned in in our school days that energy is ability to do work.

What is the nature of this property we call internal energy ? What is its origin ? How and where does it reside in the interior of the object ? We have to wait for Boltzmann to arrive, formulate statistical mechanics and answer all these questions. Until then we shall define internal energy in terms of adiabatic work.

Every time we observe a change in the (internal) energy of a system and on each of these occasions we are able to account for the change in terms of heat and work, then we can say that energy is conserved²⁴. The idea is to explicitly recognize that the system and its surroundings are separated by a boundary. Energy enters or exits through the boundary. When it enters by work, we say the work is positive; when it enters by heat we say the heat is positive. In the same fashion when energy exits the system by work we say the work is negative; when it exits the system by heat we say the heat is negative. There are only two ways - heat and work - by which such a transaction can take place and we have the law of conservation of energy expressed in thermodynamics as

$$\Delta U = W + Q. \quad (2.4)$$

I must reiterate that the quantity ΔU in the above is the change in a property of the system, when you go from an equilibrium thermodynamic state A to another equilibrium thermodynamic state B . It does not depend on the path taken. It depends only on the initial and the final states. We can not say of this about the two quantities W and Q sitting on the right hand side of the above equation.

If the two points A and B are infinitesimally close to each other in the thermodynamic phase plane, then ΔU can be expressed as an exact differential dU . Again, we can not say of this about the other two quantities sitting on the right hand side of equation (2.4). For an infinitesimal process we write the first law of thermodynamics as

$$dU = \bar{d}Q + \bar{d}W. \quad (2.5)$$

Heat can not be expressed as an exact differential. Heat is not a property of the system. Hence we have put a bar on d and we have denoted the small amount of heat as $\bar{d}Q$. Do not read $\bar{d}Q$ as change of Q . It is absurd. Q is not a thermodynamic state variable. These observations hold equally good for work as well.

²⁴ I would strongly recommend : read the first chapter of the little book of Van Ness, *Understanding Thermodynamics*, Dover (1969) where he talks about a mother, a son, thirty seven sugar cubes, and a room with two windows one named W and the other Q .

We have already seen that though \boldsymbol{dW} is not an exact differential the quantity $-\boldsymbol{dW}/P$ is an exact differential²⁵ called dV . We have $\boldsymbol{dW} = -P dV$, in an infinitesimal (quasi-static) reversible process. We can calculate the work done as

$$W_{A \rightarrow B} = - \int_A^B P dV, \quad (2.6)$$

The integral is carried out along a pre-specified quasi static reversible path taking the system from a thermodynamics state A to a thermodynamic state B , on the $P - V$ phase plane. $-1/P$ is the integrating factor that gives you an exact differential dV from an in-exact differential \boldsymbol{dW} . The expression $\boldsymbol{dW} = -P dV$ holds good only for a (quasi static) reversible processes. If the process is not reversible, then the expression given for work does not hold good.

Thus, in thermodynamics, internal energy is a state function defined for equilibrium states of a system; the difference in internal energy between two equilibrium states is given by the adiabatic work done while going from one of the states to the other.

2.4 Entropy : Statistical Mechanics

Consider a macroscopic system which can exist in more than one micro states.

- A coin has two sides labeled "Heads" - H and "Tails" - T . We say these are the two (micro) states of the coin : $\{H, T\}$.
- Consider a system of two independent fair coins; there are four micro states : $\{HH, HT, TH, TT\}$.
- A system of N independent fair coins has 2^N micro states. Each micro state is a string of N elements; each element is H or T .
- A die has six micro states - the six sides of a cube notched with $1, 2, \dots, 6$ dots.
- A point particle is specified by three position coordinates and three momentum coordinates. At any time it is represented by a point in six dimensional phase space. We imagine the six dimensional phase space to be made up of tiny six dimensional cubes. We can take the cube to have a minimum uncertainty²⁶ volume of h^3 . Then we count the number of cubes in the phase space region accessible to the single-particle system. This gives the total the number of micro states of a single particle.

²⁵ A natural question arises : Is it possible to express \boldsymbol{dQ} also in terms of some exact differential and some integrating factor ? Rudolf Emmanuel Clausius answered this question in the affirmative and in doing so he invented a new thermodynamic property called usually denoted by the symbol S . I shall tell you of this later. Suffice is to say $\boldsymbol{dQ}/T = dS$

²⁶ We have the uncertainty relation $\Delta x \Delta p_x \gtrsim h$, where h denotes the Planck's constant : $h = 6.626176 \text{ j s}$.

- Consider a system of N ideal gas molecules confined to a volume V and having energy E . A string of $6N$ number - $3N$ for specifying the positions and $3N$ for momenta, represents a micro state. The entire system is specified by a single point in the $6N$ dimensional phase space. We can count the number of cubes, each cube being of volume h^{3N} , required to fill up the phase space volume accessible to the system. This count gives the number of micro states of the system. Let us denote this count by $\widehat{\Omega}(E, V, N)$ and proceed to calculate this quantity as follows.

First we notice that for spatial coordinates, we have

$$\int dq_1 \int dq_2 \int dq_3 \cdots \int dq_{3N-2} \int dq_{3N-1} \int dq_{3N} = V^N, \quad (2.7)$$

where the integral over the three positions of each molecule extends over the volume V of the container.

The energy is given by

$$E = \sum_{i=1}^{3N} \frac{p_i^2}{2m}. \quad (2.8)$$

Since the system is isolated, the energy is a constant. The trajectory of the system is confined to the surface of a $3N$ dimensional sphere of radius $\sqrt{2mE}$. For purpose of counting the micro states, we shall consider the volume of the $3N$ dimensional sphere. This brings us to the issue of determining the volume of hyper spheres and to this we turn our attention below.

2.4.1 Volume of an N -Dimensional Sphere

The volume of an N - dimensional sphere of radius R is formally given by the integral,

$$V_N(R) = \int_{-\infty}^{+\infty} dx_1 \cdots \int_{-\infty}^{+\infty} dx_N \Theta \left(R^2 - \sum_{i=1}^N x_i^2 \right), \quad (2.9)$$

Change the coordinate system from

$$\{x_i : i = 1, N\} \text{ to } \{y_i = x_i/R : i = 1, N\}.$$

$$dx_i = R dy_i \quad \forall i = 1, N;$$

$$\Theta \left(R^2 \left[1 - \sum_{i=1}^N y_i^2 \right] \right) = \Theta \left(1 - \sum_{i=1}^N y_i^2 \right).$$

We have,

$$V_N(R) = R^N \int_{-\infty}^{+\infty} dy_1 \cdots \int_{-\infty}^{+\infty} dy_N \Theta \left(1 - \sum_{i=1}^N y_i^2 \right); \quad (2.10)$$

$$= V_N(R = 1) R^N. \quad (2.11)$$

where $V_N(R = 1)$ is the volume of an N - dimensional sphere of radius unity.

To find the volume of N -dimensional sphere of radius R , we proceed as follows.

$$V_N(R=1)R^N = \int_{-\infty}^{+\infty} dx_1 \cdots \int_{-\infty}^{+\infty} dx_N \Theta \left(R^2 - \sum_{i=1}^N x_i^2 \right). \quad (2.12)$$

Differentiate both sides of the above expression with respect to R and get,

$$NV_N(R=1)R^{N-1} = \int_{-\infty}^{+\infty} dx_1 \cdots \int_{-\infty}^{+\infty} dx_N \delta \left(R^2 - \sum_{i=1}^N x_i^2 \right) 2R. \quad (2.13)$$

Now, multiply both sides by $\exp(-R^2)dR$ and integrate over R from 0 to ∞ .

Left Hand Side:

$$LHS = NV_N(R=1) \int_0^\infty dR \exp(-R^2) R^{N-1}. \quad (2.14)$$

Let $x = R^2$; then $dx = 2RdR$. This gives

$$dR = \frac{1}{2} \frac{dx}{x^{1/2}}. \quad (2.15)$$

We get,

$$\begin{aligned} LHS &= V_N(R=1) \frac{N}{2} \int_0^\infty x^{\frac{N}{2}-1} \exp(-x) dx, \\ &= V_N(R=1) \frac{N}{2} \Gamma \left(\frac{N}{2} \right), \\ &= \Gamma \left(\frac{N}{2} + 1 \right) V_N(R=1). \end{aligned} \quad (2.16)$$

Right Hand Side :

$$\begin{aligned} RHS &= \int_0^\infty dR \exp(-R^2) \int_{-\infty}^{+\infty} dx_1 \cdots \int_{-\infty}^{+\infty} dx_N \delta \left(R^2 - \sum_{i=1}^N x_i^2 \right) 2R; \\ &\quad t = R^2 ; dt = 2RdR, \\ RHS &= \int_0^\infty dt \exp(-t) \int_{-\infty}^{+\infty} dx_1 \cdots \int_{-\infty}^{+\infty} dx_N \delta \left(t - \sum_{i=1}^N x_i^2 \right), \\ &= \int_{-\infty}^{+\infty} dx_1 \cdots \int_{-\infty}^{+\infty} dx_N \exp \left[-(x_1^2 + x_2^2 + \cdots + x_N^2) \right], \\ &= \left[\int_{-\infty}^{+\infty} dx \exp(-x^2) \right]^N = \pi^{N/2}. \end{aligned} \quad (2.17)$$

Thus we get

$$V_N(R=1) = \frac{\pi^{N/2}}{\Gamma \left(\frac{N}{2} + 1 \right)}. \quad (2.18)$$

$$V_N(R) = \frac{\pi^{N/2}}{\Gamma \left(\frac{N}{2} + 1 \right)} R^N. \quad (2.19)$$

What we require is the volume of a thin shell, confined between spheres of radius R and $R + \Delta R$. We show below that for large N this quantity is the same as the volume of the sphere.

2.4.2 An $N(\rightarrow \infty)$ Dimensional Sphere Lives on its Outer Shell

In the limit of $N \rightarrow \infty$, the volume of a thin outer shell tends to the volume of the whole sphere. This intriguing behaviour is a consequence of the power law.

$$\begin{aligned} \frac{V_N(R) - V_N(R - \Delta R)}{V_N(R)} &= \frac{R^N - (R - \Delta R)^N}{R^N}, \\ &= 1 - \left(1 - \frac{\Delta R}{R}\right)^N = 1 \text{ for } N \rightarrow \infty. \end{aligned} \quad (2.20)$$

Consider the case with $R = 1$ and $\Delta R = 0.1$. The percentage of the total volume contained in the outermost shell of an N dimensional sphere for N ranging from 1 to 100 is given in the table below.

Table 2.1. Percentage of volume of an N dimensional sphere contained in a thin outer shell between $R = 0.90$ and 1

N	$\frac{V_N(R=1) - V_N(R=0.9)}{V_N(R=1)} \times 100$	N	$\frac{V_N(R=1) - V_N(R=0.9)}{V_N(R=1)} \times 100$
1	10.000%	8	57.000%
2	19.000%	9	61.000%
3	27.000%	10	65.000%
4	34.000%	20	88.000%
5	41.000%	40	99.000%
6	47.000%	60	99.000%
7	52.000%	80	99.980%
		100	99.997%

2.4.3 Counting of Micro States

The volume of a $3N$ dimensional sphere of radius $\sqrt{2mE}$ is thus, given by

$$V_{3N}(R = \sqrt{2mE}) = \frac{(2\pi mE)^{3N/2}}{\Gamma\left(\frac{3N}{2} + 1\right)}. \quad (2.21)$$

The number of micro states of N molecules of an ideal gas confined to a volume V and with energy less than or equal to E is formally given by

$$\hat{\Omega}(E, V, N) = \frac{V^N (2\pi mE)^{3N/2}}{h^{3N} \Gamma\left(\frac{3N}{2} + 1\right)} \quad (2.22)$$

Entropy is defined as proportional to the logarithm of the number of micro states accessible to the system.

- For a coin with two micro states, $S \propto \ln 2$.
- For a die with six micro states, $S \propto \ln 6$.
- If we have a system of N independent fair coins, there are 2^N micro states. We have $S \propto N \ln 2$.
- Entropy of N non interacting particle of energy E confined to a volume V is given by

$$S \propto \ln \hat{\Omega}(E, V, N) \\ \propto N \ln V + (3N/2) \ln(E/N) + (3N/2) \ln(4\pi m/[3h^2]) + 3N/2.$$

In deriving the above, I have used the fact that $\Gamma(n+1) = n!$, and I have employed the first Stirling formula²⁷ : $N! = N^N \exp(-N)$, for large factorials. Thus, when the volume of the container increases, entropy increases because the system gets access to more number of micro states; the above formula tells you how does it increase : $S \propto \ln V$. When energy increases, entropy increases, because the system gets access to more number of micro states; the dependence is $\ln E$.

2.5 Entropic Pressure

Consider the following experiment : A gas is confined to a vertical cylinder open at the top and fitted with a movable piston. When you try to push the piston down, the gas resists and records its displeasure by trying to push the piston up. You can feel the pressure.

Now pull the piston up. There is no resistance. The gas happily expands and fills up the extra volume made available to it. The gas is all the time making efforts to increase its entropy. If what you do, decreases its entropy the gas opposes it by exerting pressure. If what you do, increases its entropy, the gas accepts it; poses no opposition to it. Thus we see that the pressure in this example is of entropic origin²⁸.

Thus, given an opportunity, the system would like to increase its entropy. In other words, in any spontaneous process, entropy increases. Given certain constraints, the system would take those numerical values for its macroscopic properties that maximize its entropy.

²⁷ First Stirling Formula : We have, $N! = N \times (N-1) \times \dots \times 3 \times 2 \times 1$. Therefore, $\ln N! [= \ln 1 + \ln 2 + \ln 3 + \dots + \ln N = \sum_{k=1}^N \ln(k) \approx \int_1^N \ln x dx = (x \ln x - x)|_1^N = N \ln N - N + 1] \approx N \ln N - N \implies N! \approx N^N \exp(-N)$

²⁸ We are familiar with pressure of mechanical origin. Consider a spring with plates fitted on either side. Catch hold of the plates and push them toward each other, thereby, compressing the spring. The spring resists and exerts pressure to throw your hands out. Try to pull the plates apart thereby increasing the spring length. The spring resists again, exerts a pressure and pulls your hands inwards. In this experiment the pressure is of mechanical origin.

For now, this picture of statistical mechanical entropy is adequate²⁹. An important point is that entropy is a (logarithmic) measure of the number of micro states of a macroscopic system. The system is all the time taking efforts to increase the number of micro states. A macroscopic system has a natural tendency to go to states of higher entropy.

2.6 Entropy : Thermodynamics

Start with the first law of thermodynamics and write heat as adiabatic work³⁰ minus actual work : $\delta Q = dU - \delta W$. For a quasi static reversible process, we have

$$\begin{aligned}\delta W &= -PdV = -P d(nRT/P) \\ &= -P \left(\frac{-nRT}{P^2} dP + \frac{nR}{P} dT \right) \\ &= \frac{nRT}{P} dP - nR dT\end{aligned}\tag{2.23}$$

Also for an ideal gas, internal energy U depends only on temperature; hence we have $dU = C_V dT$, where C_V is the heat capacity at constant volume. Therefore we have,

$$\begin{aligned}\delta Q &= (C_V + nR) dT - \frac{nRT}{P} dP \\ &= f(T, P) dT + g(T, P) dP\end{aligned}\tag{2.24}$$

In the above,

$$f(T, P) = C_V + nR \quad \text{and} \quad g(T, P) = -\frac{nRT}{P}\tag{2.25}$$

Let us check if δQ is an exact differential or inexact differential. We have

$$\frac{\partial f}{\partial P} = 0 \quad \text{and} \quad \frac{\partial g}{\partial T} = -\frac{nR}{P}\tag{2.26}$$

Thus we find

$$\frac{\partial f}{\partial P} \neq \frac{\partial g}{\partial T}\tag{2.27}$$

²⁹ In the description of entropy, I have not explicitly employed the word probability, for defining entropy. Nor have I invoked the notion of probability toward defining internal energy. We shall see later, entropy defined completely in term of probabilities of the micro states of a macroscopic system; and what we call as internal energy in thermodynamics corresponds to average energy, in statistical mechanics

³⁰ we have named adiabatic work as dU : the change in internal energy.

From this we conclude that dQ is not an exact differential and hence, Q is not a (state) function of the (state) variables P and T . Q is not a property of the ideal gas system.

What I am saying is extremely simple. If I have a (state) function ζ of (state) variables P and T , then I can write,

$$\zeta \equiv \zeta(P, T) \quad (2.28)$$

$$d\zeta = \frac{\partial \zeta}{\partial P} dP + \frac{\partial \zeta}{\partial T} dT \quad (2.29)$$

If $\zeta = \zeta(P, T)$, then

$$\frac{\partial}{\partial T} \left[\frac{\partial \zeta}{\partial P} \right] = \frac{\partial}{\partial P} \left[\frac{\partial \zeta}{\partial T} \right] \quad (2.30)$$

The above can be written as

$$\frac{\partial^2 \zeta}{\partial T \partial P} = \frac{\partial^2 \zeta}{\partial P \partial T} \quad (2.31)$$

The order of differentiation is immaterial for a state function.

2.6.1 Clausius Invents Entropy

Clausius started with the equation,

$$dQ = (C_V + nR) dT - \frac{nRT}{P} dP \quad (2.32)$$

Divide all the terms in the above equation by T and get

$$\frac{dQ}{T} = \frac{C_V + nR}{T} dT - \frac{nR}{P} dP \quad (2.33)$$

$$= f(T, P) dT + g(T, P) dP \quad (2.34)$$

In the above,

$$f(T, P) = \frac{C_V + nR}{T} \quad (2.35)$$

$$g(T, P) = -\frac{nR}{P} \quad (2.36)$$

Let us check if dQ/T is an exact differential or inexact differential. We have

$$\frac{\partial f}{\partial P} = 0 \text{ and } \frac{\partial g}{\partial T} = 0 \quad (2.37)$$

Thus dQ/T is an exact differential. Let $dS = dQ/T$, then S is state variable; it is a property of the system. Clausius named the new thermodynamic variable as entropy. Clausius writes³¹ ‘ *I have intentionally formed the word entropy so as to be as similar as possible to the word energy since the two magnitudes that are given their names are so closely related in their physical significance that a certain likeness in their names has seemed appropriate.* ’

Having invented a new thermodynamic variable entropy, Clausius asserts that the entropy has a tendency to always increase in any spontaneous processes. At best it remains constant in a reversible process. It never decreases.

- First Law : The energy of the universe is a constant
- Second Law : The entropy of the universe always increases, until it reaches a maximum and shall remain the same subsequently.

2.6.2 Heat flows from hot to cold

The second law assertion that $\Delta S \geq 0$ in all processes helps us comprehend several phenomenon that occurs in nature. For example consider a certain amount of heat moving from a heat reservoir-1 at temperature T_1 to a heat reservoir-2 at temperature T_2 . The reservoir-1 loses entropy : $dS_1 = -q/T_1$. The reservoir-2 gains entropy : $dS_2 = q/T_2$. The total change in entropy is thus

$$dS = dS_1 + dS_2 = q \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (2.38)$$

$$= q \times \frac{T_1 - T_2}{T_1 \times T_2} \quad (2.39)$$

Clausius assertion that $dS \geq 0$ implies that $T_1 \geq T_2$: Heat always moves from hot to cold.

2.7 Carnot engine and the Second Law

Consider now an engine M that draws a certain amount of heat from the heat reservoir at temperature T_1 and delivers work W , see figure below.

This is permitted as far as the first law of thermodynamics is concerned. We demand that $W = q_1$. The entropy of the reservoir decreases by q_1/T_1 . The

³¹ Clausius presented this work in Züricher naturforschende Gesellschaft on April 24, 1865; see R Clausius, *On different forms of the fundamental equations of the mechanical theory of heat and their convenience for applications*, in J Kestin (Editor), *The Second Law of Thermodynamics*, Dowden-Hutchinson-Ross, Stroudsburg, PA (1976)pp.162-193

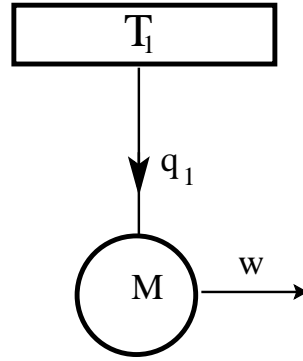


Fig. 2.3. An hypothetical engine that draws a certain amount of heat from a heat reservoir at temperature T_1 and converts the whole of it into work.

machine after delivering the work returns to its initial state to start all over again. Since entropy is a state function, there is no change in entropy of the machine. Therefore the net change in entropy in the process is $dS = -dq_1/T_1$. The second law tells that $dS \geq 0$. Hence the process of converting heat completely into work is not permitted by the second law.

Now introduce a sink at lower temperature T_2 , see figure below. The machine dumps a certain amount of heat q_2 into the sink. The sink gains an entropy of q_2/T_2 . Then we should have the following constraints:

$$q_1 - q_2 = W \quad \text{from the first law of thermodynamics (2.40)}$$

$$dS \left(= \frac{q_2}{T_2} - \frac{q_1}{T_1} \right) \geq 0 \quad \text{from the second law of thermodynamics (2.41)}$$

Consider an ideal engine for which $dS = 0$. Therefore

$$\frac{q_1}{T_1} = \frac{q_2}{T_2} \Rightarrow \frac{q_2}{q_1} = \frac{T_2}{T_1} \quad (2.42)$$

Now start with the first-law- equation,

$$W = q_1 - q_2 \Rightarrow \frac{W}{q_1} = 1 - \frac{q_2}{q_1} \Rightarrow \eta = 1 - \frac{T_2}{T_1} \quad (2.43)$$

The above is the familiar equation for the efficiency of a Carnot engine, of which we have seen earlier while discussing Carnot and his work.

Thus Clausius did what he said he would do. He had a hunch that Carnot's formula for the efficiency of an ideal heat engine, in terms of the source and sink temperatures, was correct and of fundamental import, even though he did not approve of the way Carnot arrived at the formula based on Caloric heat. But then, the caloric heat has since, given way to kinetic heat, thanks to Rumford, Mayer, and Joule. Clausius wanted to justify Carnot's principle in the light of kinetic heat. In the process he invented a new thermodynamic property called Entropy.

By demanding that entropy always increases except in ideal processes³², he derived Carnot's formula.

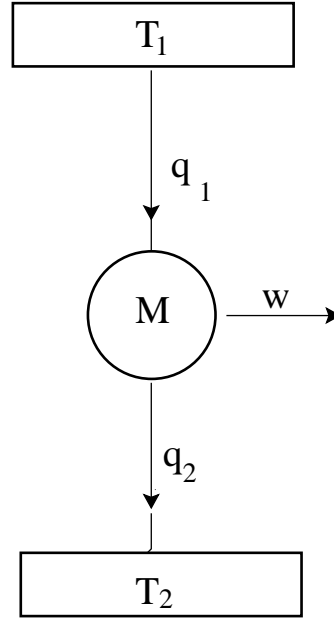


Fig. 2.4. Carnot Engine

Thus the Second law of thermodynamics can be stated as $dS \geq 0$ for any process; equality obtains for a reversible process. dS refers to change in entropy of the system plus that of the surroundings. We also know that Second law of thermodynamics is rooted in heat engine that produces work from heat. It would be interesting to see the Second law stated completely in terms of heat engines, see below.

Clausius statement of the Second law :

No process is possible whose *only final result* is the transfer of heat from a colder to a hotter body.

Kelvin-Planck statement of the Second law :

No process is possible whose *only final result* is the absorption of heat from a reservoir and conversion of the whole of heat into work.

In both the statements above, the phrase ‘ the only final result ’ is extremely profound. This phrase is there for a purpose : The familiar refrigerator transfers heat from cold to hot; but then this is not the ‘ only final result ’ ; the refrigerator is plugged to a power point; an external source does work on the refrigerator; this is what enables the refrigerator to do what it does,

³² quasi-static and reversible

In a reversible isothermal process, the gas absorbs heat and converts the whole of it into work. But then this is not the ‘ only final result ’ ; the gas also expands during the process.

The Second law can be stated in several different ways³³. From one statement, we should be able derive all other statements. I leave it to you prove that the Clausius statement of the Second law is equivalent to the Kelvin-Planck statement.

The invention of entropy and the assertion that it always increases - called the Second law of thermodynamics is going to have far-reaching consequences. It is going to change completely the way we are going to look at macroscopic phenomena. Entropy and the Second law are going to haunt us !

Thus, in thermodynamics the defining equation for entropy is

$$dS = \frac{dQ}{T}. \quad (2.44)$$

It is energy (joule) divided by temperature (kelvin). Entropy is measured in units of joule per kelvin.

2.8 Tying up loose ends

2.8.1 Boltzmann Constant

I said that in statistical mechanics, entropy is defined as proportional to logarithm of the number of micro states of a macroscopic system. Why do we need logarithm ?

The number of micro states of a composite system is the product of the number of micro states of the individual systems. A single coin has two micro states. A system of two coins has $2 \times 2 = 4$ micro states. In thermodynamics we have already defined entropy as extensive. Entropy of the individual systems add up when we combine them to form a composite system. Logarithm of a product is the sum of logarithms : $\ln(ab) = \ln a + \ln b$.

In statistical mechanics entropy is a mere number. In thermodynamics, entropy is measured in units of joules/kelvin. But we know, now, that joule and kelvin are just two units of measuring energy. The conversion factor that helps us to go from joule to kelvin is called the Boltzmann constant. It is denoted by the symbol k_B . We have $k_B = 1.3807 \times 10^{-23} \text{ j k}^{-1}$. To express statistical mechanical entropy in units of joule per kelvin, we take the proportionality constant as k_B . Thus we have,

³³ a beautiful statement of the Second law obtains when Omar Khayyam (1048 - 1131) surrenders to the irreversibility of life with the words

The Moving Finger writes; and, having writ,
 Moves on: nor all your Piety nor Wit
 Shall lure it back to cancel half a Line,
 Nor all your Tears wash out a Word of it.

$$S = k_B \ln \hat{\Omega}. \quad (2.45)$$

The above is called the Boltzmann entropy.

2.8.2 Classical Entropy is not Extensive

For an isolated system of N ideal gas molecules with energy E and confined to a volume, we found that the number of micro states is given by

$$S(E, V, N) = Nk_B \left[\ln V + \frac{3}{2} \ln \left(\frac{E}{N} \right) + \frac{3}{2} \ln \left(\frac{4\pi m}{3h^2} \right) + \frac{3}{2} \right]. \quad (2.46)$$

The first thing we notice is that the above expression for entropy is not extensive :

$$S(\lambda E, \lambda V, \lambda N) \neq \lambda S(E, V, N). \quad (2.47)$$

2.8.3 Boltzmann Counting

To restore the extensive property of entropy, Boltzmann introduced an ad-hoc notion of indistinguishable particles. He proposed that $N!$ permutations of the particles, should all be counted as one micro state since they are *indistinguishable*.

With Boltzmann counting, we have,

$$\hat{\Omega}(E, V, N) = \frac{1}{N!} \frac{V^N}{h^{3N}} \frac{(2\pi m E)^{3N/2}}{\Gamma(\frac{3N}{2} + 1)} \quad (2.48)$$

The expression for reads as,

$$S(E, V, N) = Nk_B \left[\ln \left(\frac{V}{N} \right) + \frac{3}{2} \ln \left(\frac{E}{N} \right) + \frac{3}{2} \ln \left(\frac{4\pi m}{3h^2} \right) + \frac{5}{2} \right] \quad (2.49)$$

The expression for entropy given above is extensive; it called Sackur-Tetrode equation.

Historically Boltzmann counting was proposed to resolve Gibbs paradox, which was a consequence of the non-extensive entropy. Gibbs formulated the paradox in terms of entropy of mixing of like and unlike gases.

2.8.4 Entropy of Mixing, Gibbs Paradox and its Resolution

The number of micro states of N non interacting gas molecules confined to a volume V is given by, $\hat{\Omega}(V) = V^N$, where we have retained only the dependence on V . We have ignored all other terms since they are irrelevant for the discussion below. The entropy is given by $S = N \ln(V)$ where we have set without loss of generality $k_B = 1$.

Consider a box divided by a partition into two portions by a shutter. portion 1 has N_1 molecules in volume V_1 and portion 2 has N_2 molecules in volume V_2 . Entropy of the two systems are $S_1 = N_1 \ln(V_1)$ and $S_2 = N_2 \ln(V_2)$. The two systems are in equilibrium.

Now remove the shutter and allow the gas to mix and equilibrate. We now have $N_1 + N_2$ molecules occupying a volume of $V_1 + V_2$. The entropy is $S = (N_1 + N_2) \ln(V_1 + V_2)$. Let us calculate the change in entropy when the shutter is removed. It is given by $\Delta S = S - (S_1 + S_2)$. We get,

$$\Delta S = N_1 \ln \left(\frac{V_1 + V_2}{V_1} \right) + N_2 \ln \left(\frac{V_1 + V_2}{V_2} \right). \quad (2.50)$$

We find that $\Delta S > 0$. ΔS is called entropy of mixing. Consider now a situation when $N_1/V_1 = N_2/V_2 = \rho$. The entropy of mixing can be written as,

$$\Delta S = \rho V_1 \ln \left(\frac{V_1 + V_2}{V_1} \right) + \rho V_2 \ln \left(\frac{V_1 + V_2}{V_2} \right) \quad (2.51)$$

The entropy of mixing is positive. There is some thing wrong. We expect ΔS to be zero, because there is no distinction between the system with and without the shutter.

Let us say we remove the shutter, wait for sometime and insert the shutter. We get back to the initial state. We have reversibility. Hence entropy of mixing should be zero. This is called Gibbs paradox. Boltzmann introduced the notion of indistinguishability of particles to correct for over counting of the micro states : Divide $\hat{\Omega}(V)$ by $N!$. Thus we have $\hat{\Omega} = V^N/N!$. The entropy of mixing is then, given by,

$$\Delta S = (N_1 + N_2) \ln \left(\frac{V_1 + V_2}{N_1 + N_2} \right) - N_1 \ln(V_1/N_1) - N_2 \ln(V_2/N_2) \quad (2.52)$$

$$= N_1 \ln(N_1/V_1) + N_2 \ln(N_2/V_2) - (N_1 + N_2) \ln \left(\frac{N_1 + N_2}{V_1 + V_2} \right) \quad (2.53)$$

Now let us consider the situation when $N_1/V_1 = N_2/V_2 = \rho$. We get $\Delta S = N_1 \ln(\rho) + N_2 \ln(\rho) - (N_1 + N_2) \ln(\rho) = 0$ as required. Entropy of mixing is zero. Boltzmann resolves Gibbs paradox.

Boltzmann counting can be described, at best, as a patch work. You don't demolish a well-built wall simply because it has developed a small crack. It is wise to cover the crack by pasting a paper over it. Boltzmann did just that.

A good formalism is not dismissed because of a small flaw³⁴. You look for an immediate quick-fix. Boltzmann counting provides one such quick-fix.

³⁴ Desperate and often elaborate patch work are not new to physicists. They have always indulged 'papering' when cracks appear in their understanding of science. A spectacular example is the entity aether proposed to justify the wave nature of light; Maxwell's work showed light is a wave. Waves require medium for propagation. Hence the medium aether, with exotic properties, was proposed to carry light.

In fact non extensive entropy in classical derivation is a pointer to a deeper malady. We shall discover soon, the fault is not with statistical mechanics but with classical formalism employed to describe ideal gas. For the correct resolution of the Gibbs' paradox we have to wait for the arrival of quantum mechanics and for the arrival of bosons and fermions.

2.8.5 Equivalence of Boltzmann and Clausius entropies

Let me end this lecture after making a few remarks on Boltzmann entropy and Clausius entropy. On the face of it they seem to be very different. Clausius entropy is deeply rooted in thermal phenomenon : entropy is heat divided by temperature. Boltzmann entropy is based on counting of the micro states of a system, thermal or otherwise. Let me quickly show you that these two entropies are consistent with each other for thermal systems.

Consider the Sackur-Tetrode equation, that expresses Boltzmann entropy in terms of \mathbf{E} , \mathbf{V} , and \mathbf{N} . Let us concentrate on the dependence of \mathbf{S} on \mathbf{V} which can be written as

$$\mathbf{S} = Nk_B \ln \mathbf{V} + \phi(\mathbf{E}, \mathbf{N}),$$

where ϕ is a function of \mathbf{E} and \mathbf{N} only. We have

$$\left(\frac{\partial \mathbf{S}}{\partial \mathbf{V}} \right)_{\mathbf{E}, \mathbf{N}} = \frac{Nk_B}{\mathbf{V}}. \quad (2.54)$$

The left hand side of the above equation³⁵ equals \mathbf{P}/\mathbf{T} . Therefore,

$$\frac{Nk_B}{\mathbf{V}} = \frac{\mathbf{P}}{\mathbf{T}} \Rightarrow \mathbf{PV} = Nk_B \mathbf{T}.$$

We have derived the ideal gas law.

More importantly, we have,

$$d\mathbf{S} = \frac{Nk_B}{\mathbf{V}} d\mathbf{V} = \frac{\mathbf{P} d\mathbf{V}}{\mathbf{T}} = \frac{d\mathbf{Q}}{\mathbf{T}} \quad (2.55)$$

Thus, starting from Boltzmann entropy, we have derived the thermodynamic entropy of Clausius. In the derivation of the above, I have made use of the ideal gas law $\mathbf{PV} = Nk_B \mathbf{T}$ and the fact that for an ideal gas, in an isothermal process $d\mathbf{Q} + d\mathbf{W} = 0$ which implies $d\mathbf{Q} = \mathbf{P} d\mathbf{V}$. The above equation indicates that Boltzmann entropy and Clausius entropy are indeed consistent with each other.

³⁵ for the present, assume this result. I shall derive it in the next lecture where I shall deal with partial derivatives of the fundamental equation $\mathbf{U} \equiv \mathbf{U}(\mathbf{S}, \mathbf{V}, \mathbf{N})$ or $\mathbf{S} \equiv \mathbf{S}(\mathbf{U}, \mathbf{V}, \mathbf{N})$.

3. LECTURES 6 - 8

ENTROPY, IRREVERSIBILITY, AND THE SECOND LAW

3.1 Preliminaries

We have been using the terms like quasi-static process, reversible process, and irreversible process rather freely so far. For example

- while talking about work, I said that the formula $\delta W = -PdV$ is valid only if the process is (quasi-static and) **reversible**.
- I have repeatedly emphasized that
 - only systems in **equilibrium** can be represented by points on the thermodynamic phase diagram; and
 - only a (quasi-static and) **reversible process** can be depicted by a curve in the phase diagram.
- The expression $dS = \delta Q/T$ gives the increase in entropy only when the system absorbs δQ of energy by heat **reversibly**. Hence δQ in this expression is often called reversible heat.

3.1.1 Clausius Inequality

If the process is not reversible then $dS > \delta Q/T$. This is called Clausius inequality. This should be understood as follows. The entropy change in an irreversible process is more than what you would have otherwise calculated employing the expression $\delta Q/T$. Thus, for any general process, we can write $dS \geq \delta Q/T$, wherein equality obtains when the process is (quasi - static and) reversible.

Consider a system that undergoes a cyclic process. Since S is property of the system and since the system returns to its initial state after a cycle, $dS = 0$. This is true irrespective of whether the cycle is reversible or has one or more segments that are irreversible. If the different segments that constitute the cyclic process are all reversible, then $\oint \frac{\delta Q}{T} = 0$. However if the cyclic process contains one or more irreversible segments, then, $\oint \frac{\delta Q}{T} < 0$. This is also known as Clausius inequality. Thus in general we have,

$$\oint \frac{\delta Q}{T} \leq 0, \quad (3.1)$$

where equality obtains if the cyclic process is quasi static and reversible.

It is time we get to know what exactly does one mean by a quasi static reversible process. We shall do this by considering two examples. A quasi static process, as its very name³⁶ suggests, is a process which can be viewed as if it were static - a process which is extremely slow.

3.2 Example - 1 : Adiabatic Expansion-Reversible and Irreversible

Consider a cylindrical vessel open at the top, fitted with a movable piston, and filled with some $n = 80.186$ moles of a mono atomic ideal gas. Let the cylinder be isolated by non-conducting walls so that no heat enters or exits the cylinder. Let the volume of the gas be $V_A = 1 \text{ m}^3$ and pressure $P_A = 2 \times 10^5 \text{ pa.}$, when the piston is in some position. Let us now move the piston up until the volume increases to $V_F = 2V_A = 2 \text{ m}^3$. Let us say we take some τ units of time to carry out this process. Formally we have,

$$V(t) = V_A + \frac{V_F - V_A}{\tau} \times t, \quad 0 \leq t \leq \tau. \quad (3.2)$$

The initial equilibrium state of the system can be represented by a point $A(P_A, V_A)$ in the Pressure-Volume phase diagram, see Fig. (3.1). $T_A = P_A V_A / nR = 300 \text{ k.}$

3.2.1 Switching Process

If τ is finite, the process can not be represented by a curve on the phase diagram, The system disappears from A when we start pulling the piston. When the volume reaches $V_F = 2V_A = 2 \text{ m}^3$, we stop. Then, if we wait sufficiently long, the system would come to an equilibrium state and appear at some point on the line parallel to the P -axis at $V = 2V_A = 2 \text{ m}^3$. Where exactly it will be on this line will depend on the value of τ . Let us say, the system appears at a point C , dictated by a particular value of τ . Since the system disappears at A and re-appears at C at a later time we call it a switching process and call τ the switching time. Thus, in the irreversible adiabatic process, the system switches from A to C , see Fig. (3.1). The short arrow directed from A to C indicates that the switching is from an equilibrium state A to an equilibrium state C , the process is irreversible, and hence you can not draw a continuous curve starting at A and ending at C . The process is also adiabatic.

³⁶ quasi means "having some resemblance usually by possession of certain attributes", derived from Quam (as) + si (if). For example a phonon is a quasi particle : you can treat phonon as if it is a particle. It behaves almost like a particle though strictly it is not a particle.

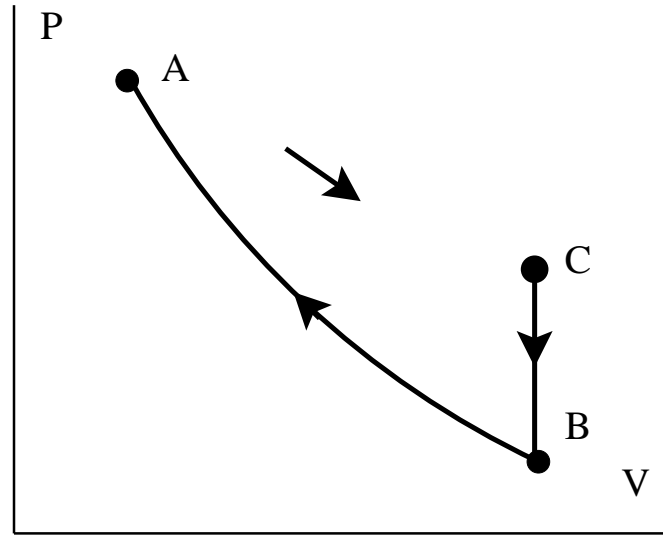


Fig. 3.1. Pressure - Volume phase diagram of an ideal gas. The system disappears at A and late appears at C. At the points A, C and B the system is in equilibrium. The process $C \rightarrow B$ and $B \rightarrow A$ are quasi static and revesible processes.

3.2.2 Quasi-static Reversible Process

Contrast this with an ideal quasi-static reversible adiabatic process which obtains in the limit $\tau \rightarrow \infty$. This process can be represented by a curve $PV^\gamma = \Theta$ describing an adiabatic process, see figure in which the points **A** and **B** are connected by a reversible adiabatic curve. Θ is a constant. $\gamma = C_P/C_V$, the ratio of the specific heats at constant pressure and constant volume. For a mono-atomic ideal gas $\gamma = 5/3$.

A quasi static reversible process is an idealization. We can imagine it as follows. The system is at **A**. Move the piston up a wee bit. The system disappears from **A** and equilibrates very quickly and re-appears at a point extremely close to **A**. Now move the piston a little bit more. Again the system disappears, equilibrates taking a very small amount of time, and appears at a point very close. Continue this until the volume becomes $V_B = 2 \times V_A = 2 \text{ m}^3$. We get a dense set of points between **A** and **B**. Slower you carry out the process, denser shall be the set of points. The line that passes through such a dense set of points, from **A** to **B** represents a quasi-static reversible process, see Fig. (3.1). Right now, do not worry about the direction of arrows marked in the figure. I shall talk about these arrows later.

The pressure and temperature can be easily calculated employing the formula $PV^\gamma = \Theta$. We get $P_B = 6.3 \times 10^4 \text{ pa.}$ and $T_B = 189 \text{ k.}$

3.2.3 Entropy and Irreversible Processes

What is the change in entropy of the system and the surroundings, when you go irreversibly and adiabatically from **A** to **C** ?

Since the process is adiabatic, there is no transaction of heat between the system and the surroundings. Therefore $\delta Q/T = 0$. Clausius inequality tells us that $dS > 0$. To calculate dS we proceed as follows.

We take the system from **C** to **B** by a convenient reversible process. The arrowed line connecting **C** to **B** denotes this quasi static reversible process. Since $V_B = V_C$, we consider a constant-volume reversible process. The change in entropy of the system when you go reversibly from **C** to **B** can be calculated as,

$$\Delta S(B \rightarrow C) = C_V \int_{T_C}^{T_B} \frac{dT}{T} = \frac{3nR}{2} \int_{250}^{189} \frac{dT}{T} = -279.7 \text{ J K}^{-1} \quad (3.3)$$

The system loses **279.7** units of entropy. Since the process is reversible, the surroundings gain an entropy of **279.7** units. Now return the system from **B** to **A** along the arrowed adiabatic curve shown in the figure. Since the system returns to the start of the cycle, the change in entropy is zero. This means that

$$\Delta S(A \rightarrow C) - 279.7 = 0.$$

There is no change in the entropy of the surroundings during the process **A** \rightarrow **C**, since the system is thermally isolated. There is no change in entropy of the surroundings during the process **B** \rightarrow **A** since it is adiabatic and reversible. The entropy of the surroundings increases by **279.7** units during the constant-volume process from **C** \rightarrow **B**.

The cyclic process **A** \rightarrow **C** \rightarrow **B** \rightarrow **A**, consists of

- an irreversible segment **A** \rightarrow **C** (adiabatic expansion)
- a reversible segment **C** \rightarrow **B** (constant - volume cooling) and
- a reversible segment **B** \rightarrow **A** (adiabatic compression).

The system starts at **A** and ends at **A** in the cyclic process; Entropy is a state variable. The change in entropy of the system in the cyclic process is therefore zero.

The change in entropy of the surroundings is **+279.7** units. The net entropy change is positive and this is because of the presence of an irreversible segment **A** \rightarrow **C** in the cyclic process **A** \rightarrow **C** \rightarrow **B** \rightarrow **A**. The whole scenario is consistent with the Second law of thermodynamics.

Also we find that for the system,

$$\oint \frac{\delta Q}{T} = -279.7 \quad (3.4)$$

The system obeys Clausius inequality : $\oint \frac{\delta Q}{T} < 0$

Let me make a simple observation before we leave this example. I said when the gas expands irreversibly and adiabatically, from V_A to $V_F = 2V_A$, there is no way we can say what shall be its pressure or temperature upon equilibration. This is not quite correct. Let me explain.

We assumed a particular finite switching time and said the system would emerge at C , for purpose of subsequent calculations. The Second law of thermodynamics tells us that the point C should be vertically above B and never below. For, if it were below B , then we need to heat the system to bring it reversibly, to B and then complete the cycle by an adiabatic and reversible compression $B \rightarrow A$. This would result in increase of entropy of the system and decrease of entropy of the surroundings; this would clearly violate the Second law of thermodynamics, and we shall see this when we do the book keeping of entropy changes in the system and the surroundings in the cyclic process.

We shall consider one more example to drive home the meaning of a quasi-static reversible process.

3.3 Example - 2 : Cooling and Heating of a Metal Coin

I have picked up this problem from Dugdale³⁷. I have a metal coin in an equilibrium state A , at 400 k. Let the heat capacity of the coin be denoted by $C_V = 1000 \text{ J k}^{-1}$. C_V is independent of temperature. The volume of the coin does not change during cooling and heating processes. The coin is cooled to an equilibrium state B at 100 k following the procedure described below.

We organize $N + 1$ heat baths³⁸ The k -th heat bath is at temperature T_k , given by,

$$T_k = 400 - \left(\frac{400 - 100}{N} \right) k. \quad (3.5)$$

We see that $T_0 = 400 \text{ k}$ and $T_N = 100 \text{ k}$. The coin constitutes the system and all the heat baths together constitute the environment.

3.3.1 Cooling Process

The coin is first plunged into bath-1 and kept inside until it comes to thermal equilibrium at T_1 . This process is repeated with bath-2 and then with bath-3 ... *etc.* Eventually when it comes out of bath- N , it is at $T = T_N = 100 \text{ k}$.

³⁷ J D Dugdale, *Entropy and its Physical Meaning*, Taylor and Francis (1998)pp.58-59

³⁸ a heat bath is one which transacts energy by heat with a system with out suffering any change in its own temperature. In other words the heat bath has infinite heat capacity. Keep a hot cup of coffee in a room. The coffee cools. Its temperature decreases. However, the temperature of the room does not increase. The room takes the heat from the cup of coffee but this does not result in increase of its temperature.

3.3.2 Change in Entropy of the coin

The coin goes from an equilibrium state \mathbf{A} to an equilibrium state \mathbf{B} . Entropy is a state function. Therefore the change in entropy of the system *i.e.*, the coin, is $(\Delta S)_S = S(\mathbf{B}) - S(\mathbf{A})$, and is given by,

$$(\Delta S)_S = C_V \int_{400}^{100} \frac{dT}{T} = -C_V \ln 4 = -1.386 C_V \text{ j k}^{-1} \quad (3.6)$$

Alternately,

$$\begin{aligned} (\Delta S)_S &= C_V \sum_{k=1}^N \int_{T_{k-1}}^{T_k} \frac{dT}{T} = C_V \sum_{k=1}^N \ln \left(\frac{T_k}{T_{k-1}} \right) \\ &= C_V \ln \left(\prod_{k=1}^N \frac{T_k}{T_{k-1}} \right) \\ &= C_V \ln \left(\frac{T_N}{T_0} \right) \\ &= -C_V \ln \left(\frac{T_0}{T_N} \right) \\ &= -C_V \ln 4 \text{ j k}^{-1} \end{aligned} \quad (3.7)$$

3.3.3 Change in Entropy of the Environment

When the coin enters the \mathbf{k} -th bath, it is at temperature T_{k-1} ; when it comes out of bath- \mathbf{k} it is at temperature T_k . It loses heat to the bath. The bath gets ΔQ of heat,

$$\Delta Q = C_V \frac{(400 - 100)}{N}. \quad (3.8)$$

The entropy of bath- \mathbf{k} changes by

$$\begin{aligned} (\Delta S)_k &= C_V \frac{300/N}{T_k} = C_V \frac{(300/N)}{400 - (300/N)k} \\ &= C_V \frac{(3/N)}{4 - (3/N)k} \text{ j k}^{-1} \end{aligned} \quad (3.9)$$

Therefore the change in the entropy of the environment is given by,

$$(\Delta S)_E = \sum_{k=1}^N (\Delta S)_k = C_V \sum_{k=1}^N \frac{3/N}{4 - (3/N)k} \quad (3.10)$$

3.3.4 Value of $(\Delta S)_E$ in the Limit of $N \rightarrow \infty$

We have

$$(\Delta S)_E = C_V \sum_{k=1}^N \frac{(3/N)}{4 - (3/N)k} \quad (3.11)$$

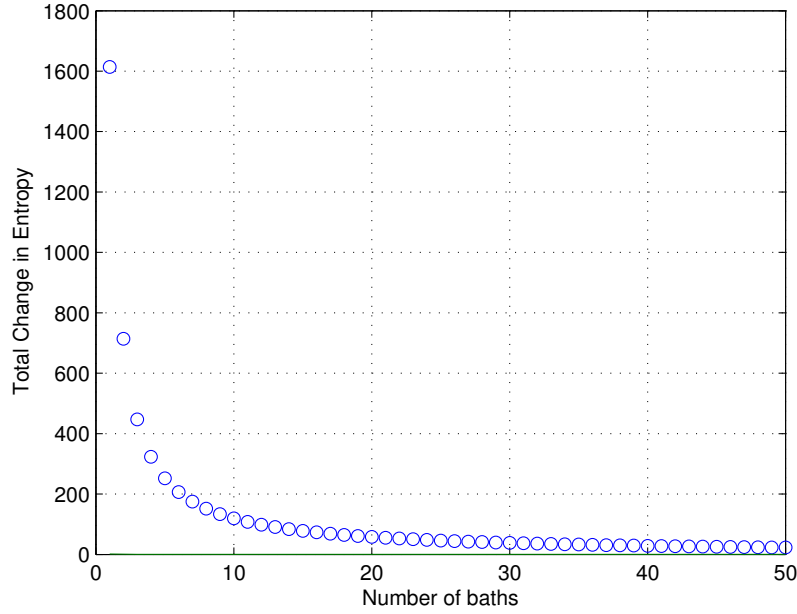


Fig. 3.2. The system *i.e.* the Coin, is cooled from 400 k to 100 k : Change in entropy of the system plus the environment denoted by the symbol ΔS , is plotted as a function of number of heat baths N . In the limit $N \rightarrow \infty$, we find that $\Delta S \rightarrow 0$. We say that in the limit $N \rightarrow \infty$, the process becomes (quasi-static and) reversible.

In the limit $N \rightarrow \infty$, the sum over k can be written as integral over $x = k/N$, where $dx = 1/N$. We get,

$$(\Delta S)_E = C_V \int_0^3 \frac{dx}{4 - x} = C_V \int_1^4 \frac{dy}{y} = +C_V \ln 4 \quad (3.12)$$

Therefore, $\Delta S = (\Delta S)_S + (\Delta S)_E = 0$.

3.3.5 Change in Entropy of the system plus the environment

The change in entropy of the system plus the environment is formally given by,

$$\Delta S = (\Delta S)_S + (\Delta S)_E.$$

We can calculate ΔS for various values of N ranging from **1** to **50**. The results on ΔS versus N are depicted in the figure below. We find that when $N \rightarrow \infty$ the total change in entropy goes to zero. $N \rightarrow \infty$ represents (quasi-static) reversible limit.

Why do we say that in the limit $N \rightarrow \infty$, the process $A \rightarrow B$ is reversible and for any finite value of N , it is irreversible ?

To answer this question, let us reverse the process and go from $B \rightarrow A$, see below.

3.3.6 Heating

Let us now reverse the process : heat the coin from **100** to **400** k by successively plunging the coin in heat baths $N-1, N-2, \dots, 1$ and eventually in the bath-**0** at **400** k.

Thus we have a cyclic process : coin is cooled from **400** to **100** k and then heated from **100** to **400** k. The coin returns to its initial state; hence change in entropy of the coin in the cyclic process is zero. Each of the baths from **1** to $N-1$, gain a certain amount of entropy while the coin gets cooled and lose the same amount of entropy when the coin gets heated. However bath- N participates only in the cooling process; it gains an entropy of $C_V \times 300/(100N)$. Bath-**0** participates only in the heating process; it loses entropy by an amount $C_V \times 300/(400N)$. Therefore the change in entropy of the environment in the cyclic process is

$$(\Delta S)_{\text{cyclic}} = C_V \frac{3}{N} \left(1 - \frac{1}{4} \right) = \frac{9C_V}{N} \quad (3.13)$$

3.3.7 Irreversible Process

For any finite N the process $A \rightarrow B$ is irreversible, because when we reverse the process, and take the system from B to A , the environment does not return to its original state; its entropy increases by an amount $9C_V/N$

3.3.8 Reversible Process

The process $A \rightarrow B$ is reversible in the limit of $N \rightarrow \infty$, because when we reverse the process, and take the system from $B \rightarrow A$, the environment returns to original state : there is no change in the entropy of the environment. Note this obtains only when $N \rightarrow \infty$.

Reversible processes are an idealization. Strictly you can not achieve a reversible process in the laboratory. However, you can make a process as close to a reversible process as required, by rendering it slower and slower.

Thus a reversible process has to be necessarily extremely slow, *i.e.* quasi static, meaning almost static.

3.4 End Remarks

The general approach followed is clear. By invoking adiabatic processes we defined a thermodynamic property called internal energy, U . However we employed internal energy in the context of processes which are not adiabatic. This allowed us to talk of change of internal energy by work as well as heat. We got the first law of thermodynamics $dU = \delta Q + \delta W$. In the same fashion, by invoking reversible processes we defined a thermodynamic property called entropy, S . We can talk of change in entropy of a system when its other properties change by thermodynamic processes. We found that if we consider the change in entropy of the system plus the change in entropy of the surroundings with which the system interacts, then this quantity is always zero in reversible processes. In other words, if the system entropy increases(decreases) in a reversible process, then the entropy of the surroundings decreases(increases) exactly by the same amount, so that the total change in entropy is always zero. Let me emphasize that this statement is true only if the process is reversible.

Having established how entropy behaves in reversible processes, we started employing entropy in the context of irreversible processes and obtained the Second law of thermodynamics. The Second law asserts that the total change in entropy in an irreversible process is always positive. Thus, in general we have $dS \geq 0$, wherein equality obtains when the process is reversible.

4. LECTURES 9 -13

PARTIAL DERIVATIVES IN THERMODYNAMICS

4.1 $U(S, V, N)$ and its partial derivatives

Let us turn our attention to some formal stuff. We start with internal energy U . We shall express U as a function of entropy S and volume V . We shall assume N to be a constant. Formally we have

$$dU = \left(\frac{\partial U}{\partial S} \right)_{V,N} dS + \left(\frac{\partial U}{\partial V} \right)_{S,N} dV \quad (4.1)$$

We have the First Law of thermodynamics

$$dU = T dS - P dV.$$

Equating the coefficients of dS and dV in the above two expressions for dU , we identify,

$$T = \left(\frac{\partial U}{\partial S} \right)_{V,N}; \quad P = - \left(\frac{\partial U}{\partial V} \right)_{S,N}. \quad (4.2)$$

4.2 $S(U, V, N)$ and its partial derivatives

In statistical mechanics or statistical thermodynamics we take entropy as a basic entity and express it as a function of energy and volume for a fixed number of molecules : $S \equiv S(U, V)$. We can change entropy by changing energy, and, volume. Formally we have

$$dS = \left(\frac{\partial S}{\partial U} \right)_{V,N} dU + \left(\frac{\partial S}{\partial V} \right)_{U,N} dV \quad (4.3)$$

We need to identify the partial derivatives in the above expression in terms of the intensive properties T and P . To this end we proceed as follows. We have,

$$dU = T dS - P dV \quad (4.4)$$

From the above we get,

$$TdS = dU + PdV \quad (4.5)$$

$$dS = \frac{1}{T}dU + \frac{P}{T}dV \quad (4.6)$$

Equating the coefficients of dU , and dV , we get

$$\left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{1}{T}; \quad \left(\frac{\partial S}{\partial V}\right)_{U,N} = \frac{P}{T}. \quad (4.7)$$

4.2.1 Properties of Partial Derivative

Thus we find the following important property of partial derivatives. If x , y and z , are three variables each dependent on the other two, then

$$\left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{\left(\frac{\partial y}{\partial x}\right)_z} \quad (4.8)$$

Another important property of partial derivatives is :

$$\left(\frac{\partial U}{\partial S}\right)_V \times \left(\frac{\partial S}{\partial V}\right)_U \times \left(\frac{\partial V}{\partial U}\right)_S = -1 \quad (4.9)$$

We see this by noticing that the left hand side of the above equation can be identified as

$$(T) \times \left(\frac{P}{T}\right) \times \left(\frac{1}{-P}\right) = -1 \quad (4.10)$$

where we have made use of the first property of the partial derivative

$$\left(\frac{\partial V}{\partial U}\right)_S = \frac{1}{\left(\frac{\partial U}{\partial V}\right)_S} = \frac{1}{(-P)} \quad (4.11)$$

In terms of x , y , and z , this property reads as,

$$\left(\frac{\partial x}{\partial y}\right)_z \times \left(\frac{\partial y}{\partial z}\right)_x \times \left(\frac{\partial z}{\partial x}\right)_y = -1 \quad (4.12)$$

4.2.2 Chemical Potential

We can include explicitly the dependence on N and write the fundamental equation $U \equiv U(S, V, N)$. The partial derivative of U with respect to N is called the chemical potential, and is usually denoted by the symbol μ . We have,

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}. \quad (4.13)$$

In the entropic picture, we have,

$$\left(\frac{\partial S}{\partial N}\right)_{U,V} = -\frac{\mu}{T}. \quad (4.14)$$

4.3 Closed System and Helmholtz Free Energy

Let us consider a closed system - a system which is in thermal contact with the surroundings. It exchanges energy but is closed to exchange of matter. The system is in thermal equilibrium with its surroundings³⁹ whence the system and its surroundings are at the same temperature. Thus temperature is a natural variable for describing the system.

Consider thermodynamics processes occurring at constant temperature. We have, from the first law of thermodynamics,

$$dU = \delta Q + \delta W \quad (4.15)$$

$$= TdS + \delta W \quad (4.16)$$

$$dU - TdS = \delta W \quad (4.17)$$

Since the temperature remains constant, we can write the above as,

$$d(U - TS) = \delta W.$$

For a process that takes the system reversibly from an equilibrium state **1** to an equilibrium state **2**, at constant temperature T , we can write,

$$(U_2 - TS_2) - (U_1 - TS_1) = W \quad (4.18)$$

where W is the work done during the isothermal reversible process $\mathbf{1} \rightarrow \mathbf{2}$. This suggests that we can treat $U - TS$ as a thermodynamic property of the system. We call it Helmholtz free energy and employ it for studying closed systems.

It is readily seen that the principle of minimum energy and maximum entropy can be combined into a single principle of minimum free energy. Spontaneously a system would go to a state with minimum free energy. We also see that work done on the system is minimum for a reversible process.

4.3.1 Free Energy and the Second Law

We can state the second law of thermodynamics as

$$W \geq \Delta F, \quad (4.19)$$

where the equality obtains for a reversible process.

³⁹ we have earlier seen that equality of temperature is a universal indicator of thermal equilibrium

4.4 Legendre Transform : General

Thus free energy provides an alternate formulation of thermodynamics suitable for describing closed system. In what follows we shall see of general alternate formulations of thermodynamics based on Legendre transform.

To start with we shall consider passage from internal energy picture suitable for studying isolated systems to free energy picture, suitable for closed systems, as a transform :

$$S \rightarrow T \text{ and } U \rightarrow F.$$

The basic idea is to view the curve $U(S)$, as an envelop of a set of tangents; each tangent is specified by its slope and the intercept. The slope is temperature, T and the intercept is Free energy, F . Thus we go from U versus S picture to F versus T picture.

Consider f , a quantity that varies when x is varied.

- We can prepare a table of values of x and the corresponding values of f . Also,
- we can trace it as a curve in the $x - f$ coordinate plane with f on the y -axis.

Let us now look for an alternate way of expressing the contents of the table or of the graph.

- Take a point $(x, y = f(x))$ on the graph.
- Draw a line tangent to the curve at this point. Let the slope of this tangent be denoted by m . Note that m depends of x . We can prepare a table with m and the corresponding x . We can draw a curve to represent the table. Will this description provide a unique correspondence to $f(x)$? We see it does not. All curves that are parallel to the curve $f(x)$ shall have the same representation. A way to distinguish one curve from the other in the family of parallel curves is to specify the intercept C for each tangent, see figure below.
- We see from the figure,

$$\frac{f(x) - C}{x} = m \quad (4.20)$$

In other words,

$$C = f(x) - m \times x \quad (4.21)$$

$$m = \frac{df}{dx} \quad (4.22)$$

- We see that $C(m)$ provides an alternate description of $f(x)$.
- We have Legendre-transformed $x \rightarrow m$ and $f \rightarrow C$.

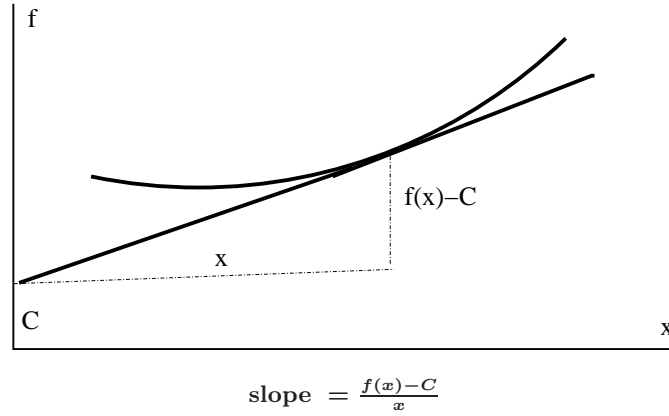


Fig. 4.1. Principle of Legendre Transform : Intercept C is expressed as a function of slope

4.4.1 Legendre Transform : $S \rightarrow T$ and $U(S, V, N) \rightarrow F(T, V, N)$

Take f as U and x as S . We see that the slope m corresponds to temperature, T . Denote the intercept by F and we have the Legendre transform : $S \rightarrow T$ and $U \rightarrow F$.

$$F(T, V, N) = U - TS; \quad T = \left(\frac{\partial U}{\partial S} \right)_{V, N} \quad (4.23)$$

We carry out the Legendre transform as follow.

Start with $U \equiv U(S, V, N)$.

Derive an expression for the partial derivative of U with respect to S . This partial derivative is a function of S, V and N .

Equate it to T and invert it to express $S \equiv S(T, V, N)$.

Replace S by this function in the expression : $U(S, V, N) - TS$.

You will get an expression involving only T, V , and N . This is the desired expression for the free energy $F(T, V, N)$.

The problem below shall illustrate the operations involved.

4.5 Free Energy : Illustrative Example

Let the fundamental equation of substance be given by

$$U(S, V, N) = \Theta \frac{N^2 + S^2}{V} \quad (4.24)$$

where Θ is a constant.

In the first step we derive an expression for temperature as a function of S, V and N . We have

$$T(S, V, N) = \left(\frac{\partial U}{\partial S} \right)_{V, N} = \Theta \frac{2S}{V} \quad (4.25)$$

In the second step, we invert the above expression and get S as a function of T , V , and N .

$$S(T, V, N) = \frac{TV}{2\Theta} \quad (4.26)$$

In the third step we carry out the Legendre transform :

$$F = U(S(T, V, N), V, N) - TS(T, V, N) \quad (4.27)$$

$$= \Theta \left(\frac{N^2 + (T^2 V^2)/(4\Theta^2)}{V} \right) - T \frac{TV}{2\Theta} \quad (4.28)$$

$$= \frac{\Theta N^2}{V} - \frac{T^2 V}{4\Theta} \quad (4.29)$$

The independent variables of F are T , V and N .

By taking the partial derivatives of F with respect to T , V , and N we obtain expressions for entropy, pressure and chemical potential respectively. We have

$$\begin{aligned} F(T, V, N) &= U - TS \\ dF &= dU - TdS - SdT \\ &= TdS - PdV + \mu dN - TdS - SdT \\ &= -PdV - SdT + \mu dN \end{aligned} \quad (4.30)$$

Thus we get,

$$P = - \left(\frac{\partial F}{\partial V} \right)_{T, N} = \Theta \frac{N^2}{V^2} + \frac{1}{4\Theta} T^2 \quad (4.31)$$

$$S = - \left(\frac{\partial F}{\partial T} \right)_{V, N} = \frac{1}{2\Theta} TV \quad (4.32)$$

$$\mu = + \left(\frac{\partial F}{\partial N} \right)_{T, V} = 2\Theta \frac{N}{V} \quad (4.33)$$

4.6 Enthalpy

Let us now consider processes taking place at constant pressure⁴⁰. We start with the first law of thermodynamics.

⁴⁰ Chemists are usually interested in such processes; the chemical reactions they study occur at constant atmospheric pressure.

$$\begin{aligned}
dU &= \delta Q + \delta W \\
&= \delta Q - PdV \\
dU + PdV &= \delta Q \\
d(U + PV) &= \delta Q \\
(U_2 + PV_2) - (U_1 + PV_1) &= Q
\end{aligned} \tag{4.34}$$

Let us denote the quantity $U + PV$ by the symbol H and call it enthalpy.

Thus the change in H when the system undergoes a reversible process, equals energy transacted by heat, or what the chemists call as *heat of reaction*.

Enthalpy increases when the chemical reaction is endothermic, *i.e.* when energy enters the system by heat. Enthalpy is negative if the process is exothermic, whence energy exits the system by heat.

4.6.1 Legendre Transform : $V \rightarrow P$ and $U(S, V, N) \rightarrow H(S, P, N)$

It is easily checked that enthalpy is a Legendre transform :

$$V \rightarrow P; \quad U(S, V, N) \rightarrow H(S, P, N) \tag{4.35}$$

$$H(S, P, N) = U + PV; \quad P = - \left(\frac{\partial U}{\partial V} \right)_{S, N}. \tag{4.36}$$

4.6.2 Enthalpy : Illustrative Example

Consider the fundamental equation,

$$U(S, V, N) = \Theta \frac{N^2 + S^2}{V} \tag{4.37}$$

An expression for pressure in terms of S, V, N can be derived, see below.

$$P(S, V, N) = - \left(\frac{\partial U}{\partial V} \right)_{S, N} = \Theta \frac{N^2 + S^2}{V^2} \tag{4.38}$$

Now take P as an independent variable and express V as a function of P :

$$V = \sqrt{\Theta \frac{N^2 + S^2}{P}} \tag{4.39}$$

Enthalpy is formally given by

$$H(S, P, N) = U(S, V, N) + PV(S, P, N).$$

Eliminating V from the above we get

$$H(S, P, N) = 2PV \quad (4.40)$$

$$= 2P \sqrt{\Theta \frac{N^2 + S^2}{P}} \quad (4.41)$$

$$= 2\Theta^{1/2} \sqrt{P (N^2 + S^2)} \quad (4.42)$$

By taking the partial derivatives of enthalpy with respect to S , P and N , we can derive expressions, see below, for T , V and μ . We have,

$$H(S, P, N) = U + PV \quad (4.43)$$

$$dH = dU + PdV + VdP \quad (4.44)$$

$$= TdS - PdV + \mu dN + PdV + VdP \quad (4.45)$$

$$= TdS + VdP + \mu dN \quad (4.46)$$

We see immediately that,

$$T = \left(\frac{\partial H}{\partial S} \right)_{P, N} = 2\Theta^{1/2} \frac{(S/N)\sqrt{P}}{\sqrt{1 + (S/N)^2}} \quad (4.47)$$

$$V = \left(\frac{\partial H}{\partial P} \right)_{S, N} = \Theta^{1/2} \frac{\sqrt{N^2 + S^2}}{\sqrt{P}} \quad (4.48)$$

$$\mu = \left(\frac{\partial H}{\partial N} \right)_{S, P} = 2\Theta^{1/2} \frac{\sqrt{P}}{\sqrt{1 + (S/N)^2}} \quad (4.49)$$

4.7 Gibbs Free Energy

Gibbs free energy is denoted by the symbol G . It obtained by carrying out Legendre transform of two variables, S and V . S is transformed to T , V is transformed to P and U gets transformed to G . Gibbs free energy is a function of T , P , and N .

4.7.1 Legendre Transform : $S \rightarrow T$, $V \rightarrow P$, and $U(S, V, N) \rightarrow G(T, P, N)$

We have,

$$G(T, P, N) = U - TS + PV; \quad T = \left(\frac{\partial U}{\partial S} \right)_{V, N}; \quad P = - \left(\frac{\partial U}{\partial V} \right)_{S, N} \quad (4.50)$$

4.7.2 Legendre Transform : $S \rightarrow T$ and $H(S, P, N) \rightarrow G(T, P, N)$

Alternately, we can obtain Gibbs free energy as a Legendre transform of enthalpy. We have $H \equiv H(S, P, N)$, and we transform $S \rightarrow T$

$$G(T, P, N) = H - TS; \quad T = \left(\frac{\partial H}{\partial S} \right)_{P, N}. \quad (4.51)$$

4.7.3 Gibbs Free Energy : An Illustrative Example

Gibbs Free Energy : Illustrative Example We have

$$H(S, P, N) = 2\Theta^{1/2} \sqrt{P(N^2 + S^2)} \quad (4.52)$$

$$\left(\frac{\partial H}{\partial S} \right)_{P,N} = T = 2\Theta^{1/2} \frac{S\sqrt{P}}{\sqrt{N^2 + S^2}} \quad (4.53)$$

Now consider T as an independent variable and express S as a function of T , P , and N . We get,

$$S = \frac{NT}{\sqrt{4\Theta P - T^2}} \quad (4.54)$$

$$G(T, P, N) = H(S(T, P, N), P, N) - TS(T, P, N) \quad (4.55)$$

$$= N\sqrt{4\Theta P - T^2} \quad (4.56)$$

By taking partial derivatives of G with respect to the variables T , P , and N , we can derive expressions for S , V , and μ . We have,

$$G = U - TS + PV \quad (4.57)$$

$$dG = -SdT + VdP + \mu dN \quad (4.58)$$

We see immediately,

$$S = - \left(\frac{\partial G}{\partial T} \right)_{P,N} = \frac{NT}{\sqrt{4\Theta P - T^2}} \quad (4.59)$$

$$V = + \left(\frac{\partial G}{\partial P} \right)_{T,N} = \frac{2\Theta N}{\sqrt{4\Theta P - T^2}} \quad (4.60)$$

$$\mu = + \left(\frac{\partial G}{\partial N} \right)_{T,P} = \sqrt{4\Theta P - T^2} \quad (4.61)$$

4.8 Euler theorem for Homogeneous Functions

Let $f(x_1, x_2, \dots, x_N)$ be an n -th order homogeneous function of x_1, x_2, \dots, x_N . We can express this formally as,

$$f(\lambda x_1, \lambda x_2, \dots, \lambda x_N) = \lambda^n f(x_1, x_2, \dots, x_N). \quad (4.62)$$

Differentiate both sides of the equation with respect to λ . We get,

$$\sum_{i=1}^N \frac{\partial f}{\partial(\lambda x_i)} \frac{\partial(\lambda x_i)}{\partial \lambda} = n\lambda^{n-1} f(x_1, x_2, \dots, x_N) \quad (4.63)$$

$$\sum_{i=1}^n x_i \frac{\partial f}{\partial(\lambda x_i)} = n\lambda^{n-1} f(x_1, x_2, \dots, x_N) \quad (4.64)$$

The above is valid for any value of λ . let $\lambda = 1$; we get, the theorem for homogeneous functions discovered by Euler⁴¹ and is given by,

$$nf(x_1, x_2, \dots, x_N) = \sum_{i=1}^N x_i \frac{\partial f}{\partial x_i}. \quad (4.65)$$

Let us apply Euler's theorem to functions in thermodynamics. The thermodynamic functions are first order homogeneous. We call first order homogeneous functions as extensive. For example the internal energy U is first order homogeneous function of S , V , and N , which are also extensive. Helmholtz free energy F is first order homogeneous function of extensive variables V and N and intensive variable T ; enthalpy is first order homogeneous in S and N , and zeroth order homogeneous in P . Gibbs' free energy is a first order homogeneous function of N ; it depends also on intensive properties T and P ; and so on. Therefore in thermodynamics we have $n = 1$.

4.8.1 Euler Relation and Internal Energy

Let us explicitly derive the Euler relation for the internal energy U , which is a first order homogeneous function of entropy S , volume V , and number of particles N . We express this formally as

$$U(\lambda S, \lambda V, \lambda N) = \lambda U(S, V, N). \quad (4.66)$$

Let us differentiate both sides of the above equation with respect to λ . We get,

$$U(S, V, N) = \frac{\partial U}{\partial(\lambda S)} \frac{\partial(\lambda S)}{\partial \lambda} + \frac{\partial U}{\partial(\lambda V)} \frac{\partial(\lambda V)}{\partial \lambda} + \frac{\partial U}{\partial(\lambda N)} \frac{\partial(\lambda N)}{\partial \lambda} \quad (4.67)$$

$$= \frac{\partial U}{\partial(\lambda S)} S + \frac{\partial U}{\partial(\lambda V)} V + \frac{\partial U}{\partial(\lambda N)} N \quad (4.68)$$

The above is valid for any number λ . Let us set $\lambda = 1$. We get,

$$U(S, V, N) = \left(\frac{\partial U}{\partial S} \right)_{V, N} S + \left(\frac{\partial U}{\partial V} \right)_{S, N} V + \left(\frac{\partial U}{\partial N} \right)_{S, V} N \quad (4.69)$$

$$= TS - PV + \mu N \quad (4.70)$$

The Euler equation above is one of the most beautiful equations in thermodynamics. It tells us, how the seven thermodynamic properties four of which are extensive and rest three intensive, are related.

⁴¹ Leonhard Euler (1707-1783) is one of the most eminent mathematicians. He is also widely considered to be the most prolific mathematician of all time.

I told you in an earlier lecture, that what resides in a thermodynamic system is energy. The energy comes into the system or exits from the system either by heat or by work. There is no way to tell the energy that has come into the system by work from the energy that has come from heat. Euler tells that you may not be able to distinguish between "Heat" and "Work", but you can definitely do a book keeping and say how much of the internal energy has come from heat and how much from $P - V$ work and/or $\mu - N$ work.

4.8.2 Euler Relation for Helmholtz Free Energy

Helmholtz free energy F is a function of T , V and N . Of the three variables V and N are extensive properties. Hence, Euler theorem reads as

$$F = \left(\frac{\partial F}{\partial V} \right)_{T,N} V + \left(\frac{\partial F}{\partial N} \right)_{T,V} N = -PV + \mu N \quad (4.71)$$

4.8.3 Euler Relation for Enthalpy

Enthalpy H is a function of S , P , and N . Of these S and N are extensive properties. Hence Euler theorem reads as,

$$H = \left(\frac{\partial H}{\partial S} \right)_{P,N} S + \left(\frac{\partial H}{\partial N} \right)_{S,P} N = TS + \mu N \quad (4.72)$$

4.8.4 Euler Relation for Gibbs Free Energy

Gibbs free energy G is a function of T , P , and N . There is only one dependent variable which is extensive, namely N . Hence Euler theorem reads as,

$$G = \left(\frac{\partial G}{\partial N} \right)_{T,P} N = \mu N \quad (4.73)$$

4.9 Gibbs-Duhem Relation

Start with the Euler relation, for the internal energy,

$$U = TS - PV + \mu N. \quad (4.74)$$

Take the derivatives on both sides and get,

$$dU = TdS - PdV + \mu dN + sdT - VdP + Nd\mu. \quad (4.75)$$

The first law of thermodynamics tells us that

$$dU = TdS - PdV + \mu dN.$$

Hence we find, $\mathbf{S}d\mathbf{T} - \mathbf{V}d\mathbf{P} + \mathbf{N}d\boldsymbol{\mu} = 0$, which can be written as,

$$d\boldsymbol{\mu} = - \left(\frac{\mathbf{S}}{\mathbf{N}} \right) d\mathbf{T} + \left(\frac{\mathbf{V}}{\mathbf{N}} \right) d\mathbf{P}. \quad (4.76)$$

Let $\mathbf{s} = \mathbf{S}/\mathbf{N}$ denote entropy per particle and $\mathbf{v} = \mathbf{V}/\mathbf{N}$ denote the volume per particle. \mathbf{s} and \mathbf{v} are now intensive properties. We can now write the above equation as,

$$d\boldsymbol{\mu} = -\mathbf{s}d\mathbf{T} + \mathbf{v}d\mathbf{P}. \quad (4.77)$$

The above is called Gibbs-Duhem⁴² relation. It tells us the three intensive properties \mathbf{T} , \mathbf{P} , and $\boldsymbol{\mu}$ are not all independent. If you know any two, the third can be obtained from them.

Gibbs - Duhem relation can be derived starting from Helmholtz free energy, enthalpy, or the Gibbs free energy . I leave this as a exercise for you.

⁴² Josiah Willard Gibbs (1839 -1903), an American physicist and one of the founding fathers of statistical mechanics; Pierre Maurice Marie Duhem (1861-1916), a French physicist, mathematician, historian and philosopher of science.

5. LECTURES 14 - 18

MAXWELL RELATIONS

5.1 Basic Idea

Let us take a look at Maxwell relations involving partial derivatives of intensive variables taken with respect to extensive variables.

We have internal energy U expressed as a function of S , and V : $U \equiv U(S, V)$. Let us take partial derivative of U with respect S first and with respect to V next. We get, in general, a function of S and V . Now let us take the partial derivative of U with respect to V first and then with respect to S next. We should get the same result.

Maxwell relations are based on this observation that the order with which we take the partial derivatives does not matter. Either way we should get the same result :

$$\left(\frac{\partial}{\partial V} \left[\left(\frac{\partial U}{\partial S} \right)_V \right] \right)_S = \left(\frac{\partial}{\partial S} \left[\left(\frac{\partial U}{\partial V} \right)_S \right] \right)_V \quad (5.1)$$

We can write the above in a more suggestive way,

$$\frac{\partial^2 U}{\partial V \partial S} = \frac{\partial^2 U}{\partial S \partial V} \quad (5.2)$$

5.1.1 Internal Energy and First Maxwell Relation

We identify that the partial derivative of $U(S, V)$ with respect to S is temperature $T(S, V)$. The negative of partial derivative of $U(S, V)$ with respect to V is pressure $P(S, V)$. Then we write,

$$\left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial P}{\partial S} \right)_V \quad (5.3)$$

The above is called the first Maxwell relation.

5.1.2 Helmholtz Free Energy and Second Maxwell Relation

We can do the same thing with Helmholtz free energy, $F(T, V)$. We have

$$\left(\frac{\partial}{\partial V} \left[\left(\frac{\partial F}{\partial T} \right)_V \right] \right)_T = \left(\frac{\partial}{\partial T} \left[\left(\frac{\partial F}{\partial V} \right)_T \right] \right)_V \quad \text{or} \quad \frac{\partial^2 F}{\partial V \partial T} = \frac{\partial^2 F}{\partial T \partial V} \quad (5.4)$$

We identify that the partial derivative of F with respect to T is $-S$; the partial derivative of F with respect to V is $-P$. Then we get the second Maxwell relation,

$$\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V \quad (5.5)$$

5.1.3 Enthalpy and Third Maxwell Relation

Consider now enthalpy H which is a function of S and P . We get,

$$\left(\frac{\partial H}{\partial P} \left[\left(\frac{\partial H}{\partial S} \right)_P \right] \right)_S = \left(\frac{\partial}{\partial S} \left[\left(\frac{\partial H}{\partial P} \right)_S \right] \right)_P \quad \text{or} \quad \frac{\partial^2 H}{\partial P \partial S} = \frac{\partial^2 H}{\partial S \partial P} \quad (5.6)$$

We identify that the partial derivative of H with respect to S is T ; the partial derivative of H with respect to P is V . Then we get the third Maxwell relation,

$$\left(\frac{\partial V}{\partial S} \right)_P = \left(\frac{\partial T}{\partial P} \right)_S \quad (5.7)$$

5.1.4 Gibbs Free Energy and Fourth Maxwell Relation

Starting with Gibbs free energy $G(T, P)$, we get,

$$\left(\frac{\partial}{\partial P} \left[\left(\frac{\partial G}{\partial T} \right)_P \right] \right)_T = \left(\frac{\partial}{\partial T} \left[\left(\frac{\partial G}{\partial P} \right)_T \right] \right)_P \quad \text{or} \quad \frac{\partial^2 G}{\partial P \partial T} = \frac{\partial^2 G}{\partial T \partial P} \quad (5.8)$$

We identify that the partial derivative of G with respect to T is $-S$; the partial derivative of G with respect to P is V . Then we get the fourth Maxwell relation,

$$-\left(\frac{\partial S}{\partial P} \right)_T = \left(\frac{\partial V}{\partial T} \right)_P \quad (5.9)$$

5.2 Mnemonic for Maxwell Relations

Maxwell relations are easy to derive. However it would be extremely useful to recall them directly, whenever we need them. There is a simple mnemonic device described in the book by Finn⁴³ that helps us write the Maxwell relation directly. Finn invites us to join the **S**ociety for **P**revention of **T**eaching **V**ectors, written as

⁴³ C B P Finn, Thermal Physics, Second Edition, Chapman and Hall (1993)pp.121-122

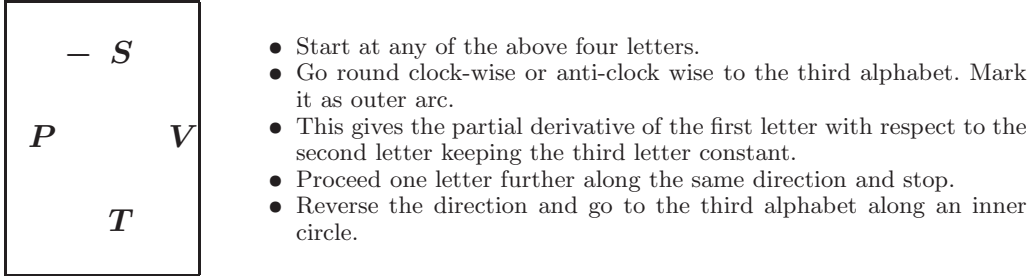


Fig. 5.1. Mnemonic base for Maxwell relations

- Get the partial derivative of the first letter with respect to the second letter keeping the third letter constant, along the inner circle.
- Maxwell relation obtains upon equating the partial derivative of the outer circle to the partial derivative of the inner circle
- When both P and S occurs in a partial derivative, put a negative sign. The negative sign on the top left corner should remind us of this.

5.2.1 Mnemonic for First Maxwell Relation from $U(S, V)$

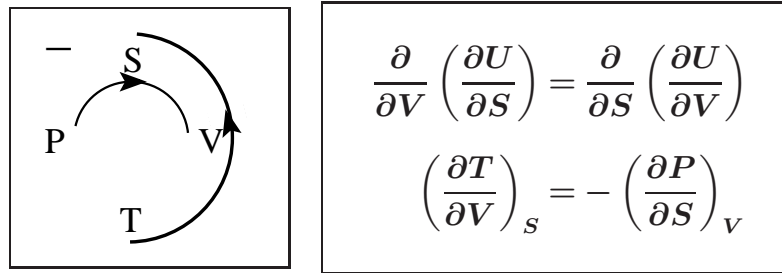


Fig. 5.2. Mnemonic for the first Maxwell relation

5.2.2 Mnemonic for Second Maxwell Relation from $F(T, V)$

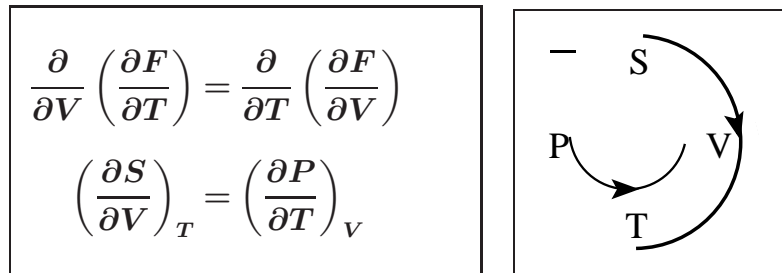


Fig. 5.3. Mnemonic for the second Maxwell relation

5.2.3 Mnemonic for Third Maxwell Relation from $H(S, P)$

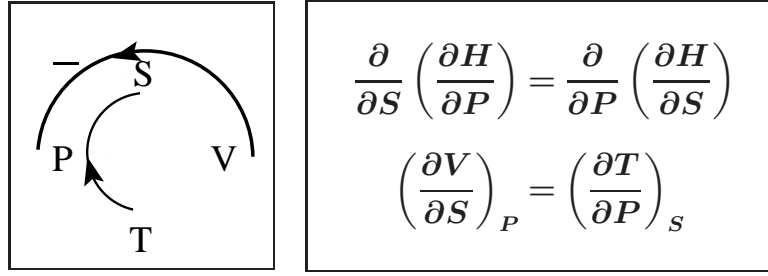


Fig. 5.4. Mnemonic for the third Maxwell relation

5.2.4 Mnemonic for Fourth Maxwell Relation from $G(T, P)$

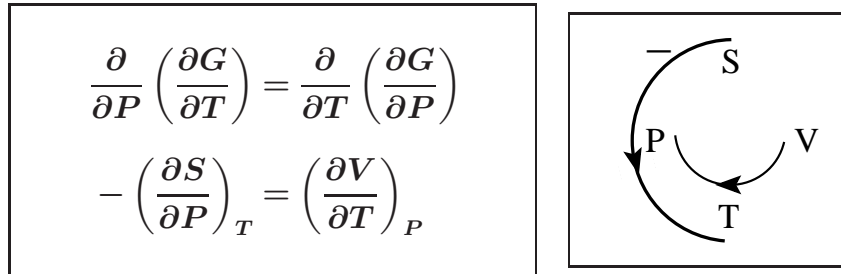


Fig. 5.5. Mnemonic for the fourth Maxwell relation

5.3 Isothermal Compression

Take a piece of metal. Squash it reversibly from an initial pressure P_1 to a final pressure $P_2 > P_1$ at constant temperature. The metal shall give away a certain amount say q of heat. Aim is to calculate q .

To this end, we start with expressing entropy as a function of temperature and pressure : $S \equiv S(T, P)$. we have,

$$dS = \left(\frac{\partial S}{\partial T} \right)_P dT + \left(\frac{\partial S}{\partial P} \right)_T dP \quad (5.10)$$

$$dq = TdS \quad (5.11)$$

$$= T \left(\frac{\partial S}{\partial T} \right)_P dT + T \left(\frac{\partial S}{\partial P} \right)_T dP \quad (5.12)$$

In the above, the first term on the right hand side is zero since the process is isothermal : $dT = 0$. Therefore,

$$d\mathbf{q} = T \left(\frac{\partial S}{\partial P} \right)_T dP \quad (5.13)$$

Employing the first Maxwell relation, the above can be written as,

$$d\mathbf{q} = -T \left(\frac{\partial V}{\partial T} \right)_P dP \quad (5.14)$$

The coefficient of thermal volume expansion at constant pressure is defined as

$$\gamma = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$$

Therefore, $d\mathbf{q} = -\gamma T V dP$, and hence $\mathbf{q} = -\gamma T V (P_2 - P_1)$. This expression for \mathbf{q} is true only if the change in volume is negligible during compression and the initial and final pressures are P_1 and P_2 respectively.

In we want to take into account the change of V during the compression process,

$$\mathbf{q} = -\gamma T \int_{P_1}^{P_2} dP V(P) dP$$

where $V \equiv V(P)$ is the dependence of the volume on pressure during the compression process.

When you squash a piece of metal it gets heated. In the quasi static reversible process considered the temperature is maintained constant; hence the energy is instantaneously liberated to the surrounding as heat. Since the system loses energy, \mathbf{q} is negative.

5.4 Adiabatic Compression

Start with $T \equiv T(S, P)$. T can change either by change of S at constant P and/or change of P at constant entropy. For an adiabatic process the change of S at constant P is zero, since there is no heat transaction with the surroundings. Hence,

$$dT = \left(\frac{\partial T}{\partial P} \right)_S dP \quad (5.15)$$

Use the following identity of the partial derivatives,

$$\left(\frac{\partial T}{\partial P} \right)_S \times \left(\frac{\partial P}{\partial S} \right)_T \times \left(\frac{\partial S}{\partial T} \right)_P = -1 \quad (5.16)$$

Take the second term. Employing a property of the partial derivatives, and the fourth Maxwell relation,

$$\left(\frac{\partial P}{\partial S}\right)_T = \frac{1}{\left(\frac{\partial S}{\partial P}\right)_T} = \frac{1}{-\left(\frac{\partial V}{\partial T}\right)_P} = -\frac{1}{\gamma V} \quad (5.17)$$

Maxwell relation gives,

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P = -\gamma V \quad (5.18)$$

We also have

$$T\left(\frac{\partial S}{\partial T}\right)_P = C_P \quad (5.19)$$

We get,

$$\left(\frac{\partial T}{\partial P}\right)_S \times \left(-\frac{1}{\gamma V}\right) \left(\frac{C_P}{T}\right) = -1 \quad (5.20)$$

Thus in an adiabatic squashing of a metal piece the rise in temperature is given by,

$$dT = \frac{\gamma VT}{C_P} dP \quad (5.21)$$

5.5 Rubber Band and Entropic Tension

When you stretch a rubber band, it develops a linear tension \mathcal{F} which opposes the stretching process; work done is $dW = +\mathcal{F}dl$ for a quasi static reversible stretching; dl is the infinitesimal increase in length. Work is done on the rubber band and hence the expression for work is consistent with the sign convention.

In an earlier lecture, see Lectures - II, while discussing about work, I had mentioned that rubber elasticity has its origin in entropy. Let me elaborate on this now. A rubber band is made of a large number of strands. Each strand is a chain of molecules. These chains are intertwined. Each chain is full of twists and turns and is in a coiled state. Take any single strand. It is obvious that the number of configurations in which the chain can organize itself is larger when the strand is coiled than when it is straight. Thus the entropy of a coiled strand is more than that of a straight strand. When you stretch a rubber band the strands untwine and straighten up. Entropy decreases. The rubber band tries to coil back and increase its entropy. This inherent tendency to increase its entropy manifests itself as a linear tension.

Let us look at the stretching of a rubber band thermodynamically. We ignore the very small change in volume that accompanies stretching. This means we can ignore $-PdV$ work compared to $+\mathcal{F}dl$ work. We can write the first law of

thermodynamics as $dU = \delta Q + \mathcal{F}dl$. Thus we have a \mathcal{F}, V, T system instead of P, V, T with $-\mathcal{F}$ replacing P in all the thermodynamic relations. In particular the Maxwell relations are modified : Replace P by $-\mathcal{F}$; and V by l . We have the modified mnemonic base for the rubber-thermodynamics, see the boxed item below.

$-S$
$-\mathcal{F} \quad l$
T

From the mnemonic we can write down the second Maxwell relation (originating from Helmholtz free energy) as,

$$\left(\frac{\partial S}{\partial l}\right)_T = -\left(\frac{\partial \mathcal{F}}{\partial T}\right)_l \quad (5.22)$$

Since S decreases with increase of l , $\left(\frac{\partial S}{\partial l}\right)_T < 0$. From the Maxwell relation we see that this is equivalent to

$$\left(\frac{\partial \mathcal{F}}{\partial T}\right)_l > 0.$$

Consider the following properties of partial derivatives,

$$\left(\frac{\partial l}{\partial T}\right)_{\mathcal{F}} = \frac{1}{\left(\frac{\partial T}{\partial l}\right)_{\mathcal{F}}} \quad (5.23)$$

$$\left(\frac{\partial \mathcal{F}}{\partial T}\right)_l \times \left(\frac{\partial T}{\partial l}\right)_{\mathcal{F}} \times \left(\frac{\partial l}{\partial \mathcal{F}}\right)_T = -1 \quad (5.24)$$

We find,

$$\left(\frac{\partial l}{\partial T}\right)_{\mathcal{F}} = -\left(\frac{\partial \mathcal{F}}{\partial T}\right)_l \times \left(\frac{\partial l}{\partial \mathcal{F}}\right)_T \quad (5.25)$$

The first term on the right hand side is positive, we have shown this just now. The second term is also positive - upon increase of tension the length of the rubber band increases. Therefore,

$$\left(\frac{\partial l}{\partial T}\right)_{\mathcal{F}} < 0.$$

The equation above tells you that when you stretch a rubber band it will cool down; or when when a stretched rubber band shrinks it will warm up.

Keep a rubber band across and touching your forehead; then stretch it; the rubber band throws out heat and you can feel it.

Hang an appropriate weight to the end of a rubber band; slightly heat the rubber band; it will shrink and the weight shall be pulled up.

5.6 First Energy Equation

We start with the first law of thermodynamics $dU = TdS - PdV$. Let us consider $U \equiv U(T, V)$ and $S \equiv S(T, V)$. we get,

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \quad (5.26)$$

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV \quad (5.27)$$

The first law of thermodynamics can now be written as

$$\begin{aligned} \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \\ = T \left(\frac{\partial S}{\partial T}\right)_V dT + T \left(\frac{\partial S}{\partial V}\right)_T dV - PdV \end{aligned} \quad (5.28)$$

- Equate the coefficients of dT and get the familiar expression,

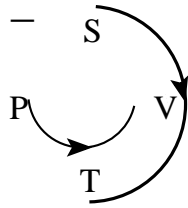
$$\left(\frac{\partial U}{\partial T}\right)_V = T \left(\frac{\partial S}{\partial T}\right)_V \quad (5.29)$$

- Equating the coefficient of dV we get,

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial S}{\partial V}\right)_T - P \quad (5.30)$$

Re write the first term on the right hand side of the above equation employing the second Maxwell relation

and get,



$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P \quad (5.31)$$

The above is called the first energy equation. An important point is that the right hand side of the first energy equation can be calculated from the equation of state.

5.6.1 First Energy Equation and Ideal Gas

We have for an ideal gas $P = Nk_B T/V$. Therefore

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{Nk_B}{V} = \frac{P}{T}$$

Substituting the above in the first energy equation, we get,

$$\left(\frac{\partial U}{\partial V}\right)_T = 0.$$

The internal energy does not depend on volume. It depends only on temperature.

5.6.2 First Energy Equation and van der Waal Gas

Let us calculate $\left(\frac{\partial U}{\partial V}\right)_T$ for van der Waal gas for which,

$$\left(P + \frac{aN^2}{V^2}\right)(V - Nb) = Nk_B T \quad (5.32)$$

We can write the equation of state for van der Waal gas as,

$$P = \frac{Nk_B T}{V - Nb} - \frac{aN^2}{V^2} \quad (5.33)$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{Nk_B}{V - Nb} - P \quad (5.34)$$

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{Nk_B T}{V - Nb} - P \quad (5.35)$$

$$= \frac{aN^2}{V^2} \quad (5.36)$$

We find that internal energy depends on volume. This is a general result. For any non-ideal gas, internal energy shall depend on both temperature and volume.

5.6.3 First energy equation in terms of γ and κ_T

First energy equation in terms of γ and κ_T The first energy equation can be expressed in terms of experimentally measurable properties of the system like isothermal compressibility denoted by the symbol κ_T and coefficient of thermal expansion denoted by the symbol γ , as follows. indexthermal expansion We have

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P \quad (5.37)$$

We can write

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{1}{\left(\frac{\partial T}{\partial P}\right)_V} \quad (5.38)$$

$$\left(\frac{\partial T}{\partial P}\right)_V \times \left(\frac{\partial P}{\partial V}\right)_T \times \left(\frac{\partial V}{\partial T}\right)_P = -1 \quad (5.39)$$

$$(5.40)$$

In terms of isothermal compressibility as κ_T and coefficient of thermal expansion γ , we can write the above equation as,

$$\left(\frac{\partial T}{\partial P}\right)_V \times \left(\frac{1}{-V\kappa_T}\right) \times (V\gamma) = -1 \quad (5.41)$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{\gamma}{\kappa_T} \quad (5.42)$$

The first energy equation can now be written as,

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{T\gamma}{\kappa_T} - P \quad (5.43)$$

5.7 Second Energy Equation

The aim is to first express U as a function of T and P ; then we shall evaluate the partial derivatives of U with respect to T and P .

To this end we write

$$U \equiv U(T, P) \quad (5.44)$$

$$dU = \left(\frac{\partial U}{\partial T}\right)_P dT + \left(\frac{\partial U}{\partial P}\right)_T dP \quad (5.45)$$

Similarly, we have,

$$S = S(T, P) \quad (5.46)$$

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP \quad (5.47)$$

and

$$V = V(T, P) \quad (5.48)$$

$$dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP \quad (5.49)$$

Begin with the first law of thermodynamics for reversible process

$$dU = TdS - PdV \quad (5.50)$$

In the above substitute for dU , dS and dV respectively from the equations above, and get,

$$\left(\frac{\partial U}{\partial T}\right)_P dT + \left(\frac{\partial U}{\partial P}\right)_T dP = T \left(\frac{\partial S}{\partial T}\right)_P dT + T \left(\frac{\partial S}{\partial P}\right)_T dP \quad (5.51)$$

$$P \left(\frac{\partial V}{\partial T}\right)_P dT - P \left(\frac{\partial V}{\partial P}\right)_T dP \quad (5.52)$$

Equating the coefficients of dT we get,

$$\left(\frac{\partial U}{\partial T}\right)_P = T \left(\frac{\partial S}{\partial T}\right)_P - P \left(\frac{\partial V}{\partial T}\right)_P \quad (5.53)$$

$$(5.54)$$

This can be written as

$$\left(\frac{\partial U}{\partial T}\right)_P = T \left(\frac{\partial S}{\partial T}\right)_P - PV\gamma \quad (5.55)$$

Equating the coefficients of dP we get,

$$\left(\frac{\partial U}{\partial P}\right)_T = T \left(\frac{\partial S}{\partial P}\right)_T - P \left(\frac{\partial V}{\partial P}\right)_T \quad (5.56)$$

$$(5.57)$$

Now employing the fourth Maxwell relation in the above, we get the second energy equation,

$$\left(\frac{\partial U}{\partial P}\right)_T = - \left[T \left(\frac{\partial V}{\partial T}\right)_P + P \left(\frac{\partial V}{\partial P}\right)_T \right] \quad (5.58)$$

$$(5.59)$$

In terms of isothermal compressibility κ_T and coefficient thermal expansion γ , the second energy equation can be written as,

$$\left(\frac{\partial U}{\partial P}\right)_T = -T\gamma V + V\kappa_T P \quad (5.60)$$

5.8 TdS Equations

The so-called TdS equations are obtained by considering S as a function of (i) T and V , (ii) T and P , and (iii) P and V .

5.8.1 First TdS equation : $S \equiv S(T, V)$

$$TdS = T \left(\frac{\partial S}{\partial T} \right)_V dT + T \left(\frac{\partial S}{\partial V} \right)_T dV \quad (5.61)$$

$$(5.62)$$

Employing the second Maxwell relation in the above, we get the first TdS equation :

$$TdS = T \left(\frac{\partial S}{\partial T} \right)_V dT + T \left(\frac{\partial P}{\partial T} \right)_V dV \quad (5.63)$$

We can write the above in terms of experimentally measurable properties of the system as follows We have

$$\left(\frac{\partial P}{\partial T} \right)_V \times \left(\frac{\partial T}{\partial V} \right)_P \times \left(\frac{\partial V}{\partial P} \right)_T = -1 \quad (5.64)$$

$$\left(\frac{\partial P}{\partial T} \right)_V \times \frac{1}{V\gamma} \times (-V\kappa_T) = -1 \quad (5.65)$$

$$\left(\frac{\partial P}{\partial T} \right)_V = \frac{\gamma}{\kappa_T} \quad (5.66)$$

$$T \left(\frac{\partial S}{\partial T} \right)_V = C_V \quad (5.67)$$

We thus have the first TdS equation,

$$TdS = C_V dT + \frac{\gamma}{\kappa_T} T dV \quad (5.68)$$

5.8.2 Second TdS equation : $S \equiv S(T, P)$

$$TdS = T \left(\frac{\partial S}{\partial T} \right)_P dT + T \left(\frac{\partial S}{\partial P} \right)_T dP \quad (5.69)$$

$$= T \left(\frac{\partial S}{\partial T} \right)_P dT - T \left(\frac{\partial V}{\partial T} \right)_P dP, \quad (5.70)$$

where we have made use of the fourth Maxwell relation. We can also write the second TdS equation as,

$$T dS = C_P dT - \gamma T V dP \quad (5.71)$$

5.8.3 Third TdS equation : $S \equiv S(P, V)$

$$dS = \left(\frac{\partial S}{\partial P} \right)_V dP + \left(\frac{\partial S}{\partial V} \right)_P dV \quad (5.72)$$

We have the following identities

$$\left(\frac{\partial S}{\partial P} \right)_V = \left(\frac{\partial S}{\partial T} \right)_V \times \left(\frac{\partial T}{\partial P} \right)_V = \frac{C_V}{T} \left(\frac{\partial T}{\partial P} \right)_V \quad (5.73)$$

$$\left(\frac{\partial S}{\partial V} \right)_P = \left(\frac{\partial S}{\partial T} \right)_P \times \left(\frac{\partial T}{\partial V} \right)_P = \frac{C_P}{T} \left(\frac{\partial T}{\partial V} \right)_P \quad (5.74)$$

Thus we get the third TdS equation,

$$TdS = C_V \left(\frac{\partial T}{\partial P} \right)_V dP + C_P \left(\frac{\partial T}{\partial V} \right)_P dV, \quad (5.75)$$

which can also be written as,

$$TdS = C_V \frac{\kappa_T}{\gamma} dP + \frac{C_P}{V\gamma} dV \quad (5.76)$$

6. LECTURES 19 - 20

Joule Cooling and Joule-Kelvin Throttling

Under Preparation

7. LECTURES 21 - 25

VAN DER WAALS EQUATION OF STATE AND ELEMENTS OF PHASE TRANSITION

$$7.1 \quad PV = Nk_B T \Rightarrow (P + aN^2/V^2)(V - Nb) = Nk_B T$$

The equation of state for an ideal gas is $PV = Nk_B T$. It provides a reasonably good description of the behaviour of air near room temperatures. Real gases are not ideal. An equation of state for a non-ideal gas was proposed by Johannes Diderik van der Waals (1837 - 1923). in the year **1873**. van der Waals retained the basic structure of the ideal gas law and made empirical corrections to P and V , based on heuristic arguments.

7.1.1 A Molecule is of Finite Size

The first correction comes from realizing that a molecule is not a geometrical point with zero volume. A molecule occupies a finite, though tiny, space. We have already seen of Lennard-Jones potential, see Eq. (2.1) and Fig. (2.2.1), which tells us that when two molecules come very close to each other, they repel each other rather strongly. The repulsion increases steeply with decrease of the inter-molecular distance. Effectively each molecule has a tiny private space which it owns exclusively; it does not permit any other molecule to come into its private space. The excluded volume for a molecule can be taken as $b = (4/3)\pi\sigma^3$, where σ is the 'size' parameter appearing in the Lennard-Jones potential, see Eq. (2.1). There are N molecules. If the volume of the container is V then the volume available for the N molecules to move freely around is $V - Nb$. The value of b shall differ from one substance to another. For some chosen materials, these are given in Table (7.1).

van der Waals argued that this is the volume we have to use in the ideal gas law and not the volume of the container. With this correction, the equation of state reads as $P(V - Nb) = Nk_B T$. We notice that

$$\frac{Nk_B T}{V - Nb} > \frac{Nk_B T}{V}. \quad (7.1)$$

The above implies that the pressure after correction to the volume is more than the pressure before correction. Repulsion at short range leads to an increase of

pressure, as indeed one would expect. Each molecule pushes out its neighbours and as a consequence, overall there is an increase in pressure.

While the strong, short-range repulsion leads to increase of pressure, the weak, long range attraction leads decrease of pressure, see below.

7.1.2 Molecules Attract Each Other

A molecule in the interior, is attracted by all the molecules surrounding it; hence it does not experience on the average any net force. Of course it will be subjected to a tiny fluctuating force whose average over time is zero. Such a statistical cancellation does not obtain for a molecule near the wall of the container. It is pulled by the molecules present in the interior; there are no molecules in the opposite side to cancel, statistically, the force. As a result a molecule near a wall of the container experiences a net pull inwards. This diminishes the effect of impact on the wall; the pressure thus, becomes less. The reduction in pressure depends on two factors.

1. The number of molecules that pull and
2. the number of molecules that get pulled.

Hence we can say $P \rightarrow P - a(N/V)^2$ where a is a proportionality constant. The value of a shall differ from material to material. For some chosen substances the value of a is given in Table (7.1).

7.2 van der Waals Equation of State

Incorporating the corrections to pressure and volume, we get,

$$P = \frac{Nk_B T}{V - Nb} - \frac{aN^2}{V^2} \quad (7.2)$$

The above can be written in a more familiar form,

$$\left(P + \frac{aN^2}{V^2}\right) (V - Nb) = Nk_B T \quad (7.3)$$

7.2.1 V_c , P_c , and T_c for a van der Waals Gas

Let $v = V/N$ denote the specific volume of a molecule. We can write the van der Waals equation of state as

$$\left(P + \frac{a}{v^2}\right) (v - b) = k_B T \quad (7.4)$$

We can re-write the above as a cubic equation in v , see below.

Material	a (pa m ⁶)	b (m ³ mol ⁻¹)
Helium	0.00346	2.371×10^{-5}
Neon	0.0212	1.710×10^{-5}
Hydrogen	0.00245	2.661×10^{-5}
Carbon-di-Oxide	0.396	4.269×10^{-5}
Water Vapour	0.5471	3.052×10^{-5}

Table 7.1. The constants a and b of van der Waals equation of state

$$v^3 - \left(b + \frac{k_B T}{P}\right) v^2 + \frac{a}{P} v - \frac{ab}{P} = 0 \quad (7.5)$$

In general the above cubic equation has three roots, which we denote by the symbols v_1 , v_2 , and v_3 . We write the equation of state as

$$(v - v_1)(v - v_2)(v - v_3) = 0 \quad (7.6)$$

The three roots v_1 , v_2 , and v_3 depend on P , T , a , and b . Consider a situation where $v_1 = v_2 = v_3 = v_c$. Also when the three roots of v are the same, let $P = P_c$ and $T = T_c$. We can determine v_c , P_c , and T_c as described below.

Formally we have,

$$(v - v_c)^3 = 0 \quad (7.7)$$

$$v^3 - (3v_c) v^2 + (3v_c^2) v - (v_c^3) = 0 \quad (7.8)$$

Compare Eq. (7.8) with Eq. (7.5) and equate the coefficients of equal powers of v . We get,

$$3v_c = b + \frac{k_B T}{P}; \quad 3v_c^2 = \frac{a}{P}; \quad \text{and} \quad v_c^3 = \frac{ab}{P}. \quad (7.9)$$

We can get v_c , P_c and T_c solving the above three equations. These are,

$$v_c = 3b; \quad P_c = \frac{1}{27} \frac{a}{b^2}; \quad k_B T_c = \frac{8}{27} \frac{a}{b}. \quad (7.10)$$

We can obtain the same results by taking the first and second derivatives of P with respect to v and setting them to zero⁴⁴.

⁴⁴ P_c , v_c , and T_c are those values of P , v and T respectively, at which both first and second derivatives of P with respect to v vanish. To calculate the critical pressure, volume and temperatures we proceed as follows.

$$P = \frac{k_B T}{v - b} - \frac{a}{v^2}; \quad \frac{dP}{dv} = -\frac{k_B T}{(v - b)^2} + \frac{2a}{v^3}; \quad \frac{d^2 P}{dv^2} = \frac{2k_B T}{(v - b)^3} - \frac{6a}{v^4}$$

Setting $\frac{dP}{dv} = \frac{d^2 P}{dv^2} = 0$ and solving the resulting algebraic equations gives v_c , P_c and T_c .

Let us measure v in units of v_c , P in units of P_c , and T in units of T_c . Accordingly we set, $\hat{v} = v/v_c$, $\hat{P} = P/P_c$ and $\hat{T} = T/T_c$. In terms of the scaled variables \hat{v} , \hat{P} and \hat{T} , the van der Waals equation of state reads as,

$$\hat{P} = \frac{8}{3} \frac{\hat{T}}{\hat{v} - (1/3)} - \frac{3}{\hat{v}^2} \quad (7.11)$$

$$\left(\hat{P} + \frac{3}{\hat{v}^2}\right) \left(\hat{v} - \frac{1}{3}\right) = \frac{8\hat{T}}{3} \quad (7.12)$$

Notice that in the above equation of state, the material-dependent properties a and b do not appear. The pressure *versus* volume of a van der Waals gas is plotted in Fig. (7.1) for $\hat{T} = 1.2, 1.0$ and 0.8 .

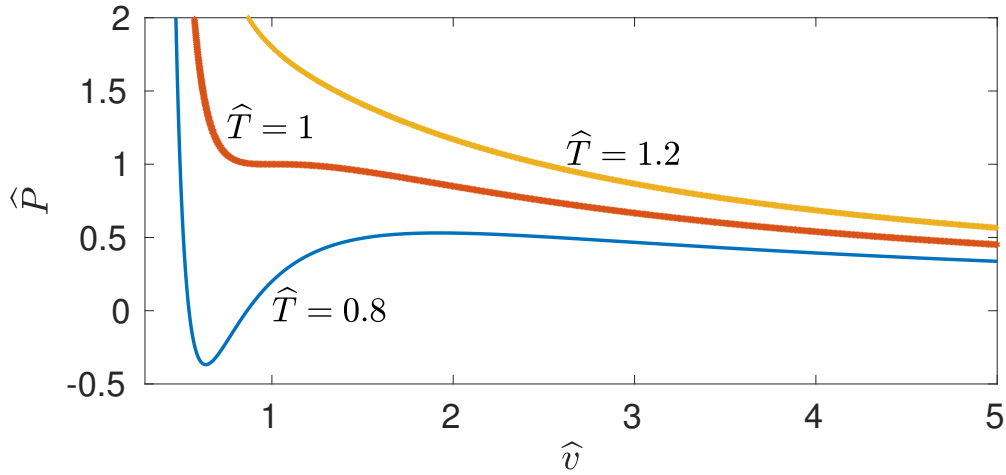


Fig. 7.1. \hat{P} *versus* \hat{V} for three values of \hat{T} .

At high temperatures ($\hat{T} > 1$) the van der Waals gas behaves somewhat, like an ideal gas. When you confine a given quantity of the gas to smaller and smaller volumes, the pressure increases smoothly; at very small volumes, the pressure increases rather steeply with decrease of volume and goes to infinity in the limit of $\hat{v} \rightarrow 1/3$ (or $v \rightarrow b$ or $V \rightarrow Nb$). For an ideal gas, the limiting divergent behaviour obtains when v or $V \rightarrow 0$.

7.2.2 Isotherm at Low T for a van der Waals Gas

At low temperatures ($\hat{T} < 1$) the phase diagram exhibits some seemingly peculiar behaviour. Keeping the temperature at a constant low value, if we compress the gas, its pressure increases initially; upon further compression, the pressure falls down and then starts increasing and eventually goes to infinity rapidly as $\hat{v} \rightarrow 1/3$. The important point is that there exists regions of temperature, pressure and

volume, in which if you compress the gas its pressure drops instead of increasing. How do we understand this behaviour ?

7.2.3 G at Low Temperatures for a van der Waals Gas

To this end, let us investigate the behaviour of Gibbs free energy at low temperatures. For a fixed T and P , the equilibrium value of V a fluid system is determined by minimizing the Gibbs free energy.

Gibbs free energy G is a function of T , P , and, N . It is obtained by Legendre transform of $S \rightarrow T$, $V \rightarrow P$ and $U \rightarrow G$ and the defining equations are,

$$G(T, P, N) = U(S, V, N) - TS + PV; \quad T = \left(\frac{\partial U}{\partial S} \right)_{V, N}; \quad P = - \left(\frac{\partial U}{\partial V} \right)_{S, N}$$

We have,

$$dG = +V dP - S dT + \mu dN \quad (7.13)$$

Let us investigate the behaviour of G at constant temperature and at a constant quantity of material. Accordingly, in the equation above, we set $dT = 0$ and $dN = 0$. Therefore,

$$dG = V dP \quad (7.14)$$

$$\left(\frac{\partial G}{\partial V} \right)_{T, N} = V \left(\frac{\partial P}{\partial V} \right)_{T, N} \quad (7.15)$$

We can write Eq. (7.15), in terms of scaled variables. Note $\hat{G} \equiv \hat{G}(\hat{T}, \hat{v})$. We have,

$$\left(\frac{\partial \hat{G}}{\partial \hat{v}} \right)_{\hat{T}} = \hat{v} \left(\frac{\partial \hat{P}}{\partial \hat{v}} \right)_{\hat{T}} \quad (7.16)$$

The Right Hand Side of the above equation can be obtained from the van der Waals equation of state, see Eq. (7.11). We have,

$$\hat{P} = \frac{8\hat{T}}{3\hat{v} - 1} - \frac{3}{\hat{v}^2} \quad (7.17)$$

$$\left(\frac{\partial \hat{P}}{\partial \hat{v}} \right)_{\hat{T}} = - \frac{(8\hat{T}) \times 3}{(3\hat{v} - 1)^2} + \frac{6}{\hat{v}^3} \quad (7.18)$$

$$\begin{aligned}
\left(\frac{\partial \hat{G}}{\partial \hat{v}}\right)_{\hat{T}} &= -\frac{(8\hat{T})3\hat{v}}{(3\hat{v}-1)^2} + \frac{6}{\hat{v}^2} \\
&= -\frac{(8\hat{T})(3\hat{v}-1+1)}{(3\hat{v}-1)^2} + \frac{6}{\hat{v}^2} \\
&= -\frac{8\hat{T}}{3\hat{v}-1} - \frac{8\hat{T}}{(3\hat{v}-1)^2} + \frac{6}{\hat{v}^2} \tag{7.19}
\end{aligned}$$

$$\hat{G}(\hat{T}, \hat{v}) = -\frac{8\hat{T}}{3} \ln(3\hat{v}-1) + \frac{8\hat{T}}{3} \frac{1}{3\hat{v}-1} - \frac{6}{\hat{v}} + \phi(\hat{T}) \tag{7.20}$$

For a fixed temperature, the equation above gives Gibbs free energy as a function of volume, upto an additive constant. The van der Waals equation gives pressure as a function of volume for a fixed temperature. Combining these two we can express the Gibbs free energy as function of pressure. We have plotted \hat{G} against \hat{P} at $\hat{T} = 0.8$ in figure (7.2) below.

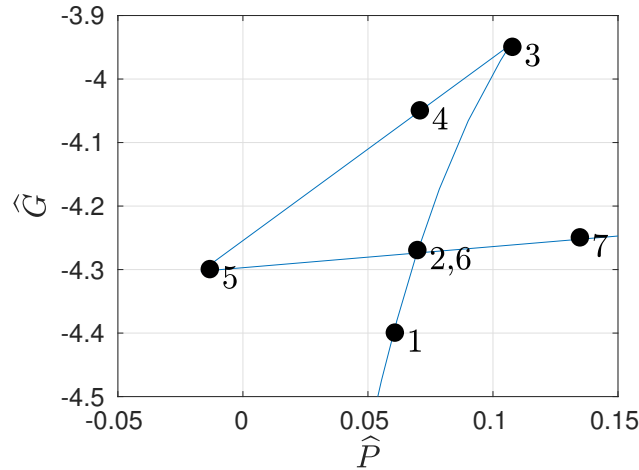


Fig. 7.2. Gibbs free energy (scaled) *versus* pressure (scaled) for isotherm at $\hat{T} = 0.8$. The points marked 1 – 7 correspond to the states indicated in the isotherm below in Fig.(7.3).

From Fig. (7.2) we observe that the thermodynamic states corresponding to the points on the loop $2 \rightarrow 3 \rightarrow 4 \rightarrow 5 \rightarrow 6$ should be unstable since for every such state there exists a state with lower Gibbs free energy. Note, (stable) equilibrium states are characterized by minimum Gibbs free energy.

The isotherm underlying Fig. (7.2) is shown in Fig. (7.3).

How do we locate the points 2 and 6 so that I can draw an horizontal line connecting these two points which incidentally passes through 4 ? The states on this line have all the same free energy since this line is isobaric and isothermal. Let me remind you that G is a function of T , P and N . Also this constant free

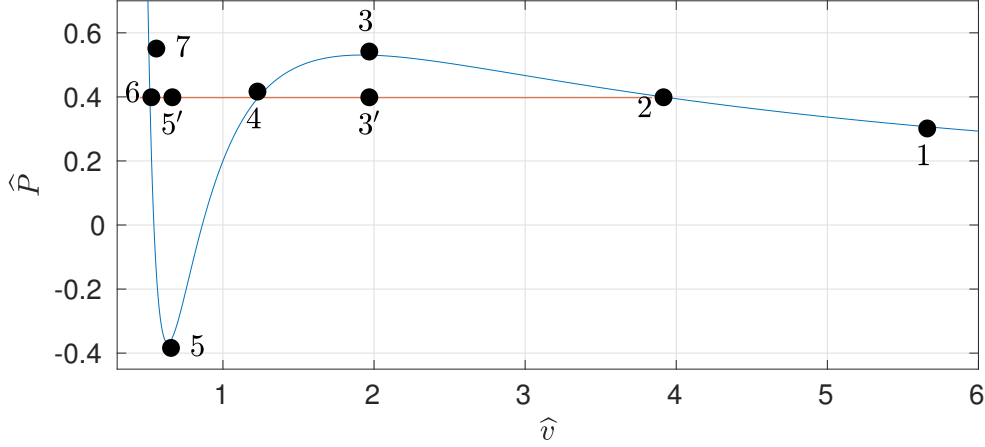


Fig. 7.3. Isotherm at $\hat{T} = 0.8$: Pressure (scaled) *versus* volume (scaled), see Eq. (7.11)

energy is less than the free energy on the points lying on the unstable segment $2 \rightarrow 3 \rightarrow 4 \rightarrow 5 \rightarrow 6$.

7.2.4 Maxwell Construction

To locate the horizontal line passing through **2**, **4**, and **6** we proceed as follows. Look at Fig. (7.2). First we observe the integral of $d\hat{G}$ over the loop $C : 2 \rightarrow 3 \rightarrow 4 \rightarrow 5 \rightarrow 6$ is zero.

$$\oint_C d\hat{G} = 0 \quad : \quad C = 2 \rightarrow 3 \rightarrow 4 \rightarrow 5 \rightarrow 6 \quad (7.21)$$

To evaluate the above integral we recognize that $d\hat{G} = \hat{v}d\hat{P}$ at constant \hat{T} and N . Thus the integral over $d\hat{G}$ equals integral over $\hat{v}d\hat{P}$, which is best seen in the isotherm plotted with \hat{v} on the y-axis and \hat{P} on the x axis. Figure (7.4) depicts such a curve with the points 1 to 7 marked on it.

We have

$$\int_C \hat{v}d\hat{P} = \int_2^3 \hat{v}d\hat{P} + \int_3^4 \hat{v}d\hat{P} + \int_4^5 \hat{v}d\hat{P} + \int_5^6 \hat{v}d\hat{P} = 0 \quad (7.22)$$

$$= \left(\int_2^3 \hat{v}d\hat{P} - \int_4^3 \hat{v}d\hat{P} \right) - \left(\int_5^4 \hat{v}d\hat{P} - \int_6^5 \hat{v}d\hat{P} \right) = 0 \quad (7.23)$$

Inn the above, the integrals in the first bracket on the RHS, give the area of the loop $2 \rightarrow 3 \rightarrow 4 \rightarrow 2$. The integrals in the second bracket correspond to the area in the lo op $4 \rightarrow 5 \rightarrow 6 \rightarrow 4$

Now look at Fig. (7.3). The above statement of equal areas means that the points **2**, **4** and **6** fall on the horizontal line which is positioned in such a way that

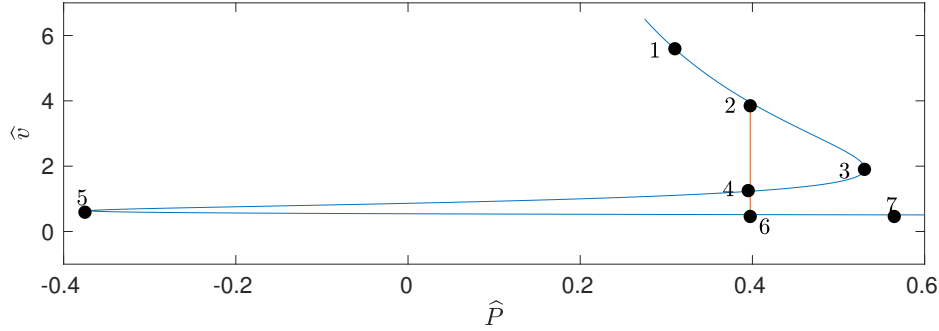


Fig. 7.4. Isotherm at $\hat{T} = 0.8$: Volume (scaled) *versus* Pressure (scaled), at $\hat{T} = 0.8$ see Eq. (7.11)

the area contained in the closed loop $2 \rightarrow 3 \rightarrow 4 \rightarrow 2$ is the same as the area contained in the closed loop $4 \rightarrow 5 \rightarrow 6 \rightarrow 4$. The horizontal line can be located either graphically or numerically. Drawing a straight line to ensure equality of enclosed areas, as described above, is called the Maxwell construction.

7.2.5 Vapour - Liquid Phase Transition

Look at the figure (7.3); at point **1**, the fluid system is in a homogeneous vapour state; when you confine the system to smaller and smaller volume, its pressure increases smoothly; the system manages to retain its homogeneous vapour state, until it reaches the point **2**. The pressure at **2** is the maximum the system can withstand if it wants to remain in a homogeneous vapour state. Upon further confinement, the states on the van der Waals curve are metastable. A metastable state is an unstable state. The system can not remain in a homogeneous vapour phase in the meta stable state. By a mechanism called nucleation, liquid droplets are formed locally at several points in vapour system The system remains in metastable state until it reaches the point **3**. Note that in this segment $2 \rightarrow 3$, the slope of the pressure - volume curve is negative; this ensures that isothermal compressibility is positive.

Beyond the point **3** and in the segment $3 \rightarrow 4 \rightarrow 5$ the system is unstable. The slope of the pressure *versus* temperature curve is positive; isothermal compressibility is negative which is un-physical. Hence in this region the system can not remain in a homogeneous phase (liquid or gas); it will spontaneously breaks into two phases by a a mechanism called spinodal decomposition. Beyond **5** and in the segment $5 \rightarrow 6$ the system is again metastable. Beyond **6**, the system is in a homogeneous liquid phase. On the Maxwell line, the vapour and liquid coexist. We have already seen that at all the states on the entire Maxwell line $2 \rightarrow 3' \rightarrow 4 \rightarrow 5' \rightarrow 6$, the Gibbs free energy is smaller at points on the Maxwell line compared to that at the corresponding states on the van der Waals curve. As we move on the Maxwell line, from point **2** toward the point **6**, more and

more of vapour gets converted into liquid. At **6** the phase transition from vapour state to liquid state is complete.

Upon further confinement, the pressure of the liquid increases and goes to infinity when $\hat{v} \rightarrow 1/3$ (same as $V \rightarrow Nb$). The volume drops abruptly from $\hat{v}(\mathbf{2})$ to $\hat{v}(\mathbf{6})$ at constant pressure. The transition from vapour to liquid phase is discontinuous. Hence it is called discontinuous or first order phase transition.

7.2.6 $T - V$ Phase Diagram of a van der Waals Gas

From the isotherm at $\hat{T} = 0.8$ depicted in Fig. (7.3) we find the points **2** and **6** are the end points of the Maxwell line. As we increase the temperature, the two points move toward each other; the length of the Maxwell line becomes smaller and smaller. In the limit of $\hat{T} \rightarrow 1$ the two points merge and we call it a critical point for which $\hat{T} = \hat{v} = \hat{P} = 1$. Let us plot the value of \hat{v} of the points **2** and **6** for various values of \hat{T} from say **0.8** to **1**. These points are plotted on a graph with \hat{T} on the y-axis and \hat{v} on the axis. The temperature - volume phase diagram is schematically shown in Fig. (7.5).

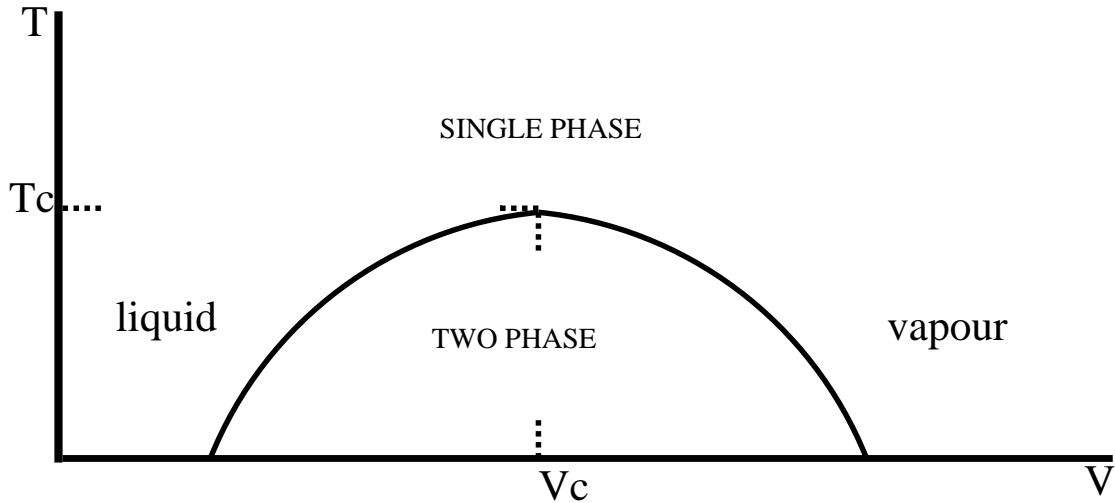


Fig. 7.5. Schematic of a Temperature-Volume Phase Diagram

The interior of the dome is the two phase region and the exterior is the single phase region. The curve that separates the single phase and the two-phase regions has two wings, one on the right - the vapour side and the other on the left - the liquid side. If the system enters the dome straight down through the apex whose coordinates are (V_c, T_c) , the phase transition is continuous - second order phase transition. If the system enters the dome at any other point where $V \neq V_c$, the phase transition is first order.

Now consider the segment from **3'** to **5'** on the Maxwell line depicted in Fig. (7.3). These two points are the vertical projections of the points **3** and **5** from the

van der Waals curve. The states on the segment of the van der Waals line between **3** and **5** are unstable⁴⁵. As the temperature increases from $\hat{T} = 0.8$ to **1**, the points **3'** and **5'** come closer and closer to each other and in the limit $\hat{T} \rightarrow 1$ they merge at the critical point. Let us plot the value of \hat{v} of the points **3'** and **5'** for various values of \hat{T} from say **0.8** to **1**. These points are plotted on a graph with \hat{T} on the y-axis and \hat{v} on the axis. These data generate a dome inside the dome defining the two-phase region, as depicted Fig (7.6). The region inside the smaller dome is unstable.

The system in a meta stable state the region outside the inner dome but inside the outer dome. In the metastable region, the phenomenon of nucleation is the mechanism that is responsible for the emergence of new phase.

Inside the inner dome, the system is unstable and breaks up locally and spontaneously into two phases by a mechanism called Spinodal decomposition. The inner unstable region and the outer meta stable region is separated by the spinodal curve, indicated in Fig. (7.6).

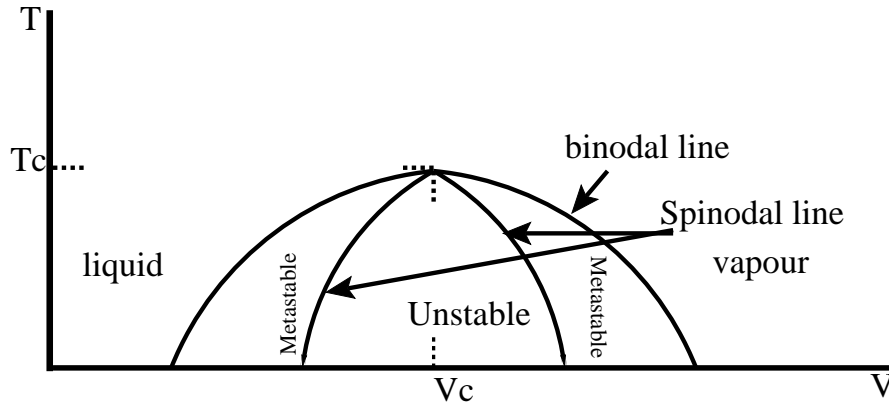


Fig. 7.6. Schematic Temperature-Volume Phase Diagram

7.2.7 $P - T$ Phase Diagram for a van der Waals Gas

Maxwell construction tells us that for each isotherm below the critical temperature, there exists a well defined pressure at which the vapour-liquid phase transition takes place. Let us name it as vapour pressure curve. The liquid and gas coexist on this curve. The vapour - pressure curve terminates at the critical point. Figure (7.7) depicts the schematic of the pressure temperature phase diagram for the van der Waals fluid.

It is indeed astonishing that simple corrections to pressure and volume in the ideal gas law, which led to the van der Waals equation state, could capture the es-

⁴⁵ the thermal expansion coefficient is negative since the slope of the van der Waals curve is positive in the region between the points **3** and **5**.

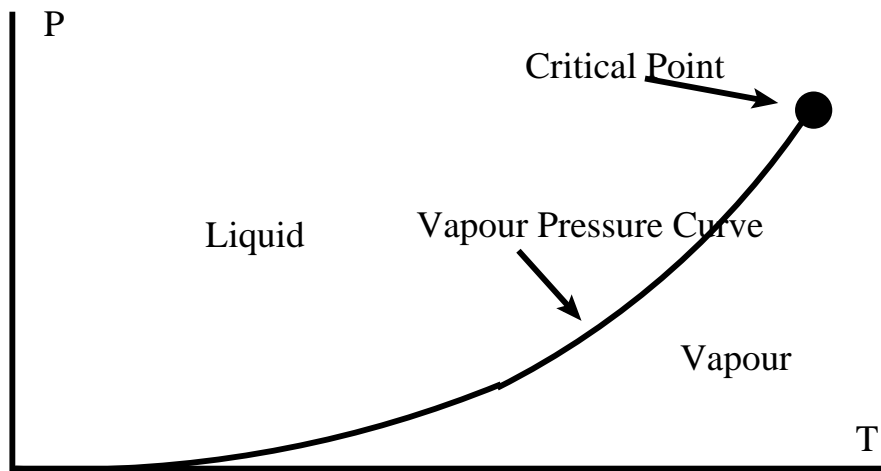


Fig. 7.7. A Schematic of the Pressure-Temperature Phase Diagram

essential contents of vapour-liquid phase transition. The transition is discontinuous - the properties of the system change abruptly. The vapour pressure curve terminates at a critical point. The phase transition at the critical point is continuous.

We have looked at only the vapour pressure curve on the pressure temperature phase diagram of a simple fluid system. There are several other interesting features in the phase diagram of a simple substance. We have the melting line that separates solid and liquid phases; the sublimation line at low temperatures and pressure, which separates the solid and gaseous phases; the tri-critical point at which the three coexistence curves meet. The solid, liquid and the gaseous phases coexist at the tri-critical point. The slope of the coexistence curve holds a vital information about how certain physical properties change upon phase transformation and this is enshrined in the Clausius - Clapeyron equation. We shall see of these, briefly, in what follows.

7.3 Phase Transition - An Elementary Introduction

We expect a substance to be in solid phase at low temperatures and high pressures. It will be in a gaseous state at high temperatures and low pressures. Figure (7.8) depicts the phase diagram of a normal substance.

An astonishing thing about phase transition is that a sharp line separates two phases. The solid and Gas are separated by the sublimation line; the solid and fluid phases are separated by the melting line; the liquid and the gas phases are separated by the vapour pressure line which terminates at a critical point. Beyond the critical point there is no distinction between liquid and vapour states. We call it a fluid phase - which include both liquid state and gaseous state. The two adjacent phases coexist on the line separating them. We call it a co-existence line. The three co-existence curves meet at the triple point.

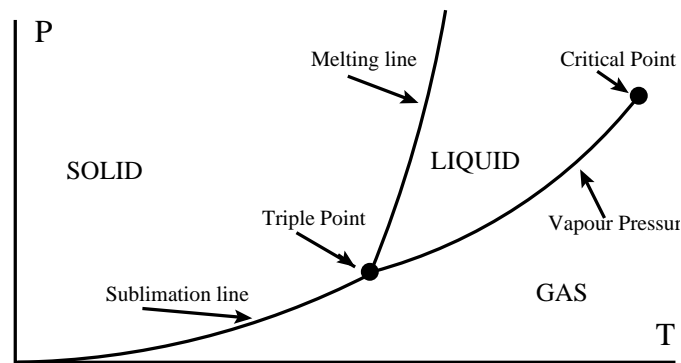


Fig. 7.8. Schematic of Pressure-Temperature Phase behaviour of a Normal Substance

That different phases are separated by a sharp line implies even an infinitesimally small change in pressure or temperature across the coexistence line drives the system from one phase to the other. The molecules of the substance that undergo phases transition organize themselves differently in the two phases. These two kinds of organization require different energies. The difference in the energies is called latent heat. Hence you have to supply or remove the latent heat to bring about phase transition.

The vapour pressure line terminates at the critical point. To the best of our experimental knowledge the melting line does not terminate. It goes on and on *ad infinitum*. The distinction between the liquid phase and the gaseous phase decreases as you move toward the critical point. The difference disappears at the critical point. We have second order phase transition at the critical point. The transition is continuous and there is no latent heat. Unlike the first order transition which occurs abruptly unannounced, the second order phase transition gives adequate warning signals when it arrives. The fluctuations grow larger and larger as you approach the phase transition temperature from either directions - *i.e.* from liquid to gas or from gas to liquid.

7.3.1 Clausius - Clapeyron Equation

Consider two points on either side of the melting line but very close to it. A molecule residing in the solid phase has no compelling reason to migrate to liquid phase and *vice versa*. However on the melting line, a molecule can live on both phases with equal comfort. With equal ease it can migrate from the solid phase to liquid phase or *vice versa*. If μ_1 and μ_2 are the chemical potential of the two phases, then $\mu_1(T, P) = \mu_2(T, P)$ for a point T, P on the melting line. Consider a neighbouring point on the melting line. Let its coordinates be $T + \Delta T, P + \Delta P$. We have,

$$\mu_1(T + \Delta T, P + \Delta P) = \mu_2(T + \Delta T, P + \Delta P) \quad (7.24)$$

$$\begin{aligned} \mu_1(T, P) + \Delta T \left(\frac{\partial \mu_1}{\partial T} \right)_P + \Delta P \left(\frac{\partial \mu_1}{\partial P} \right)_T = \\ \mu_2(T, P) + \Delta T \left(\frac{\partial \mu_2}{\partial T} \right)_P + \Delta P \left(\frac{\partial \mu_2}{\partial P} \right)_T \end{aligned} \quad (7.25)$$

$$\Delta T \left[\left(\frac{\partial \mu_1}{\partial T} \right)_P - \left(\frac{\partial \mu_2}{\partial T} \right)_P \right] = \Delta P \left[\left(\frac{\partial \mu_2}{\partial P} \right)_T - \left(\frac{\partial \mu_1}{\partial P} \right)_T \right] \quad (7.26)$$

$$\Delta T(-s_1 + s_2) = \Delta P(v_2 - v_1) \quad (7.27)$$

$$\frac{dP}{dT} = \frac{s_2 - s_1}{v_2 - v_1} \quad (7.28)$$

In the above, we have made use of Gibbs-Duhem relation⁴⁶ for going from Eq. (7.26) to (7.27).

Equation (7.28) tells us that the slope of the co-existence line is determined by the entropies and volumes of the two phases. We can write Eq. (7.28) in a more convenient form as follows. We have $\mathbf{S} = N\mathbf{s}$ and $\mathbf{V} = N\mathbf{v}$. Also $\mathbf{S}_2 - \mathbf{S}_1 = \mathcal{L}/T$, where \mathcal{L} denotes the latent heat. Let $\Delta \mathbf{V} = \mathbf{V}_2 - \mathbf{V}_1$. We have then,

$$\frac{dP}{dT} = \frac{L}{T \Delta V} \quad (7.29)$$

The above is called the Clausius-Clapeyron equation. Consider the schematic phase diagram shown in Fig. (7.8). Let subscript **1** refer to solid phase and **2** to liquid. It is quite obvious that $\mathbf{S}_2 > \mathbf{S}_1$: A solid is ordered and liquid is disordered. The melting line has a positive slope. This means $\mathbf{V}_2 > \mathbf{V}_1$. A given amount of substance occupies more space when in liquid phase than when in solid phase. When a solid melts it expands.

7.3.2 Anomalous Expansion of Water

Now consider the phase diagram for water, shown below. The melting has a negative slope. Since entropy of water is more than the entropy of ice, the volume of water must be less than that of ice; only then the slope of the vapour pressure line shall be negative.

⁴⁶ $d\mu = -s dT + v dP$.

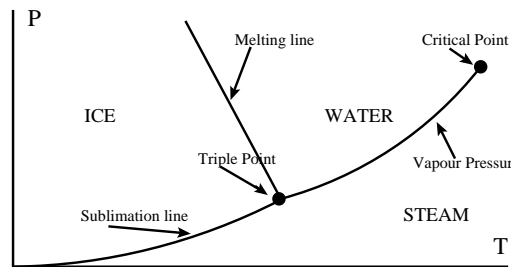


Fig. 7.9. Pressure-Temperature phase diagram of water

The floating ice on the top of water acts as an insulator impeding freezing of water underneath. The water underneath does not freeze even during peak of winter, enabling fish and other aquatic life forms and organisms to survive. Of course anomalous expansion of water leads to bursting of water pipelines in winter, a nuisance indeed !

In other words, when water freezes into ice it expands. Hence do not keep a glass bottle of water in a freezer. The bottle will break when water freezes to into ice. A major advantage of the anomalous expansion is that a lake freezes in winter from top to bottom. Ice floats on water. Icebergs on lakes and ponds are a consequence of the anomalous expansion of water.

8. LECTURES 26 - 30

WORK, AND HEAT : MICROSCOPIC INTERPRETATION, FLUCTUATIONS AND THE SECOND LAW

8.1 Micro-Macro Connections

Corresponding to every thermodynamic property, we have, in statistical mechanics, a random variable. The average of this random variable over a suitable ensemble⁴⁷, or equivalently over the corresponding probability distribution, equals the value of the thermodynamic property. Thus, statistical mechanics provides us with a machinery to calculate macroscopic properties from the properties of its microscopic constituents - atoms and molecules, and interactions amongst them.

For example we saw that the mechanical pressure in thermodynamics corresponds to the sum of the momenta transferred to the wall of the container by a very large number molecular impacts. The internal energy in thermodynamics corresponds to the sum of the kinetic energies and the interaction energies of the atoms and molecules of the macroscopic body. Statistical mechanics provides several such examples of micro-macro connections.

When a macroscopic body absorbs a quantity q of reversible heat, at constant temperature T , its entropy increases by q/T . What is the microscopic counterpart of entropy in statistical mechanics ? Answer : Boltzmann entropy.

Ludwig Eduard Boltzmann defined entropy completely in terms of the probabilities of the micro states of a macroscopic system. Formally we have

$$S = -k_B \sum_i p_i \ln p_i, \quad (8.1)$$

where a micro state is indexed by the integer i , and its probability denoted by the symbol p_i . The sum runs over all the micro states of the macroscopic system under the given constraints. The Boltzmann constant ensures that, we measure entropy in units of joules per kelvin. Thus we have $S \equiv S(p_1, p_2, \dots)$: Entropy is a function of the probabilities of the micro states.

A natural question that arises in this context relates to the microscopic nature of work and heat - the two principal ingredients of thermodynamics, and to this issue we turn our attention below.

⁴⁷ micro canonical ensemble for isolated system, canonical ensemble for a closed system, and grand canonical ensemble for an open system *etc.*

8.1.1 Work and Heat

In thermodynamics, work and heat are two processes by which a macroscopic system transacts energy with its surroundings or with another macroscopic system. Therefore let us recall the micro - macro connection for the internal energy described in Lecture Notes -2. Whatever we discussed in Lecture Notes -2, can be formally expressed as,

$$U = \langle E \rangle = \sum_i p_i \epsilon_i, \quad (8.2)$$

where ϵ_i is the energy of the micro state indexed by i and p_i its probability. Thus internal energy is a function of the energies of micro states and of their probabilities : $U \equiv U(\epsilon_1, \epsilon_2, \dots, p_1, p_2, \dots)$.

We can change U by two ways.

1. Change $\{\epsilon_i : i = 1, 2, \dots\}$, keeping $\{p_i : i = 1, 2, \dots\}$ unchanged. The change in internal energy brought about this way corresponds to work⁴⁸.
2. Change $\{p_i : i = 1, 2, \dots\}$ keeping $\{\epsilon_i : i = 1, 2, \dots\}$ unchanged⁴⁹. The change in internal energy brought about in this fashion is called heat⁵⁰.

We express the above two processes formally as,

$$dU = \sum_i p_i d\epsilon_i + \sum_i^* \epsilon_i dp_i \quad (8.3)$$

In the second term on the right hand side of the above equation, I have superscripted the summation sign with a star to remind us of the constraint that $\sum_i dp_i = 0$.

8.1.2 Micro to Macro : Work

We start with the first term on the right hand side of Eq. (8.3). We keep in mind that the probabilities are kept constant. We have,

$$\sum_i p_i d\epsilon_i = \sum_i p_i \frac{\partial \epsilon_i}{\partial V} dV = \frac{\partial}{\partial V} \left(\sum_i p_i \epsilon_i \right) dV = \frac{\partial U}{\partial V} dV = -P dV$$

⁴⁸ In a quantum mechanical description, the micro states are the eigenstates; $\{\epsilon_i : i = 1, 2, \dots\}$ are the energies of the eigenstates; the energy eigenvalues will change when you change the boundary condition of the underlying Schrödinger equation. Changing the boundary condition is the equivalent to changing the volume. Work results of when volume changes. Hence it is correct to call this term as work.

⁴⁹ ensure $\sum_i dp_i$ equals zero, since the total probability is unity.

⁵⁰ In statistical mechanics, entropy is purely of probabilistic origin. In thermodynamics, it is the product of change in entropy and temperature that corresponds to heat. Hence this change in energy brought about by changing the probabilities should correspond to heat.

8.1.3 Micro to Macro : Heat

We start with the second term on the right hand side of Eq. (8.3). We keep in mind that the energies are kept constant. We have,

$$\sum_i^* \epsilon_i dp_i = \sum_i^* \epsilon_i \frac{\partial p_i}{\partial S} dS = \frac{\partial}{\partial S} \left(\sum_i \epsilon_i p_i \right) dS = \frac{\partial U}{\partial S} dS = T dS$$

8.1.4 Work, Heat, Children, and escalator

Let me illustrate the microscopic nature of heat and work by an analogy involving children playing in an escalator.

Let the rungs of the escalator be labeled (and re-labeled, when the escalator moves) by integers that stand for their energies. The energy of a rung at any instant of time is determined by how far above it is from a reference level **0** at entry point of the escalator. A fixed number, say ***N***, of children are playing - going up and down - in the escalator. At a particular instant of time let ***n_i*** be the number children in the rung labeled by ***i***. Figure (8.2) depicts a schematic of the escalator-children system; the children depicted as filled circles on the rungs labeled by their energies. We have taken ***N* = 10**. To begin with we have ***n₁* = 4; *n₂* = 2; *n₃* = 1; *n₄* = 3**. The other rungs are unoccupied and do not contribute to energy. The energy of the system is

$$E_0 = (1 \times 4) + (2 \times 2) + (3 \times 1) + (4 \times 3) = 23 \text{ units.}$$

The first step is a work step. The escalator moves up; the distribution of children remains the same. Each rung moves up by two energy units carrying with it the children it holds. We relabel the rungs by their new energy values. Thus the rungs labelled **1, 2, 3, 4** are relabelled and the new labels are **3, 4, 5, 6**. In the revised labelling the distribution is given by ***n₃* = 4; *n₄* = 2; *n₅* = 1; *n₆* = 3** and all other rungs are unoccupied. At the end of the first work step the energy of the system is

$$E_1^W = (3 \times 4) + (4 \times 2) + (5 \times 1) + (6 \times 3) = 43 \text{ units.}$$

The energy has increased. Hence in this step work is done on the system.

The next step is a heat step. The escalator does not move. But the children move and the distribution change to ***n₂* = 2; *n₃* = 1; *n₄* = 1; *n₅* = 3; *n₆* = 1; *n₇* = 2**. The energy of the system after the first heat step is

$$E_1^H = (2 \times 2) + (3 \times 1) + (4 \times 1) + (5 \times 3) + (6 \times 1) + (7 \times 2) = 56 \text{ units.}$$

The energy has increased. This means that in the first heat step system has drawn energy from the thermostat.

We have depicted two more work and heat steps in Fig. (8.2).

8.2 Work Fluctuations : Jarzynski Identity

Consider a closed system in thermal equilibrium with a thermostat at temperature $T = 1/(k_B\beta)$. Consider a process in which we change a macroscopic property, denoted by the symbol λ of the system from a value λ_1 to another value λ_2 , following the time protocol, $\lambda(t) = \lambda_1 + \tau^{-1}(\lambda_2 - \lambda_1)t$, with $0 \leq t \leq \tau$. The system is under the influence of the thermostat at temperature T , throughout the experimental process. If τ is finite, we call it a switching process : the system disappears from A at the start of the the process. It continues to be in a non-equilibrium state even after the completion of the process. However, if you wait long enough after the process is completed the system will equilibrate purely by heat exchange and appear at a point B . Since the system disappears from A and appears at B we call it a switching process.

Fix the value of switching time τ , carry out the process and calculate or measure the work done. If you repeat the switching experiment employing the same protocol, you will get, in general, a different value for the work done. Repeat the switching experiment several times and collect an ensemble of work values. Let $\rho(W; \tau)$ denote the probability distribution describing the ensemble.

Jarzynski work fluctuation theorem⁵¹ says,

$$\langle \exp(-\beta W) \rangle = \exp(-\beta \Delta F), \quad (8.4)$$

where the angular brackets denote averaging over W -ensemble, see below.

$$\langle \exp(-\beta W) \rangle = \int_{-\infty}^{+\infty} dW \exp(-\beta W) \rho(W; \tau). \quad (8.5)$$

The Jarzynski identity is remarkable in the sense that it relates an equilibrium property of the system to non equilibrium measurements made on it. The left hand side of Jarzynski identity, see Eq. (8.4), is based on irreversible processes (for finite τ) while the right hand side involves equilibrium free energies.

8.2.1 Reversible limit : $\tau \rightarrow \infty$

Consider the case with $\tau \rightarrow \infty$. The switching process becomes reversible in this limit. The entire process can be represented by a curve in the pressure-volume phase diagram. Every time you carry out the experiment you will get the same work value $W = W_R$. The reversible work W_R equals the change in free energy : $W_R = \Delta F = F(B) - F(A)$.

We have $\rho(W; \tau \rightarrow \infty) = \delta(W - W_R)$. Therefore,

$$\int_{-\infty}^{+\infty} \exp(-\beta W) \delta(W - W_R) dW = \exp(-\beta W_R) \quad (8.6)$$

⁵¹ C Jarzynski, Physical Review Letters **78**, 2690 (1997)

Then from Jarzynski identity we get, $\exp(-\beta W_R) = \exp(-\beta \Delta F)$ which implies that $W_R = \Delta F$. The work fluctuation theorem gives the thermodynamic identity namely the work done in a reversible isothermal process equals the change in free energy.

8.2.2 Dissipation \propto fluctuations : $0 \ll \tau \ll \infty$

When τ is large, a large number of micro states of the system contribute to deciding the consequences of the switching experiment. Then by virtue of the central limit theorem⁵², we expect the distribution of W to be Gaussian. Let ζ_1 ($= \langle W \rangle$) denote the first cumulant (the mean) of the Gaussian and ζ_2 ($= \sigma^2$) the second cumulant (the variance).

$$\rho(W; 0 \ll \tau \ll \infty) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-\frac{1}{2} \frac{(W - \zeta_1)^2}{\sigma^2}\right) \quad (8.7)$$

For a Gaussian, the third and higher order cumulants are zero. We have

$$\begin{aligned} \langle \exp(-\beta W) \rangle &= \frac{1}{\sigma\sqrt{2\pi}} \int_{-\infty}^{+\infty} dW \exp(-\beta W) \exp\left(-\frac{1}{2} \frac{(W - \zeta_1)^2}{\sigma^2}\right) \\ &= \exp\left[-\beta\zeta_1 + \frac{\beta^2}{2!}\zeta_2\right] \end{aligned} \quad (8.8)$$

From Jarzynski identity we get,

$$\begin{aligned} \exp\left[-\beta\zeta_1 + (1/2)\beta^2\zeta_2\right] &= \exp(-\beta\Delta F) \\ -\beta\zeta_1 + (1/2)\beta^2\zeta_2 &= -\beta\Delta F \\ \langle W \rangle - (1/2)\beta\sigma_W^2 &= \Delta F \end{aligned} \quad (8.9)$$

⁵² Let $\{x_i = X_i(\omega) : i = 1, 2, \dots, N\}$ be a set of N independent, identically distributed, and finite variance random variables, with a common probability distribution $f(x)$. Let $Y = (1/N) \sum_{i=1}^N X_i$, be their sum. The probability distribution of the random variable Y is formally given by,

$$f_Y(y) = \int_{-\infty}^{+\infty} dx_1 \int_{-\infty}^{+\infty} dx_2 \cdots \int_{-\infty}^{+\infty} dx_N \prod_{i=1}^N f(x_i) \delta\left(y - N^{-1} \sum_{i=1}^N x_i\right)$$

Multiply both sides of the above by $\exp(-\beta y)$ and carry out an integration over y from $-\infty$ to $+\infty$. Make use of the property of the delta function : $\int_{-\infty}^{+\infty} g(x) \delta(x - x_0) = g(x_0)$, while carrying out the integration on the right hand side. We get $\phi_Y(\beta) = [\phi_X(\beta \rightarrow \beta/N)]^N$, where $\phi_X(\beta) = \int_{-\infty}^{+\infty} dx \exp(-\beta x) f(x)$. Therefore,

$$\phi_Y(\beta) = \exp\left[\sum_{n=1}^{\infty} \frac{(-\beta/N)^n}{n!} \zeta_n\right]^N = \exp\left[-\beta\zeta_1 + \frac{\beta^2}{2} \frac{\zeta_2}{N} + \mathcal{O}(1/N^2)\right]$$

Thus when $N \rightarrow \infty$, the third and higher order cumulants of Y go to zero and the distribution of y tends to a Gaussian with mean $\langle y \rangle = \langle x \rangle$ and variance $\sigma_Y^2 = \sigma_X^2/N$.

The quantity $\langle W \rangle - \Delta F$ is called the dissipation or dissipative work⁵³ Callen and Welton showed that in a thermostatted process, dissipation is proportional to fluctuation and we have the Callen-Welton theorem,

$$\langle W \rangle - \Delta F = \frac{1}{2} \beta \sigma_W^2 \quad (8.10)$$

which says that dissipation is proportional work fluctuations.

Figure (8.1) depicts the Gaussian distribution of work. $\langle W \rangle = 60$ units of energy; $W_R = 40$; $\sigma_W^2 = 160$; The area under the curve for $W \leq W_R$ is sometimes called the probability of violation of the Second law, since in this regime W is less than W_R . However we must remember that $\langle W \rangle$ is always greater than W_R consistent with the Second law; also see the next section.

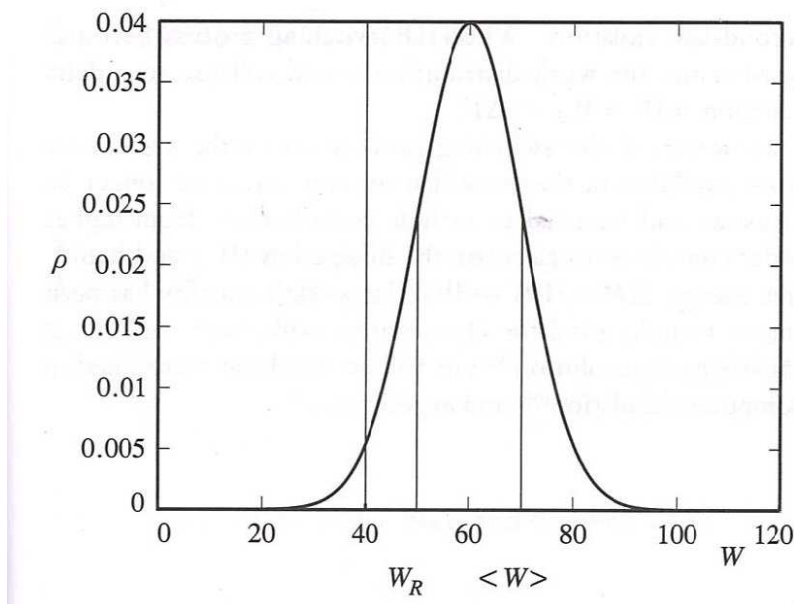


Fig. 8.1. Gaussian distribution of work. $\langle W \rangle = 60$; $\sigma^2 = 160$; $W_R = \Delta F = 40$

When the switching time τ increases two things happen.

1. $\sigma_W \rightarrow 0$.
2. $\langle W \rangle \rightarrow W_R$.

In the reversible limit, the work distribution tends to a delta function centered at W_R consistent with thermodynamic wisdom.

⁵³ A work performed irreversibly is called dissipative work. For example when you stir a cup of coffee with a spoon, you do dissipative work. Imagine a resistor R immersed in a fluid. A current i passes through the resistor for a duration of say t units of time. The work done is $i^2 R t$. This is dissipative work or irreversible work.

8.2.3 Jarzynski Identity and the Second Law

The exponential is a convex function⁵⁴. Hence,

$$\langle \exp(-\beta W) \rangle \geq \exp(-\beta \langle W \rangle) T \quad (8.11)$$

The Left Hand Side of the above is $\exp(-\beta \Delta F)$ according to jarzynski identity, Therefore,

$$\exp(-\beta \Delta F) \geq \exp(-\beta \langle W \rangle) \quad (8.12)$$

The above is equivalent to $\langle W \rangle \geq \Delta F$, which is a statement of the second law⁵⁵.

8.3 Heat Fluctuations : Crooks' Identity

Consider a closed system in thermal equilibrium with a thermostat at temperature $T = 1/(k_B \beta)$. Let $\Omega = \{\mathbf{x}_1, \mathbf{x}_2, \dots\}$ denote the set of all possible micro states of the closed system. Consider a sequence of micro states visited by the system at discrete times starting from \mathbf{X}_0 at time 0. Let us denote the sequence by

$$\mathcal{F} : \mathbf{X}_0 \rightarrow \mathbf{X}_1 \rightarrow \dots \rightarrow \mathbf{X}_{N-1} \rightarrow \mathbf{X}_N,$$

where the subscript is the discrete time index and $\mathbf{X}_i \in \Omega : i = 1, 2, \dots, N$. This sequence of micro states is a result of the system transacting energy with the thermostat by a heat processes. Our aim is to discover a good mathematical model for generating and characterizing such a sequence. To this end we shall turn our attention below.

Let $P(\mathcal{F})$ be the probability for the sequence \mathcal{F} . From Bayes' theorem we have,

$$P(\mathbf{X}_N, \mathbf{X}_{N-1}, \dots, \mathbf{X}_0) = P(\mathbf{X}_N | \mathbf{X}_{N-1}, \mathbf{X}_{N-2}, \dots, \mathbf{X}_0) \times P(\mathbf{X}_{N-1}, \mathbf{X}_{N-2}, \dots, \mathbf{X}_0) \quad (8.13)$$

Let us assume

$$P(\mathbf{X}_N | \mathbf{X}_{N-1}, \mathbf{X}_{N-2}, \dots, \mathbf{X}_0) = P(\mathbf{X}_N | \mathbf{X}_{N-1}), \quad (8.14)$$

This means that the future depends only on the present and not on the past. This is called Markovian assumption and

$$\mathbf{X}_0 \rightarrow \mathbf{X}_1 \rightarrow \dots \rightarrow \mathbf{X}_{N-1} \rightarrow \mathbf{X}_N$$

⁵⁴ A convex function is one for which $\lambda f(\mathbf{x}_1) + (1 - \lambda)f(\mathbf{x}_2) \geq f(\lambda \mathbf{x}_1 + (1 - \lambda)\mathbf{x}_2)$ for any $\mathbf{x}_1, \mathbf{x}_2$ belonging to the domain of f and $0 < \lambda < 1$. If we think of λ as the probability for \mathbf{x}_1 and $1 - \lambda$ as the probability of \mathbf{x}_2 , then the Left Hand Side of the above equation is $\langle f(\mathbf{x}) \rangle$ and the Right Hand Side is $f(\langle \mathbf{x} \rangle)$. Generalizing we can that the function $f(\mathbf{x})$ is convex if $\langle f(\mathbf{x}) \rangle \geq f(\langle \mathbf{x} \rangle)$, where the angular brackets denote averaging over the probability distribution of the random variable \mathbf{x} .

⁵⁵ Start with Clausius inequality, which is a consequence of the Second law of thermodynamics, and process as follows : $dS \geq q/T \Rightarrow q \leq TdS \Rightarrow dU - q \geq dU - TdS \Rightarrow dU - q \geq d(U - TS)$ (T remains constant) $\Rightarrow W \geq dF$.

which obeys such a condition is called a Markov chain. Once the present is specified, the future is independent of the past.

Under Markovian condition, the expression for the joint probability of the chain of micro states, simplifies to

$$\begin{aligned}
 P(\mathbf{X}_N, \mathbf{X}_{N-1}, \dots, \mathbf{X}_0) &= P(\mathbf{X}_N | \mathbf{X}_{N-1}) \times P(\mathbf{X}_{N-1}, \mathbf{X}_{N-2} \dots \mathbf{X}_0) \\
 &= P(\mathbf{X}_N | \mathbf{X}_{N-1}) \times P(\mathbf{X}_{N-1} | \mathbf{X}_{N-2}) \times P(\mathbf{X}_{N-2}, \mathbf{X}_{N-3} \dots, \mathbf{X}_0), \\
 &= \dots \dots \dots, \\
 &= P(\mathbf{X}_N | \mathbf{X}_{N-1}) \times P(\mathbf{X}_{N-1} | \mathbf{X}_{N-2}) \times \dots \times P(\mathbf{X}_1 | \mathbf{X}_0) \times P(\mathbf{X}_0).
 \end{aligned} \tag{8.15}$$

Since we are interested in equilibrium properties of the closed system, we consider a sequence of states visited by an equilibrium system : The conditional probability, $P(\mathbf{X}_i | \mathbf{X}_{i-1})$ is independent of the time index. In other words

$$P(\mathbf{X}_i = \mathcal{X}_\mu | \mathbf{X}_{i-1} = \mathcal{X}_\nu) = W_{\mu,\nu}, \tag{8.16}$$

and this quantity is independent of time. We call it time homogeneous Markov chain. Once we know the transition probability matrix \mathbf{W} and initial probabilities of all the micro states, we can calculate the probability of any given Markov Chain.

The transition probability matrix \mathbf{W} is a square matrix of size $\hat{\Omega}$. We have

$$0 \leq W_{\mu,\nu} \leq 1 \quad \forall \quad \mu, \nu \tag{8.17}$$

$$\sum_{\mu=1}^{\hat{\Omega}} W_{\mu,\nu} = 1 \quad \forall \quad \nu. \tag{8.18}$$

\mathbf{W} is called Markov matrix or stochastic matrix. Its elements are all between zero and unity. The elements of each column add to unity⁵⁶

We consider time homogeneous Markov chain. Let $P(\mathcal{X}_j, n)$ be the probability for the system to be in micro state \mathcal{X}_j at discrete time n . Let $W_{i,j}$ denote the probability for transition from micro state \mathcal{X}_j to micro state \mathcal{X}_i in one time step. We have

$$W_{i,j} = P(\mathcal{X}_i | \mathcal{X}_j), \tag{8.19}$$

the conditional probability that the system is in micro state \mathcal{X}_i at any instant of time given it was in micro state \mathcal{X}_j at the previous instant of time. The probabilities obey the Master equation given below.

$$P(\mathcal{X}_i; n+1) = \sum_{j: j \neq i} P(\mathcal{X}_j, n) W_{i,j} + P(\mathcal{X}_i, n) W_{i,i} \tag{8.20}$$

$\sum_i W_{i,j} = 1 \quad \forall \quad j$. Therefore,

$$W_{i,i} = 1 - \sum_{j: j \neq i} W_{j,i}. \tag{8.21}$$

⁵⁶ In addition, if the elements of each row also add to unity, then the transition probability matrix is doubly stochastic

We can write the above as

$$\begin{aligned}
 P(\mathcal{X}_i; n+1) &= \sum_{j \neq i} P(\mathcal{X}_j, n) W_{i,j} + P(\mathcal{X}_i, n) \left(1 - \sum_{j : j \neq i} W_{j,i} \right) \\
 &= P(\mathcal{X}_i, n) + \sum_{j \neq i} [P(\mathcal{X}_j, n) W_{i,j} - P(\mathcal{X}_i, n) W_{j,i}] \\
 &= P(\mathcal{X}_i, n) + \sum_{j=1}^{\hat{\Omega}} [P(\mathcal{X}_j, n) W_{i,j} - P(\mathcal{X}_i, n) W_{j,i}] \quad \forall i \quad (8.22)
 \end{aligned}$$

8.3.1 Balance Condition

When the system equilibrates we have $P(\mathcal{X}_i, n+1) = P(\mathcal{X}_i, n) = \pi(\mathcal{X}_i) \forall i$. Therefore we have

$$\sum_j [\pi(\mathcal{X}_j) W_{i,j} - \pi(\mathcal{X}_i) W_{j,i}] = 0.$$

This is called the balance condition which ensures that the Markov chain eventually equilibrates.

8.3.2 Detailed Balance Condition

Look at the balance condition given as a sum over j for each i . We can make a stricter demand that each term in the sum be zero. Then we get the detailed balance condition :

$$\pi(\mathcal{X}_j) \times W_{i,j} = \pi(\mathcal{X}_i) \times W_{j,i} \quad \forall i, j = 1, 2, \dots, \hat{\Omega}.$$

An important consequence of this is that detailed balance ensures that the Markov chain is reversible; hence it is most suited for describing an equilibrium system. For, no matter what kind of observations you make on an equilibrium system, you can not tell which direction time moves. Both directions are equally plausible and equally unverifiable. Equilibrium is a time-reversal invariant state. Detailed balance captures this subtle property.

8.3.3 Time Reversed Markov Chain

At discrete time N let us reverse the Markov chain and get

$$\mathcal{R} : \mathbf{X}_N \rightarrow \mathbf{X}_{N-1} \rightarrow \dots \rightarrow \mathbf{X}_1 \rightarrow \mathbf{X}_0.$$

A little thought will tell you the chain \mathcal{R} is also a Markov chain : for, the future in \mathcal{R} (which is past in \mathcal{F}) is independent of past in \mathcal{R} (which is future in \mathcal{F}) once

the present in \mathcal{R} (which is the same as present in \mathcal{F}) is specified. Hence the time reversed chain is also Markovian.

Let us denote the transition probability matrix of the time reversed chain by the symbol $\mathbf{W}^{(\mathcal{R})}$. We have

$$\begin{aligned} W_{i,j}^{(\mathcal{R})} &= P(X_n = \mathcal{X}_i | X_{n+1} = \mathcal{X}_j) = \frac{P(X_n = \mathcal{X}_i, X_{n+1} = \mathcal{X}_j)}{\pi(\mathcal{X}_j)} \\ &= \frac{P(X_{n+1} = \mathcal{X}_j | X_n = \mathcal{X}_i) \pi(\mathcal{X}_i)}{\pi(\mathcal{X}_j)} \\ &= W_{j,i} \frac{\pi(\mathcal{X}_i)}{\pi(\mathcal{X}_j)} \end{aligned} \quad (8.23)$$

The condition for reversibility is $W_{i,j}^{(\mathcal{R})} = W_{i,j}$. The transition probability matrix should be the same for both Markov chains - the time forward and the time reversed. Hence on the left hand side of the above equation replace $W_{i,j}^{(\mathcal{R})}$ by $W_{i,j}$ and reorganize the terms. Then the condition for reversibility reads as,

$$W_{i,j} \pi(\mathcal{X}_j) = W_{j,i} \pi(\mathcal{X}_i). \quad (8.24)$$

We immediately recognize this as detailed balance condition. Thus a Markov chain of micro states of an equilibrium system obeys detailed balance condition and hence is reversible.

Now we have a good mathematical model - a reversible Markov chain, to describe an equilibrium closed system transacting energy with the thermostat by heat processes. We need an algorithm that will give us the right transition matrix obeying detailed balance. Consider two micro states \mathcal{X}_i , and \mathcal{X}_j of the equilibrium closed system. Let ϵ_i and ϵ_j denote their energies. Also let $\pi_i \propto \exp(-\beta\epsilon_i)$ and $\pi_j \propto \exp(-\beta\epsilon_j)$ be their probabilities. These are also called Boltzmann weight. Let $r = \pi_j/\pi_i = \exp[-\beta(\epsilon_j - \epsilon_i)]$. Metropolis algorithm prescribes that $W_{j,i} = \min(1, r)$. It is easily verified that the Metropolis algorithm obeys detailed balance condition : Let $\pi_i > \pi_j$. Then $W_{i,j} = 1$ and $W_{j,i} = \pi_j/\pi_i$; Therefore $W_{i,j}\pi_j = \pi_j$ and $W_{j,i}\pi_i = (\pi_j/\pi_i)\pi_i = \pi_j$, consistent with the detailed balance condition.

8.3.4 Crooks identity

Now we are ready to state Crooks' identity about heat fluctuations. Let $Q(\mathcal{F})$ be the energy transacted by the system with the thermostat, during a forward sequence of micro states starting from \mathbf{X}_0 . Let $P(\mathcal{F}|\mathbf{X}_0)$ be the conditional probability of the forward Chain given the initial micro state \mathbf{X}_0 . Let $P(\mathcal{R}|\mathbf{X}_N)$ be the conditional probability of reverse chain, given the initial micro state \mathbf{X}_N . Crooks' identity ⁵⁷ says

⁵⁷ G E Crooks, Journal of Statistical Physics **90** 1481(1998)

$$\frac{P(\mathcal{F}|X_0)}{P(\mathcal{R}|X_N)} = \exp[-\beta Q(\mathcal{F})]. \quad (8.25)$$

where $Q(\mathcal{F})$ is the energy transacted by heat in the forward process.

8.3.5 Crooks' Identity : A Back-of-the-Envelope Calculation

Let me illustrate Crooks' identity on a back-of-the-envelope problem described below.

We refer to the children-in-the-escalator analogy discussed earlier and depicted in Fig. (8.2).

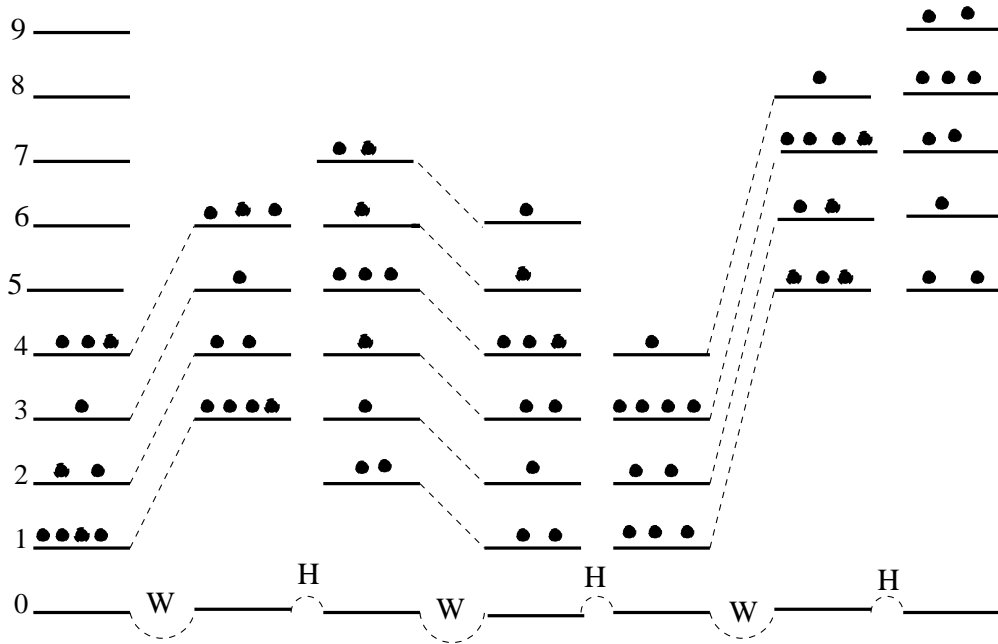


Fig. 8.2. A work step is followed by a heat step. Three consecutive pairs of work and heat steps are shown. There are ten children placed at different rungs labelled by their energies. The work step consists of the elevator moving up or down - the rungs move up or down carrying the children along with them. The children in each rung remain stay put. The movement of occupied rungs are indicated by dashed line connecting a rung before and after the work step. In the heat step, the elevator stands still. The children move up or down the rungs. The distribution of children changes. The first heat step changes the distribution from $\{n_3 = 4, n_4 = 2, n_5 = 1, n_6 = 3\}$ to $\{n_2 = 2, n_3 = 1, n_4 = 2, n_5 = 3, n_6 = 1, n_7 = 1\}$. The work and heat steps are also marked as W and H at the bottom of the figure.

There are ten children, marked as filled circles in the figure, positioned at various rungs of an escalator. The rungs are labelled by their energy levels. Only the occupied rungs are shown in the figure.

Initial Distribution. To begin we have children occupying the rungs labelled 1, 2, 3, 4. The energy of the system is +23 units.

First Work Step. The escalator goes up by two units. The rungs go up carrying along with them the children; there occurs no change in the distribution of the children. The rungs are re-labelled : $i \rightarrow i + 2$. This is a work step. At the end of the first work step, the energy is **43** units; it has increased by **20** units.

First Heat Step. The work step is followed by a heat step in which the escalator does not move but the children do. The heat step increases the energy of the system from **43** to **46**, an increase by **3** units. The probability for this to happen is ω^3 , where we have taken $\omega = \exp(-\beta)$.

Second Work Step. The second work step shifts the energy from **46** to **33** a decrease by **13** units. The probability for the work step is unity.

Second Heat Step. The heat step that follows, reduces the energy further by **10** units. The probability of such a heat step unity. At the end of the second heat step, the system has **23** units of energy.

Third Work Step. The work step that follows, the third one, increases the energy from **23** to **63** units. The probability of the work step is unity.

Third Heat Step. The heat step that follows, increases it further to **72** units. The increment is by **9** units and the probability such a heat step is ω^9 .

Verification of Crooks' identity. We have,

$$\begin{aligned} P(\mathcal{F}|X_0) &= \omega^3 \times 1 \times \omega^9 = \omega^{12} \\ P(\mathcal{R}|X_N) &= 1 \times \omega^{10} \times 1 = \omega^{10} \\ \frac{P(\mathcal{F}|X_0)}{P(\mathcal{R}|X_N)} &= \omega^2 \end{aligned} \tag{8.26}$$

The net energy transacted in the forward process, by heat is given by,

$$Q(\mathcal{F}) = (46 - 43) + (23 - 33) + (72 - 63) = 2 \text{ units.} \tag{8.27}$$

Therefore $\exp(-\beta Q) = \omega^2$, verifying Crooks' identity.

8.4 End Remarks

In these lectures I have dealt with microscopic description of heat and work. Heat originates from change of probabilities of micro states; work has its origin in change of the energies of the micro states. We discussed at length of the mathematical machinery, like cumulant expansion, central limit theorem *etc.* required for characterizing work fluctuations. We found that from an ensemble of work values obtained from non equilibrium switching experiments, we can extract equilibrium free energies. More importantly we found a way to estimate the probability for work done in a switching experiment to be less than reversible work. We learned of reversible Markov chains, for describing heat fluctuations. We found a dissipative segment of

a Markov chain is overwhelmingly more probable than its reverse, a fact beautifully quantified in Crooks' identity.

The work and heat fluctuation theorems tell us the of the probability for a macroscopic system to behave in a way opposite to the way dictated by the Second law of thermodynamics. We found that the probability of the so-called Second law violation is exponentially small for large systems.

In a sense the fluctuation theorems bring the curtains down on the dramatic narrative started by James Clerk Maxwell⁵⁸ half and one century ago, when he invented a demon to violate the Second law of thermodynamics. Maxwell's argument was simple : if entropy is of probabilistic origin, and this is what statistical mechanics would like us believe, then the Second law is of statistical origin. If so, the Second law can be violated with nonzero probability.

The fluctuation theorems of Jarzynski, and Crooks provide us with a quantitative measure of what a Maxwell's demon⁵⁹ can accomplish, in small systems and/or over small time-intervals of observation

⁵⁸ J C Maxwell, letter to P G Tait dated 11 December 1867, reproduced in G C Knot, *Life and Scientific Work of Peter Guthrie Tait*, Cambridge University Press (1924)p.213

⁵⁹ For information on Maxwell's demon, see H S Leff, and A F Rex (Eds.) *Maxwell's Demon : Entropy, Information, and Computing*, Adam Higler, Bristol (1990); *ibid*, *Maxwell's Demon*, Princeton University Press (1990); *ibid*, *Maxwell's Demon - 2 : Entropy, Classical and Quantum Information, Computing*, Institute of Physics (2003).

WORKED EXAMPLES

9.1 $PV^\gamma = \Theta$: Adiabatic process

Starting from the first law of thermodynamics, show that an adiabat⁶⁰ of an ideal gas is described by $PV^\gamma = \Theta_1$, or equivalently, $TV^{\gamma-1} = \Theta_2$, or $P^{1-\gamma}T^\gamma = \Theta_3$, where $\Theta_i : i = 1, 2, 3$ are constants and $\gamma = C_P/C_V$. For a mono atomic ideal gas $\gamma = 5/3$.

Solution

Start with the first law of thermodynamics.

$$\begin{aligned} dU &= \delta Q + \delta W; \quad \delta Q = 0 \text{ (adiabat)} \Rightarrow dU = \delta W \\ C_V dT &= -PdV \end{aligned} \quad (9.28)$$

Now start with the ideal gas law and proceed as follows.

$$\begin{aligned} PV &= nRT; \quad PdV + VdP = nRdT \\ dT &= \frac{1}{nR} (PdV + VdP) \\ C_V dT &= \frac{C_V}{nR} (PdV + VdP) \end{aligned} \quad (9.29)$$

From Eq. (9.28) and Eq. (9.29) we get, $-PdV = (C_V/nR) (PdV + VdP)$. Replace nR by $C_P - C_V$, and⁶¹, get,

$$\begin{aligned} -PdV &= \frac{C_V}{C_P - C_V} (PdV + VdP) \Rightarrow PdV = \frac{1}{\gamma - 1} (PdV + VdP) \\ -1 &= \frac{1}{\gamma - 1} \left(1 + \frac{VdP}{PdV} \right) \\ \frac{dP}{P} &= -\gamma \frac{dV}{V} \\ PV^\gamma &= \Theta_1 \end{aligned} \quad (9.30)$$

where Θ_1 is a constant.

The other two equations can be obtained by noting that $PV = nRT$.

⁶⁰ a quasi static reversible adiabatic process is often referred to as an adiabat.

⁶¹ To show this, we start with enthalpy $H(S, P) = U + PV$ where $P = -(\partial U / \partial V)_S \Rightarrow dH = dU + d(PV) = dU + d(nRT)$ since $PV = nRT$; $C_P dT = C_V dT + nRdT$; $C_P - C_V = nR$

- Substitute $P = nRT/V$ in Eq. (9.30) and get $TV^{\gamma-1} = \Theta_2$
- Substitute $V = nRT/P$ in Eq. (9.30) and get, $P^{1-\gamma}T^\gamma = \Theta_3$

9.2 Work done in an adiabatic process

Show that the work done in a (quasi static reversible adiabatic process in an ideal gas depends only on the initial and final temperatures.

Solution

For an adiabat, $PV^\gamma = \Theta$. Initial state $A = P_1, V_1, T_1 = P_1V_1/(nR)$. Final state $B = P_2, V_2, T_2 = P_2V_2/(nR)$.

$$\begin{aligned}
 W &= - \int_A^B P dV = -\Theta \int_{V_1}^{V_2} dV/V^\gamma = \Theta \frac{V_2^{-\gamma+1} - V_1^{-\gamma+1}}{\gamma - 1} \\
 &= \frac{P_2V_2^\gamma V_2^{-\gamma+1} - P_1V_1^\gamma V_1^{-\gamma+1}}{\gamma - 1} \\
 &= \frac{P_2V_2 - P_1V_1}{\gamma - 1} \\
 &= \frac{nR(T_2 - T_1)}{\gamma - 1} \quad (9.31)
 \end{aligned}$$

9.3 Work done in an isothermal process : ideal and van der Waal gas

Consider a quasi-static reversible process in which n moles of an ideal gas expands isothermally from an initial volume of V_1 to a final volume of V_2 .

- Derive an expression for work done
- What is the energy transacted by heat
- Derive an expression for the work done by the van der Waal gas

Solution

- Work done in an isothermal process :

$$\begin{aligned}
 dW &= -PdV; \quad P = nRT/V; \\
 &= -nRTdV/V \quad (9.32)
 \end{aligned}$$

$$W = -nRT \int_{V_1}^{V_2} \frac{dV}{V} = -nRT \ln(V_2/V_1) \quad (9.33)$$

(ii) Energy transacted by heat :

For an isothermal process in an ideal gas $dU = 0$;

From first law : $dU = dQ + dW$.

Therefore $dQ = -dW = +nRT \ln(V_2/V_1)$

(iii) Work done in van der Waal gas : the van der Waal equation of state is

$$\left(P + a \frac{n^2}{V^2}\right) (V - nb) = nRT \quad (9.34)$$

a and b are van der Waal constants; R is universal gas constant. We can write the above in a convenient form,

$$P = a \frac{n^2}{V^2} + \frac{nRT}{V - nb} \quad (9.35)$$

Work done is

$$\begin{aligned} W &= - \int_{V_1}^{V_2} P dV = -an^2 \int_{V_1}^{V_2} \frac{dV}{V^2} - nRT \int_{V_1}^{V_2} \frac{dV}{V - nb} \\ &= an^2 \left(\frac{1}{V_1} - \frac{1}{V_2} \right) - nRT \ln \left(\frac{V_2 - nb}{V_1 - nb} \right) \end{aligned} \quad (9.36)$$

9.4 An adiabat is steeper than an isotherm

C B P Finn, *Thermal Physics* (Second edition) Nelson Thornes (1993)P.223 (3.10)

Show that an adiabat for an ideal gas is steeper by a factor γ than an isotherm at a point on the $P - V$ phase diagram.

Solution

Adiabat :

$$\begin{aligned} PV^\gamma &= \Theta \Rightarrow P = \Theta V^{-\gamma} \Rightarrow \frac{\partial P}{\partial V} = -\Theta \gamma V^{-\gamma-1} \\ &= -(PV^\gamma) \gamma V^{-\gamma-1} \\ &= -\gamma \frac{P}{V} \end{aligned} \quad (9.37)$$

Isotherm :

$$\begin{aligned} PV &= \Theta \Rightarrow P = \Theta V^{-1} \Rightarrow \frac{\partial P}{\partial V} = -\Theta V^{-2} \\ &= -(P V) V^{-2} \\ &= -\frac{P}{V} \end{aligned} \quad (9.38)$$

9.5 Adiabats don't meet

Show that no two adiabats meet at a point.

Solution

Proof by *reductio ad absurdum*. Assume two adiabats meet at **A** on the pressure - volume phase diagram as shown in Fig. (9.3).

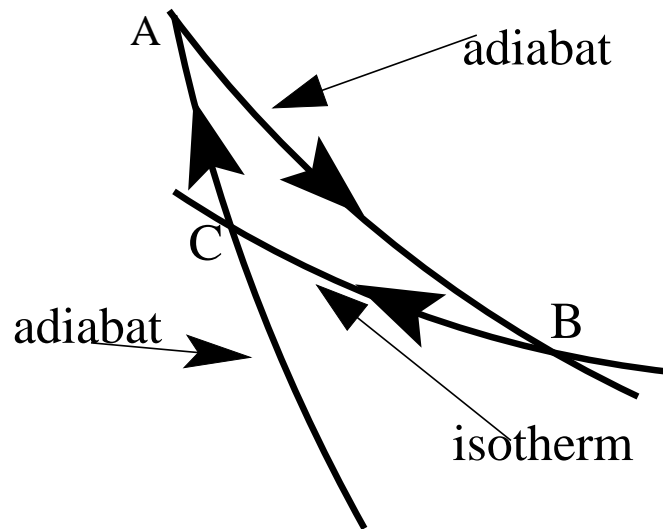


Fig. 9.3. *Reductio ad absurdum* : Two adiabats are assumed to meet at **A**; An isotherm intersects them at **B** and **C** and forms a cycle $A \rightarrow B \rightarrow C \rightarrow A$.

$A \rightarrow B$ and $A \rightarrow C$ are the two adiabats meeting at **A**. Let $B \rightarrow C$ be an isotherm cutting both the adiabats. By this construction we have a cycle $A \rightarrow B \rightarrow C \rightarrow A$. Assume a machine starts at **A**. Let the working substance be ideal gas, The machine goes to **B** adiabatically; the gas expands and does work. It is then compressed isothermally as it goes from $B \rightarrow C$. During this process work is done on the system and equivalent heat is absorbed from a heat reservoir at temperature **T**. In the least leg of the cycle the gas undergoes adiabatic compression and the machine returns to its initial state. There is no change in the entropy of the machine, since its thermodynamic state at the end is the same as it was at the beginning. The heat source loses entropy since it supplies heat to the machine during isothermal compression $B \rightarrow C$. Note there is no transaction of heat during the two adiabats, $A \rightarrow B$ and $C \rightarrow A$ and hence no change in entropy. There is a net work done which equals the area enclosed by the three curves. But then there is a decrease in entropy and is not permitted by the Second law.

Also according to Carnot's principle, to get extract work, heat has to fall from hot to cold. But in the cycle under consideration we have only the hot source; the cold sink is not there. Hence no two adiabats meet.

9.6 $C_P - C_V$

See D Kondepudi, and Ilya Prigigine, *Modern Thermodynamics : from heat engines to dissipative structures*, John Wiley (1998)p.45

Starting from the first law of thermodynamics, show that,

$$C_P - C_V = \left[P + \left(\frac{\partial U}{\partial V} \right)_T \right] \left(\frac{\partial V}{\partial T} \right)_P.$$

In the above, C_P is heat capacity at constant pressure; C_V is heat capacity at constant volume; For an ideal gas, show that the above reduces to $C_P - C_V = nR$.

Solution

Start with $U \equiv U(T, V)$.

$$dU = \left(\frac{\partial U}{\partial T} \right)_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV = \delta Q + \delta W \quad (9.39)$$

$$\begin{aligned} \delta Q &= \left(\frac{\partial U}{\partial T} \right)_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV - \delta W \\ &= \left(\frac{\partial U}{\partial T} \right)_V dT + \left[P + \left(\frac{\partial U}{\partial V} \right)_T \right] dV \end{aligned} \quad (9.40)$$

If the system is heated at constant volume, no work is done. Hence $\delta Q = dU$. Therefore,

$$C_V = \frac{\delta Q}{\Delta T} = \left(\frac{\partial U}{\partial T} \right)_V \quad (9.41)$$

If the system is heated at constant pressure, we proceed as follows.

$$\delta Q = C_V dT + \left[P + \left(\frac{\partial U}{\partial V} \right)_T \right] dV \quad (9.42)$$

$$C_P = \frac{\delta Q}{dT} = C_V + \left[P + \left(\frac{\partial U}{\partial V} \right)_T \right] \left(\frac{\partial V}{\partial T} \right)_P \quad (9.43)$$

$$C_P - C_V = \left[P + \left(\frac{\partial U}{\partial V} \right)_T \right] \left(\frac{\partial V}{\partial T} \right)_P \quad (9.44)$$

If you want to increase the temperature of the system keeping it at constant pressure, you have to supply additional heat to compensate for the accompanying

volume expansion. The right hand side of the above equation corresponds to this additional heat.

What we have above is a very general statement. For an ideal gas, U depends only on T ; it is independent of V . Hence

$$\left(\frac{\partial U}{\partial V}\right)_T = 0.$$

Also for an ideal gas,

$$V = \frac{nRT}{P}$$

Therefore,

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{nR}{P}$$

It follows then $C_P - C_V = nR$

9.7 Exact and inexact differentials

We have, $\Delta f = \alpha dx + \gamma x/y dy$. Show that Δf is not an exact differential by : (i) Method -1 : calculate the changes occurring in the quantity f along the following two paths, $(2, 2) \rightarrow (3, 2) \rightarrow (3, 3)$ and $(2, 2) \rightarrow (2, 3) \rightarrow (3, 3)$, and show they are different (ii) Method - 2 : Take the partial derivative of the pre factors of dx with respect to y and that of dy with respect to x and show they are different.

Divide all the terms in the given equation by x ; let $\Delta g = \Delta f/x$. Show that Δg is a perfect differential following the two methods listed above.

Solution

It is given that $\Delta f = \phi(x, y)dx + \psi(x, y)dy$, where $\phi * x, y = \alpha$ and $\psi(x, y) = \gamma x/y$.

(i) Change in f along the two paths

(a) path-1 : $(2, 2) \rightarrow (3, 2) \rightarrow (3, 3)$ is given by,

$$\begin{aligned} \delta(\text{Path} - 1) &= \int_2^3 dx \phi(x, y = 2) + \int_2^3 dy \psi(x = 3, y) \\ &= \alpha \int_2^3 dx + 3\gamma \int_2^3 dy/y \\ &= \alpha + 3\gamma \ln(3/2) \end{aligned} \tag{9.45}$$

(b) path-2 :

$$\begin{aligned}
\delta(\text{Path} - 2) &= \int_2^3 dy \psi(x=2, y) + \int_2^3 dy \phi(x, y=3) \\
&= 2\gamma \int_2^3 dy/y + \alpha \int_2^3 dx \\
&= \alpha + 2\gamma \ln(3/2)
\end{aligned} \tag{9.46}$$

Therefore $\delta f(\text{path} - 1) \neq \delta(\text{path} - 2)$. This is sufficient (though not necessary) to show that Δf is not an exact differential.

(ii) We find

$$\left(\frac{\partial \phi}{\partial y}\right)_x = 0; \quad \left(\frac{\partial \psi}{\partial x}\right)_y = \alpha/y \tag{9.47}$$

Thus,

$$\left(\frac{\partial \phi}{\partial y}\right)_x \neq \left(\frac{\partial \psi}{\partial x}\right)_y \tag{9.48}$$

Therefore Δf is not a perfect differential. This condition is necessary and sufficient to show that Δf is not a perfect differential.

(iii) Diving both sides of the given equation by x we get

$$\Delta g = \frac{\Delta f}{x} = \alpha \frac{1}{x} dx + \gamma \frac{1}{y} dy \tag{9.49}$$

We have $\phi(x, y) \stackrel{\partial U}{=} \alpha/x$ and $\psi(x, y) = \gamma/y$.

The change in g along path-1 is given by,

$$\begin{aligned}
\delta(\text{Path} - 1) &= \int_2^3 dx \phi(x, y=2) + \int_2^3 dy \psi(x=3, y) \\
&= \alpha \int_2^3 dx/x + \gamma \int_2^3 dy/y \\
&= \alpha \ln(3/2) + \gamma \ln(3/2)
\end{aligned} \tag{9.50}$$

The change in g along path-2 is given by,

$$\begin{aligned}
\delta(\text{Path} - 2) &= \int_2^3 dy \psi(x=2, y) + \int_2^3 dy \phi(x, y=3) \\
&= \gamma \int_2^3 dy/y + \alpha \int_2^3 dx/x \\
&= \alpha \ln(3/2) + \gamma \ln(3/2)
\end{aligned} \tag{9.51}$$

We find that $\delta(\text{path} - 1) = \delta(\text{path} - 2)$. This condition is necessary for δg to be a perfect differential, but not sufficient.

We find

$$\left(\frac{\partial \phi}{\partial y}\right)_x = \left(\frac{\partial \psi}{\partial x}\right)_y = 0 \tag{9.52}$$

The above is a necessary and sufficient condition for Δg to an exact differential

9.8 Iso-entropic process

A particular system obeys the fundamental equation,

$$U = A \frac{N^3}{V^2} \exp\left(\frac{S}{Nk_B}\right),$$

where A (joule metre²) is a constant. Initially the system is at $T = 317.48$ kelvin, and $P = 2 \times 10^5$ pascals. The system expands reversibly until the pressure drops to a value of 10^5 pascals, by a process in which the entropy does not change. What is the final temperature ?

HINT: Derive expressions for temperature T and pressure P by taking partial derivatives of U with respect to S and V respectively. Find a relation between P and T for a quasi static reversible process in which the entropy and number of particles N remain the same.

Solution

$$T(S, V) = \left(\frac{\partial U}{\partial S}\right)_{V, N} = \frac{1}{V^2} \frac{AN^2 \exp(S/NR)}{R} = \frac{1}{V^2} \phi_1(S) \quad (9.53)$$

$$P(S, V) = -\left(\frac{\partial U}{\partial V}\right)_{S, N} = \frac{2}{V^3} AN^3 \exp(S/NR) = \frac{1}{V^3} \phi_2(S) \quad (9.54)$$

$$\frac{T^{1/2}}{P^{1/3}} = \phi_3(S) \quad (9.55)$$

It is given that entropy does not change during the process of expansion. Therefore,

$$\frac{T^{1/2}}{P^{1/3}} = \Theta \quad (9.56)$$

where Θ is a constant. Therefore,

$$\frac{T_1^{1/2}}{P_1^{1/3}} = \frac{T_2^{1/2}}{P_2^{1/3}} \Rightarrow \left(\frac{T_1}{T_2}\right)^{1/2} = \left(\frac{P_1}{P_2}\right)^{1/3} \quad (9.57)$$

It is given : $T_1 = 317.47$ kelvin; $P_1 = 2 \times 10^5$ pascals; and $P_2 = 10^5$ pascals. Therefore $T_2 = 2^{-2/3} \times 317.48 = 200$ kelvin

9.9 Joule's ideal gas engine

The cycle $A \rightarrow B \rightarrow C \rightarrow D \rightarrow A$ of an ideal gas engine proposed by Joule is depicted on a $P - V$ phase diagram below. There are four segments - quasi static and reversible. The segments $A \rightarrow B$ (volume increases) and $C \rightarrow D$ (volume decreases) are isobaric; the segments $B \rightarrow C$ (expansion) and $D \rightarrow A$ (compression) are adiabats.

- (i) Find the energy transacted by heat and work in each of the four segments of the cycle
- (ii) Find the entropy change in each of the four segments of the cycle.
- (iii) Show that the efficiency of the engine is given by $\eta = 1 - (P_1/P_2)^\alpha$, where $\alpha = (\gamma - 1)/\gamma$ and $\gamma = C_P/C_V = 5/3$ for mono atomic ideal gas.

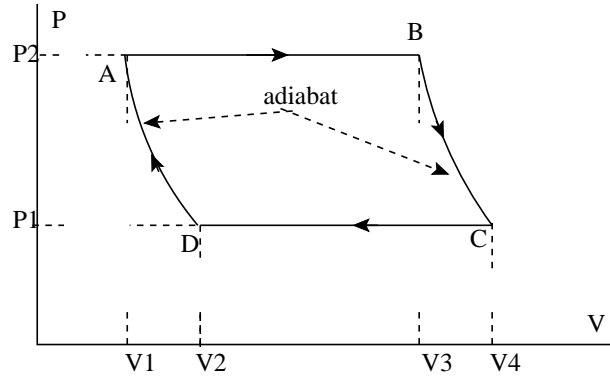


Fig. 9.4. A reversible cycle of Joule's engine

Solution

- (i) Segment $A \rightarrow B$

$$dW = -P_2 dV \quad (9.58)$$

$$W(A \rightarrow B) = -P_2 \int_{V_1}^{V_3} dV = -P_2(V_3 - V_1) \quad (9.59)$$

$W(A \rightarrow B)$ is negative. Work is done by the system.

$$dQ = C_P dT = (5/2)P_2 dV \quad (9.60)$$

$$Q(A \rightarrow B) = C_P \int_A^B dT = (5/2)P_2(V_3 - V_1) \quad (9.61)$$

$Q(A \rightarrow B)$ is positive; heat is absorbed by the system. Segment $B \rightarrow C$

$$W(B \rightarrow C) = -\frac{P_2 V_3 - P_1 V_4}{\gamma - 1}; \quad Q(B \rightarrow C) = 0 \quad (9.62)$$

$W(B \rightarrow C)$ is negative; work is done by the system

Segment $C \rightarrow D$

$$W(C \rightarrow D) = -P_1 \int_{V_4}^{V_2} dV = P_1(V_4 - V_2) \quad (9.63)$$

$W(C \rightarrow D)$ is positive : work is done on the system

$$Q(C \rightarrow D) = -\frac{5P_1(V_4 - V_2)}{2} \quad (9.64)$$

$Q(C \rightarrow D)$ is negative; heat is liberated by the system.

Segment $D \rightarrow A$

$$W(D \rightarrow A) = \frac{P_2 V_1 - P_1 V_2}{\gamma - 1} : Q(D \rightarrow A) = 0 \quad (9.65)$$

$W(D \rightarrow A)$ is positive; work is done on the system.

(ii) Calculation of entropy

$$\begin{aligned} S(B) &= S(A) + \int_{A \rightarrow B} \frac{dQ}{T} = S(A) + \frac{5nR}{2} \int_{V_1}^{V_3} \frac{dV}{V} \\ &= S(A) + \frac{5nR}{2} \ln(V_3/V_1) \end{aligned} \quad (9.66)$$

$$S(C) = S(B) \quad (9.67)$$

$$S(D) = S(C) + \frac{5nR}{2} \ln(V_2/V_4) \quad (9.68)$$

$$\text{Adiabat : } PV^\gamma = \Theta \Rightarrow P^{1/\gamma}V = \Theta$$

$$\text{Adiabat } B \rightarrow C : P_2^{1/\gamma}V_3 = P_1^{1/\gamma}V_4$$

$$\text{Adiabat } D \rightarrow A : P_1^{1/\gamma}V_2 = P_2^{1/\gamma}V_1$$

$$\frac{V_3}{V_1} = \frac{V_4}{V_2} ; P_2^{1/\gamma}(V_3 - V_1) = P_1^{1/\gamma}(V_4 - V_2)$$

(iii) Efficiency of a Joule's engine

$$\begin{aligned}
 \eta &= \frac{W}{Q_1} = 1 - \frac{Q_2}{Q_1} = 1 - \frac{Q(C \rightarrow B)}{Q(A \rightarrow B)} \\
 &= 1 - \frac{P_1(V_4 - V_2)}{P_2(V_3 - V_1)} \\
 &= 1 - \frac{P_1 P_2^{1/\gamma}}{P_2 P_1^{1/\gamma}} \\
 &= 1 - \left(\frac{P_1}{P_2} \right)^{1-(1/\gamma)} \quad (9.69)
 \end{aligned}$$

9.10 Cyclic Process : Rectangle in $S - V$ Plane

See N Newman, J Ruhl, S Staggs, and, S Thorset, *Princeton Problems in Physics with Solutions*, Universities Press (2000)p.24 and p.153

n mols of an ideal gas engine goes through a (quasi-static) reversible cyclic process depicted in Entropy - Volume phase plane, depicted below.

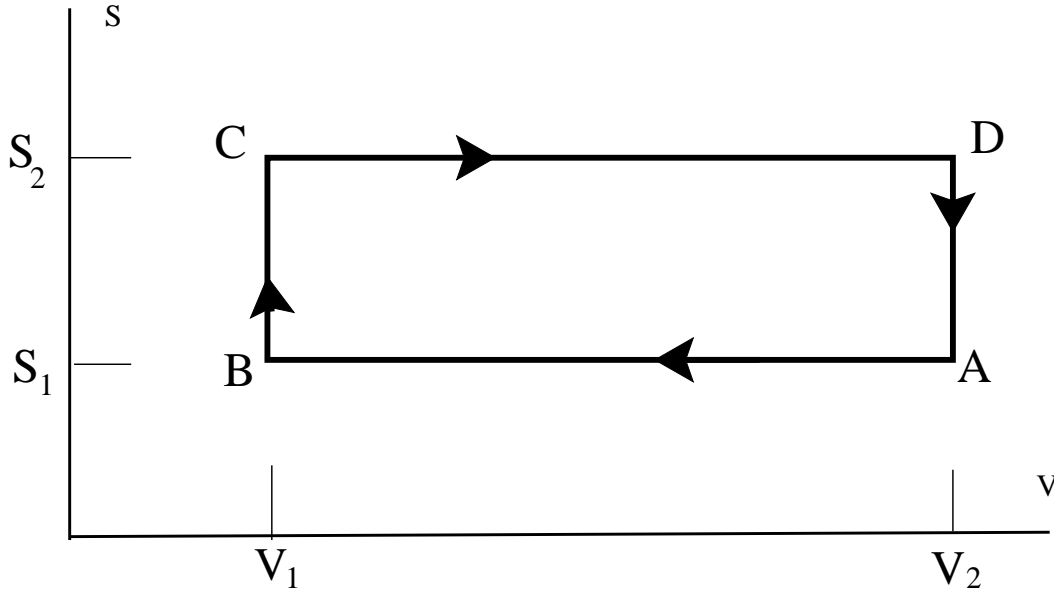


Fig. 9.5. A reversible cycle in $S - V$ phase plane

C_V denotes the heat capacity at constant volume. It is independent of temperature. Show that the efficiency of the engine is given by

$$\eta = 1 - \left(\frac{V_1}{V_2} \right)^{nR/C_V} .$$

where R is the universal gas constant.

Solution

Let us first derive an expression for temperature as a function of entropy and volume : $T \equiv T(S, V)$, see below.

$$\begin{aligned} dU &= TdS - PdV \\ TdS &= dU + PdV \\ &= C_V dT + nRT \frac{dV}{V} \\ dS &= C_V \frac{dT}{T} + nR \frac{dV}{V}; \end{aligned} \quad (9.70)$$

$$\begin{aligned} \int dS &= C_V \int \frac{dT}{T} + nR \int \frac{dV}{V} \\ S &= C_V \ln T + nR \ln V + \text{a constant} \\ \ln T &= \frac{S}{C_V} - \frac{nR}{C_V} \ln V + \text{a constant} \end{aligned} \quad (9.71)$$

$$T = \alpha \exp(S/C_V) V^{-nR/C_V} \quad (9.72)$$

where α is a constant.

There are four segments : 1. $A \rightarrow B$ 2. $B \rightarrow C$ 3. $C \rightarrow D$ and 4. $D \rightarrow A$.

Work is done only during the segments $C \rightarrow D$ and $A \rightarrow B$.

Consider segment $C \rightarrow D$.

$$\begin{aligned} W(C \rightarrow D) &= - \int_{V_1}^{V_2} P dV \\ &= -nR \int_{V_1}^{V_2} T \frac{dV}{V} \\ &= -\alpha nR \int_{V_1}^{V_2} dV V^{-(nR/C_V)-1} \exp(S_2/C_V) \\ &= +\alpha C_V \exp(S_2/C_V) \left[V^{-nR/C_V} \right]_{V_1}^{V_2} \\ &= +\alpha C_V \exp(S_2/C_V) \left[V_2^{-nR/C_V} - V_1^{-nR/C_V} \right] \end{aligned} \quad (9.73)$$

Similarly we can calculate $W(A \rightarrow B)$. Thus we have

$$W(C \rightarrow D) = -\alpha C_V \exp(S_2/C_V) \left[V_1^{-nR/C_V} - V_2^{-nR/C_V} \right] \quad (9.74)$$

$$W(A \rightarrow B) = +\alpha C_V \exp(S_1/C_V) \left[V_1^{-nR/C_V} - V_2^{-nR/C_V} \right] \quad (9.75)$$

The total work done is given by $W = W(C \rightarrow D) + W(A \rightarrow B)$.

$$W = -\alpha C_V \left[V_1^{-nR/C_V} - V_2^{-nR/C_V} \right] \times \left[\exp(S_2/C_V) - \exp(S_1/C_V) \right] \quad (9.76)$$

Note : W is negative; the engine delivers work.

The transaction of heat occurs during the segments $B \rightarrow C$ and $D \rightarrow A$. During the process $B \rightarrow C$, entropy increases. Hence heat is absorbed. Let us denote the quantity of heat absorbed by the symbol q_1 . We have,

$$\begin{aligned} q_1 &= \int_{S_1}^{S_2} T dS \\ &= \alpha V_1^{-nR/C_V} \int_{S_1}^{S_2} \exp(S/C_V) dS \\ &= \alpha C_V V_1^{-nR/C_V} \left[\exp(S_2/C_V) - \exp(S_1/C_V) \right] \end{aligned} \quad (9.77)$$

The efficiency of the engine is formally given by,

$$\begin{aligned} \eta &= \frac{|W|}{q_1} \\ &= 1 - \left(\frac{V_1}{V_2} \right)^{nR/C_V} \end{aligned} \quad (9.78)$$

9.11 Isothermal expansion and Helmholtz Free Energy

One hundred moles of a gas at **300** K expand isothermally from a volume of **1** m³ to a volume of **2** m³. What is the change in Helmholtz free energy, $F(T, V, N)$, if the gas obeys equation of state of

- (a) an ideal gas $PV = nRT$;
- (b) a van der Waal's gas : $(P + an^2/V^2)(V - nb) = nRT$. $a = 0.4261$ pa m⁶ (mol)⁻²; $b = 37.406 \times 10^{-6}$ m³ (mol)⁻¹.

Solution

First we show that the work done in a reversible process equals the change in free energy.

$$dU = dQ + dW \quad (9.79)$$

$$dW = dU - dQ = dU - TdS \quad (9.80)$$

$$= d(U - TS) \text{ since } dT = 0 \text{ for an isotherm} \quad (9.81)$$

$$= dF \quad (9.82)$$

Alternately,

$$F = U - TS \quad (9.83)$$

$$dF = dU - TdS - SdT \quad (9.84)$$

$$= -PdV - SdT \quad (9.85)$$

$$P = - \left(\frac{\partial F}{\partial V} \right)_T \quad (9.86)$$

$$dW = -PdV \quad (9.87)$$

$$= \left(\frac{\partial F}{\partial V} \right)_T dV \quad (9.88)$$

$$= dF \quad (9.89)$$

$$\text{Ideal Gas : } W = - \int_{V_1}^{V_2} PdV = -nRT \int_{V_1}^{V_2} \frac{dV}{V} = -nRT \ln(V_2/V_1)$$

$$\begin{aligned} \text{Hence, } F(T, V_2, n) - F(T, V_1, n) &= W = -nRT \ln(V_2/V_1) \\ &= -100 \times 8.314 \times 300 \times \ln 2 \\ &= -1.729 \times 10^5 \text{ J} \end{aligned}$$

van der Waal Gas

$$\begin{aligned} W &= - \int_{V_1}^{V_2} PdV = -nRT \int_{V_1}^{V_2} \frac{dV}{V - nb} + an^2 \int_{V_1}^{V_2} \frac{dV}{V^2} \\ &= -nRT \ln \left(\frac{V_2 - nb}{V_1 - nb} \right) - an^2 \left(\frac{1}{V_2} - \frac{1}{V_1} \right) \end{aligned}$$

Hence we have

$$F(T, V_2, n) - F(T, V_1, n) = W = -1.721 \times 10^5 \text{ J.}$$

9.12 Internal energy is an extensive property

The internal energy U of a single component thermodynamic system expressed as a function of entropy S , volume V , and number of particles N is of the form $U(S, V, N) = a S^{4/3} V^\alpha$ where a and α are constants.

- (i) What is the value of α ?
- (ii) What is the temperature of the system ?
- (iii) What is the pressure of the system ?
- (iv) The pressure of the system obeys a relation given by $P = \omega U/V$, where ω is a constant. Find the value of ω .
- (v) if the energy of the system is held constant, the pressure and volume are related by $PV^\gamma = \text{constant}$. Find γ .

Solution

(i)

$$U(S, V) = a S^{4/3} V^\alpha$$

U , S , and V are extensive properties of a thermodynamic system. U is an extensive function of S and V . In other words U is a first order homogeneous function of S and V .

$$U(\lambda S, \lambda V) = \lambda U(S, V)$$

We have,

$$\begin{aligned} a \lambda^\alpha + (4/3) S^{4/3} V^\alpha &= \lambda S^{4/3} V^\alpha \\ \lambda^\alpha + (4/3) &= \lambda \Rightarrow \alpha + \frac{4}{3} = 1 \Rightarrow \alpha = -\frac{1}{3} \end{aligned}$$

(ii) The temperature of the system is given by,

$$U(S, V) = a S^{4/3} V^{-1/3} ; T(S, V) = \left(\frac{\partial U}{\partial S} \right)_V = \frac{4a}{3} \left(\frac{S}{V} \right)^{1/3}$$

(iii) The pressure of the system is given by,

$$P(S, V) = - \left(\frac{\partial U}{\partial V} \right)_S = \frac{a}{3} \left(\frac{S}{V} \right)^{4/3}$$

(iv) We have,

$$U = \frac{a S^{4/3}}{V^{1/3}} ; a S^{4/3} = U V^{1/3}$$

Substitute the above in the expression for P , see below

$$P = \frac{a S^{4/3}}{3 V^{4/3}} = \frac{U V^{1/3}}{3 V^{4/3}} = \frac{1}{3} \frac{U}{V}$$

Therefore $\omega = 1/3$.

(v) We have

$$U = \frac{a S^{4/3}}{V^{1/3}} ; P = \frac{a S^{4/3}}{3 V^{4/3}} ; \frac{U}{P} = 3V$$

$$PV = \text{constant if } U \text{ is held constant}$$

Therefore $\gamma = 1$.

9.13 Adiabatic leaking

adapted from C B P Finn, *Thermal Physics*, Nelson Thornes (Second edition) (1993)p.224 3.13

A thermally insulated chamber contains **1000** moles of mono-atomic ideal gas⁶² at **10** atm. pressure. Its temperature is **300** K. The gas leaks out slowly through a valve into the atmosphere. The leaking process is adiabatic⁶³, quasi static, and reversible.

- (i) How many moles of gas shall be left in the chamber eventually?
- (ii) What shall be the temperature of the gas left in the chamber ?

$$1 \text{ atm} = 0.981 \times 10^6 \text{ Pa} ; \gamma = C_P/C_V = 5/3$$

Solution

The gas in the chamber leaks out because of the pressure difference. The pressure in the chamber decreases as the gas leaks out. The leaking continues until the chamber is at the same pressure as the atmosphere. Since the chamber is thermally insulated there is no transaction of energy by heat between the chamber and the

	Initial pressure	P_i	10 atm
	Final pressure	P_f	1 atm
surroundings. We have,	Initial amount of gas	n_i	1000 moles
	Final amount of gas	n_f	?
	Initial temperature	T_i	300 K
	Final temperature	T_f	?

- Apply ideal gas law to the n_f moles of gas left in the chamber. We have

$$P_i^{1-\gamma} T_i^\gamma = P_f^{1-\gamma} T_f^\gamma$$

From the above we get,

$$\frac{T_f}{T_i} = \left(\frac{P_f}{P_i} \right)^{(\gamma-1)/\gamma} \Rightarrow T_f = 119.4K$$

•

$$P_i V = n_i R T_i ; P_f V = n_f R T_f ; \frac{P_f}{P_i} = \frac{n_f}{n_i} \frac{T_f}{T_i}$$

$$\frac{n_f}{n_i} = \left(\frac{T_f}{T_i} \right)^{-1} \frac{P_f}{P_i}$$

$$\frac{n_f}{n_i} = \left(\frac{P_f}{P_i} \right)^{1/\gamma}$$

$$n_f = 1000 \times 10^{-3/5} = 251.2 \text{ moles}$$

⁶² $PV = nRT$

⁶³ $PV^\gamma = \Theta$.

9.14 Processes in $P - V$ phase diagram : Energy transacted by heat and work

See C B P Finn, *Thermal Physics*, Nelson Thornes (1993)p.222; Problem: 3.4

Consider the (quasi-static) reversible processes depicted in the Pressure-Volume phase diagram below.

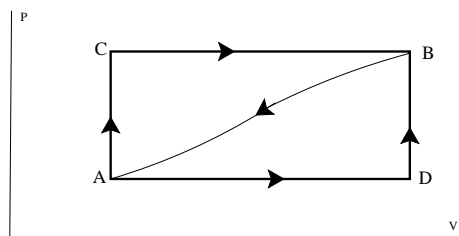


Fig. 9.6. A Quasi-static reversible process in $P - V$ phase plane

- When the system goes through the path $A \rightarrow C \rightarrow B$ it absorbs an energy of **80 joules** by heat and does work of **30 joules**.
- When it goes along the path $A \rightarrow D \rightarrow B$, the work done by the system is **10 joules**.
What is the energy transacted by heat ? Does it absorb or throw away heat ?
- The system travels from B to A along the curly path shown in the figure. During this process, **20 joules** of work is done on the system.
What is the energy transacted by heat ?
- If $U(A) = 0$, and $U(D) = 40$ joules, What is the energy transacted by heat during the process $A \rightarrow D$? What is the energy transacted by heat during $D \rightarrow B$

Solution

It is given that in the path $A \rightarrow C \rightarrow B$, the energy transacted by heat Q , and work W are given by $Q = 80 \text{ j}$; $W = -30 \text{ j}$. Therefore $U(B) - U(A) = Q + W = 50 \text{ j}$. For the path $A \rightarrow D \rightarrow B$, $W = -10 \text{ j}$, and $Q = [U(B) - U(A)] - W = 50 - (-10) = 60 \text{ j}$.

For the curly path $B \rightarrow C$, $W = 20 \text{ j}$ and $Q = U(A) - U(B) - W = (-50 - 20) = -70 \text{ j}$. Energy exits by heat during the process $B \rightarrow C$.

Consider the path $A \rightarrow D \rightarrow B$. Work is done only in the segment $A \rightarrow D$. Notice that volume does not change in segment $D \rightarrow B$, hence no work is done.

It is given that during the process $A \rightarrow D \rightarrow B$, the work done by the system is **10 j**. Therefore, $W(A \rightarrow D) = -10 \text{ j}$;

$$Q(A \rightarrow D) = U(D) - U(A) - W = 50 \text{ j};$$

$$Q(D \rightarrow B) = Q(A \rightarrow D \rightarrow B) - Q(A \rightarrow D) = 60 - 50 = 10$$

9.15 $P - T$, $V - T$, and $P - V$ phase diagrams

One mole of an ideal gas is in thermal equilibrium at temperature **100 k**, and pressure 1.0×10^5 pa. Call it the initial state and denote it by **A**. It goes to a final state **D**, at **400 k** and 8×10^5 pa, by two different reversible processes :

Process-1 : There are two steps. In the first step the system goes from **A** to **B** whence the volume remains constant and the temperature increases to **400 k**. In the second step the system goes from **B** to the final state **D** isothermally.

Process-2 : There are two steps. In the first step, the system goes from **A** to **C** whence the pressure remains the same and the temperature increases to **400 k**. In the second step the system goes from **C** to the final state **D** isothermally.

$C_V = 3nR/2$; $C_P = 5nR/2$; $R = 8.314 \text{ J K}^{-1} (\text{mole})^{-1}$. n number of moles = 1.

- Sketch both the processes in a single graph sheet with P on the y axis and T on the x axis.
- Sketch both the processes in a single graph sheet with P on the x axis and V on the Y axis.
- Calculate the energy transacted by heat and work at each step of the two processes.
- Calculate the change in entropy and show that it is independent of the path

Solution

Pressure versus Temperature Plot : In the path $A \rightarrow B$, V is a constant; P is a linear function of T passing through origin and with a slope nR/V . The P versus T plot is given below, see Fig. (9.7) Left. **Volume versus Temperature Plot :** In the path $A \rightarrow C$, P is constant. Hence V a linear function of T with a slope nR/P and passing through the origin. Volume versus temperature plot is shown in the figure below, see Fig. (9.7) Right.

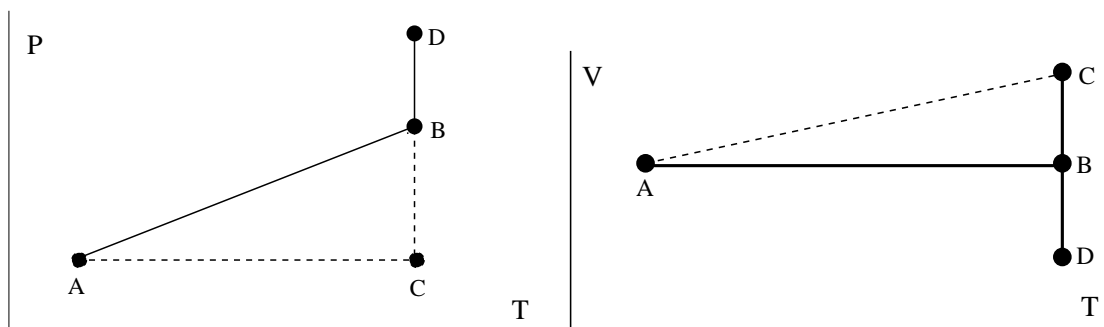


Fig. 9.7. Left : P versus T ; Right : V versus T ; Process -1 : $A \rightarrow B \rightarrow D$. Process - 2 : $A \rightarrow C \rightarrow D$

Pressure *versus* Volume Plot The Pressure *versus* Volume plot is shown in the figure below.

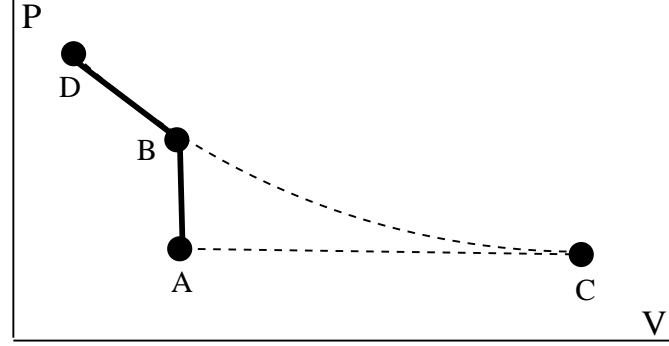


Fig. 9.8. Process -1 : $A \rightarrow B \rightarrow D$. Process -2 : $A \rightarrow C \rightarrow D$

Work and Heat during the given two processes

Process - 1 : $A \rightarrow B \rightarrow D$

Segment $A \rightarrow B$

Energy transacted by heat is given by,

$$Q(A \rightarrow B) = C_V \int_{T_A}^{T_B} dT = (3nR/2) \times (400 - 100) = 3741.30 \text{ J}$$

Volume does not change during this segment. Hence no work is done.

$W(A \rightarrow B) = 0$.

Segment $B \rightarrow D$

The process is isothermal compression. For an ideal gas, this means $dU = 0$; since according to the first law of thermodynamics

$$U(D) - U(B) = Q(B \rightarrow D) + W(B \rightarrow D),$$

we have $Q(B \rightarrow D) = -W(B \rightarrow D)$. To calculate $W(B \rightarrow D)$ we proceed as follows.

$$\begin{aligned} W(B \rightarrow D) &= - \int_B^D P dV = -nRT_B \int_B^D \frac{dV}{V} = nRT_B \int_{P_D}^{P_B} \frac{dP}{P} \\ &= nRT_B \ln(P_D/P_B) \end{aligned}$$

We have $P_D = 8 \times 10^5 \text{ pa}$. We need to calculate P_B .

For an ideal gas $P_A V_A = T_A$ and $P_B V_B = T_B$.

Since $V_A = V_B$, we have $P_B/T_B = P_A/T_A$.

This gives $P_B = P_A \times T_B/T_A \Rightarrow \underline{P_B = 4 \times 10^5 \text{ pa.}}$

Therefore,

$$\begin{aligned} W(B \rightarrow D) &= nRT_B \ln(8/4) = 1 \times 8.314 \times 400 \times \ln 2 = +2305.13 \text{ J} \\ Q(B \rightarrow D) &= -W(B \rightarrow D) = -2305.13 \text{ J} \end{aligned}$$

Therefore for the Process - 1, we have,

$$\begin{aligned} Q(A \rightarrow B \rightarrow D) &= Q(A \rightarrow B) + Q(B \rightarrow D) = 3741.30 - 2305.13 \text{ J} \\ &= +1436.17 \text{ J} \\ W(A \rightarrow B \rightarrow D) &= W(A \rightarrow B) + W(B \rightarrow D) = 0.0 + 2305.13 \text{ J} \\ &= +2305.13 \text{ J} \\ \Delta U &= U(B) - U(A) = 1436.17 + 2305.13 = +3741.30 \text{ J} \end{aligned}$$

Process - 2 : $A \rightarrow C \rightarrow D$

Segment $A \rightarrow C$

$$\begin{aligned} Q(A \rightarrow C) &= C_P(T_C = T_A) = (5nR/2)300 = +6235.50 \text{ J} \\ W(A \rightarrow C) &= - \int_{V_A}^{V_C} P dV = -P_A(V_C - V_A) = -nR(T_C - T_A) \\ &= -2494.20 \text{ J} \end{aligned}$$

Segment $C \rightarrow D$

The process is isothermal. This implies $Q = -W$.

$$\begin{aligned} W(C \rightarrow D) &= - \int_C^D P dV = -nRT \int_{V_C}^{V_D} \frac{dV}{V} = +nRT \int_{P_C}^{P_D} \frac{dP}{P} \\ &= +nRT \ln 8 \\ &= +6915.39 \text{ J} \\ Q(C \rightarrow D) &= -6915.39 \text{ J} \end{aligned}$$

Therefore for the Process - 2, we have,

$$\begin{aligned} Q(A \rightarrow C \rightarrow D) &= Q(A \rightarrow C) + Q(C \rightarrow D) \\ &= +6235.50 - 6915.39 = -679.89 \text{ J} \\ W(A \rightarrow C \rightarrow D) &= W(A \rightarrow C) + W(C \rightarrow D) \\ &= -2494.20 + 6915.39 = +4421.19 \text{ J} \\ \Delta U &= U(D) - U(A) \\ &= -679.89 + 4421.19 = +3741.30 \text{ J} \end{aligned}$$

Calculation of Entropy

We take $S(A) = 0$, with out loss of generality.

$$S(B) = C_V \int_{100}^{400} \frac{dT}{T} = (3/2)nR \ln 4 = 17.29 \text{ j k}^{-1}$$

$$S(C) = C_P \int_{100}^{400} \frac{dT}{T} = (5/2)nR \ln 4 = 28.81 \text{ j k}^{-1}$$

Process - 1 : $A \rightarrow B \rightarrow D$

The segment $B \rightarrow D$ is isothermal. Therefore $dQ = -dW = PdV$.

We get $dS = dQ/T = PdV/T = nRdV/V = -nRdP/P$.

$P_D = 8 \times 10^4$ pa.; $P_B = 4 \times 10^5$ pa.

$$\begin{aligned} S(D) &= S(B) - nR \int_{P_B}^{P_D} \frac{dP}{P} = 17.29 - nR \ln 2 = 17.29 - 5.76 \\ &= 11.53 \text{ j k}^{-1} \end{aligned}$$

Process - 2 : $A \rightarrow C \rightarrow D$

The segment $A \rightarrow D$ is isothermal. Therefore $dQ = -dW = PdV$. We get $P_D = 8 \times 10^4$ pa.; $P_C = P_A = 1.0 \times 10^5$ pa.

$$\begin{aligned} S(D) &= S(C) - nR \int_{P_C}^{P_D} \frac{dP}{P} \\ &= 17.29 - 3nR \ln 2 = 28.82 - 17.29 = 11.53 \text{ j k}^{-1} \end{aligned}$$

9.16 Right Triangle : cyclic process in $P - V$

One hundred moles of an ideal gas goes through a quasi-static reversible cyclic process $C \rightarrow A \rightarrow B \rightarrow C$ depicted on the Pressure-Volume phase plane given below.

Let $P(C) = P(B) = p = 10^5$ pa; $P(A) = 2p$; $V(A) = V(C) = v = 3 \text{ m}^3$; and $V(B) = 2v$. Let D be a point on the cycle, at which the temperature is maximum. Let $S(C) = 0$.

(i) Find D and $T(D)$.

(ii) Depict the cycle in Temperature-Entropy phase plane.

Solution

Since $PV = nRT$, we have $T(A) = T(B) = 2pv/(nR) = 721.674 \text{ k}$;
 $T(C) = pv/(nr) = 360.247 \text{ k}$

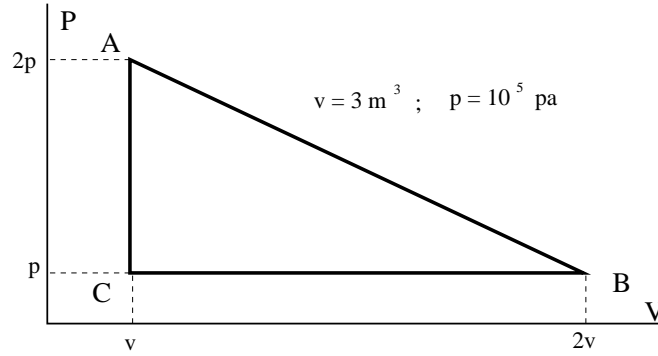


Fig. 9.9. A Quasi-Static Reversible Cycle in $P - V$ phase plane

Segment $C \rightarrow A$

As the system moves from C to A reversibly, volume remains constant at v and the pressure increases from p to $2p$. Let x be a parameter that varies from 0 to 1. When the system is at C , $x = 0$; when the system is at A , $x = 1$. We have $P(x) = xp + p$; $T(x) = vp(1 + x)/(nR)$; and

$$S(x) = S(C) + C_V \int_0^x \frac{dx}{1 + x} = C_V \ln(1 + x).$$

We can express T as a function of S , by eliminating x ; we get,

$$S = C_V \ln \left(\frac{nRT}{pv} \right) \quad \text{or} \quad T = \frac{pv}{nR} \exp(S/C_V).$$

Segment $A \rightarrow B$

As the system goes from A to B , volume increases from v to $2v$ and pressure decreases from $2p$ to p . Let y be a parameter that varies from 0 to 1. When the system is at A , the value of y is 0; and when the system is at B , $y = 1$. We have,

$$V(y) = v(1 + y); \quad P(y) = p(2 - y); \quad T(y) = \frac{pv(1 + y)(2 - y)}{nR}$$

We find that $\frac{dT}{dy} = \frac{pv}{nR}(1 - 2y)$. The derivative vanishes at $y = 1/2$. Hence

T is extrema at $y = 1/2$. We have, $\frac{d^2T}{dy^2} = -\frac{2pv}{nR} < 0$. At $y = 1/2$, the temperature is maximum. $y = 1/2$ corresponds to the mid point of the segment AB . We have $T(y = 1/2) = 9pv/[4nR]$.

Calculation of entropy

$$\begin{aligned} S(y) &= S(C) + C_V \int_p^{p(2-y)} \frac{dP}{P} + C_P \int_v^{v(1+y)} \frac{dV}{V} \\ &= C_V \ln(2 - y) + C_P \ln(1 + y) \end{aligned} \quad (9.90)$$

Segment $B \rightarrow C$

When the system goes from $B \rightarrow C$, volume decreases from $2v$ to v ; pressure remains constant at p . Let $0 \leq z \leq 1$ be a parameter. We have,

$$\begin{aligned} V(z) &= v(2 - z) \\ T(z) &= \frac{pv(2 - z)}{nR} \\ S(z) &= S(C) - C_P \int_1^z \frac{dz}{2 - z} \\ &= C_P \ln(2 - z) \end{aligned}$$

The Cycle in the $T - S$ phase plane is shown below.

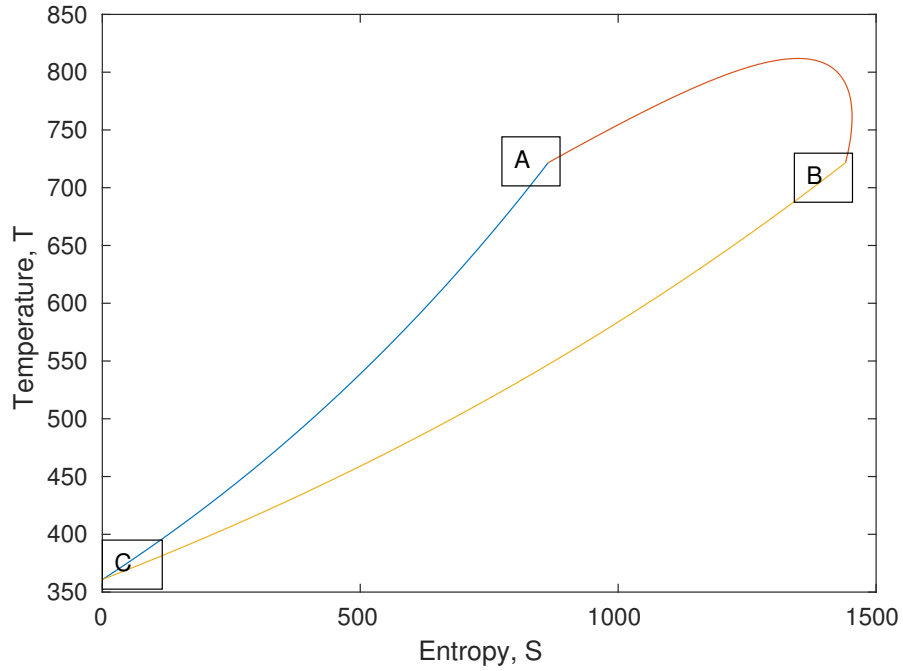


Fig. 9.10. The cycle represented in $P - V$ phase plane in figure (9.16), plotted in $T - S$ phase plane

9.17 $S(P)$ from Gibbs Free Energy

Gibbs free energy of a gas is given by $G = RT \ln(P/P_0) - ATP$, where R is the universal gas constant; A and P_0 constants. Derive an expression for entropy as a function of pressure

Solution

Gibbs free energy is obtained by Legendre transform :

$$S \rightarrow T, \quad V \rightarrow P, \quad \text{and} \quad U(S, V, N) \rightarrow G(T, P, N)$$

$$G = U - TS + PV; \quad \left(\frac{\partial U}{\partial S} \right)_{V,N} = T; \quad \left(\frac{\partial U}{\partial V} \right)_{S,N} = -P$$

Therefore

$$S = - \left(\frac{\partial G}{\partial T} \right)_P = AP - R \ln(P/P_0).$$

9.18 Isothermal compression of water

One kilogram of water is compressed isothermally from at **20°** Celsius from one atmosphere to **20** atmosphere pressure. What is the energy transacted by heat and by work ?

isotherm compressibility⁶⁴ of water $\kappa_T = 0.5 \times 10^{-4} \text{ atm}^{-1}$ $1 \text{ atm} = 1.01325 \times 10^5 \text{ pa}$. Coefficient of thermal expansion⁶⁵ for water is $\gamma = 2.0 \times 10^{-4}$ per °Celsius. Assume there is no change in volume of water upon application of pressure.

Solution

Energy transacted by work

$$V \equiv V(T, P); \quad dV = \left(\frac{\partial V}{\partial T} \right)_P dT + \left(\frac{\partial V}{\partial P} \right)_T dP$$

Compression is isothermal and reversible. Therefore $dT = 0$ in the above.

State 1 : $P=P_1=1 \text{ atm}$. ; $T=20^\circ\text{C}$; State 2 : $P=P_2=20 \text{ atm}$; $T=20^\circ\text{C}$;

$$dV = \left(\frac{\partial V}{\partial P} \right)_T dP; \quad dW = -P dV \quad (9.91)$$

$$\begin{aligned} W &= - \int_1^2 P dV \\ &= - \int_1^2 P \frac{\partial V}{\partial P} dP \\ &= \kappa_T V \int_1^2 P dP \\ &= \kappa_T V (P_2^2 - P_1^2)/2 \\ &= 0.9975 \text{ joules} \end{aligned} \quad (9.92)$$

⁶⁴ Isothermal compressibility $\kappa_T = -(1/V)(\partial V/\partial P)_T$.

⁶⁵ Coefficient of thermal expansion $\gamma = (1/V)(\partial V/\partial T)_P$.

Energy transacted by heat

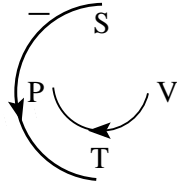
$$S \equiv S(T, P); \quad dS = \left(\frac{\partial S}{\partial T} \right)_P dT + \left(\frac{\partial S}{\partial P} \right)_T dP \quad (9.93)$$

Compression is isothermal and reversible. Therefore $dT = 0$ in the above.

$$dS = \left(\frac{\partial S}{\partial P} \right)_T dP; \quad dQ = +T dS \quad (9.94)$$

$$Q = \int_1^2 T dS \quad (9.95)$$

$$= \int_1^2 T \left(\frac{\partial S}{\partial P} \right)_T dP \quad (9.96)$$



$$-\left(\frac{\partial S}{\partial P} \right)_T = \left(\frac{\partial V}{\partial T} \right)_P$$

$$\begin{aligned} Q &= -T \int_1^2 \left(\frac{\partial V}{\partial T} \right)_P dP = -\gamma TV \int_1^2 dP \\ &= -\gamma TV (P_2 - P_1) = -112.82 \text{ joules} \end{aligned}$$

PROBLEMS

10.1 Problems Set - 1

- (1) For a cylinder, $\Delta V = 2\pi RHdR + \pi R^2dH$, where R denotes the radius and H the height. Show that ΔV is a perfect differential. Express V as a function of R and H .
- (2) Let

$$\Delta f = (2xy - y^2) dx + (2xy - x^2) dy.$$

- (a) Consider the following two paths :
 - (i) $(1, 1) \rightarrow (2, 1) \rightarrow (2, 2)$ and (ii) $(1, 1) \rightarrow (1, 2) \rightarrow (2, 2)$.
Calculate the changes in the quantity along these two paths.
 - (b) Calculate partial derivatives of the pre factors of dx and dy and find if df is an exact or inexact differential.
- (3) Consider a system of n moles of ideal gas.

$$\Delta q = C_V dT + PdV$$

is the energy transacted by heat in a quasi static reversible process. C_V is the heat capacity at constant volume. For an ideal gas $PV = nRT$. Express the energy transacted by heat as follows :

$$\Delta q = \phi(T, P) dT + \xi(T, P) dP.$$

Derive expressions for the functions $\phi(T, P)$ and $\xi(T, P)$. Show that Δq is not a perfect differential. Now consider the quantity $\Delta q/T$. Call it ΔS and show it is a perfect differential.

- (4) Consider the thermodynamic phase plane with T on the X axis and P on the Y axis. One mole of a mono atomic ideal gas is at an equilibrium state⁶⁶ represented by the point $A = (270 \text{ k}, 1 \text{ atm.})$. It is taken quasi statically and reversibly from state A to state $B = (370 \text{ k}, 2 \text{ atm.})$ as described below.
 - (i) **Process - 1** : $A \rightarrow C \rightarrow B$, where $C = (370 \text{ k}, 1 \text{ atm.})$. During the process $A \rightarrow C$ pressure remains constant and during the process $C \rightarrow B$, temperature remains constant. Calculate the energy transacted by heat and work for each segment of the process and for the whole process $A \rightarrow C \rightarrow B$. Calculate also the change in internal energy and entropy during the process.

⁶⁶ only equilibrium states can be represented by points in the thermodynamic phase diagram.

- (ii) **Process – 2** : $A \rightarrow D \rightarrow B$, where $D = (270 \text{ k}, 2 \text{ atm.})$. The process $A \rightarrow D$ is isothermal. The process $D \rightarrow B$ is isobaric. Calculate the energy transacted by heat and work in each segment and the whole of the process $A \rightarrow D \rightarrow B$. Calculate the change in internal energy and entropy.
- (5) Show that for a mono atomic ideal gas $PV^\gamma = \Theta$ for an adiabatic process. Here Θ is a constant. What is γ ? Derive similar equations of state involving 1. P and T and 2. V and T .
- (6) Consider quasi static and reversible expansion of a mono atomic ideal gas from $V_1 = 1$ litre to $V_2 = 2$ litres. Initial pressure of the gas is $P_1 = 2$ atm. and temperature $T_1 = 300$ k. If the expansion is adiabatic calculate the energy transacted by work. Let the adiabatic expansion take the system from
- $A = (P_1 = 2 \text{ atm.}, V_1 = 1 \text{ litre}, T_1 = 300 \text{ k})$ to $B = (P_2, V_2 = 2 \text{ litre}, T_2)$.
- Let $W_{A \rightarrow B}^A$ denote the work done. Consider now an isothermal expansion from
- A to C : $C = (P_3, V_3 = V_2 = 2 \text{ litre}, T_3 = T_1 = 300 \text{ k})$.
- Calculate the energy transacted by heat and work.
- Consider a quasi static reversible process that takes the system from C to B . Calculate the energy transacted by heat and work during the process $C \rightarrow B$. Thus we have two processes I : $A \rightarrow B$: adiabatic and process II : $A \rightarrow C \rightarrow B$ where the segment $A \rightarrow C$ is isothermal. Show that difference in the work done in processes I and II equals heat transacted in process II - a statement of the first law of thermodynamics.
- (7) Consider Carnot engine on the thermodynamic phase plane with volume on the X axis and pressure on the Y axis. Derive an expression for the efficiency of the Carnot engine : the energy transacted by work divided the energy taken from the source by heat.
- Depict the Carnot engine on temperature-entropy phase diagram and derive an expression for the efficiency.
- (8) At 0°C ice melts with a latent heat of fusion of **334.92** kilo joules per kilogram. Calculate the entropy change if one kilogram of ice melts completely into water at 0° C .

10.2 Problems Set - 2

- (10) For an ideal gas $PV = nRT$, where n is the number of moles and R measured in units of $\text{J k}^{-1} \text{ mole}^{-1}$, is the universal gas constant. Work done in a quasi static reversible process involving infinitesimal change in volume at constant pressure is $dW = -PdV$. The bar on d for work, is to remind us that work is not a property of the system. dW is a small quantity but not an infinitesimal; it is not an exact differential; W is not a property of the system; it a

property of the process. It depends on the path. You have to integrate $-P dV$ along the path describing the process to get the work done. The path has to be necessarily quasi static and reversible.

Calculate the energy transacted by work by an ideal gas in the following quasi static reversible processes

- (i) Isothermal : from V_1 to V_2 .
 - (ii) Isothermal : from P_1 to P_2 .
 - (iii) Isobaric (pressure is kept constant at P) : from V_1 to V_2 .
 - (iv) Isobaric (at constant pressure P) : from T_1 to T_2 .
 - (v) Adiabatic : from V_1 to V_2 .
- (11) A particular gas obeys the equation of state given by,

$$\left(P + \frac{an^2}{V}\right) (V - nb) = nRT.$$

In the above n is the number of moles of the gas; a and b are constants.

$R = 8.314 \text{ J K}^{-1} \text{ mole}^{-1}$ is the universal gas constant. The gas expands by a quasi static, reversible isothermal process from an initial state (P_1, V_1) to a final state

$(P_2 < P_1, V_2 > V_1)$. Find an expression for the energy transacted by work. Tell whether work is done on the system or by the system.

- (12) Calculate the change in entropy when 1 kg. of nitrogen is taken from a pressure from 1 bar at temperature 300 K to a pressure 3 bars and temperature 500 K. For nitrogen $C_P = 1041,6 \text{ J K}^{-1} \text{ kg}^{-1}$.

Assume nitrogen behaves like an ideal gas.

1 bar = 100 k Pa; 1 pa = 1 N m⁻².

$R = 8.314 \text{ J K}^{-1} \text{ mole}^{-1}$;

nitrogen weighs 28 g mole⁻¹.

- (13) A fundamental equation⁶⁷ of a single component substance is given by ⁶⁸,

$$U = \left(\frac{v_0 \theta}{R^2}\right) \frac{S^2}{NV},$$

where v_0 , θ , and, R are constants.

(i) First check if U is an extensive.

(ii) Find the three equations of state⁶⁹ :

$$T \equiv T(S, V, N), P \equiv P(S, V, N), \text{ and } \mu = \mu(S, V, N).$$

⁶⁷ A fundamental equation is one which expresses an extensive property as a (first order homogeneous) function of other extensive properties.

⁶⁸ Taken from H B Callen, *Thermodynamics and an Introduction to Thermostatistics* (Student Edition) Wiley India (2002)p.39; Problems 2.2-1, - 2.2-3

⁶⁹ An equation of state expresses an intensive property as a (zero-th homogeneous) function of its extensive properties.

- (iii) Show that T , P , and each is a zeroth order homogeneous function of S, V, N .
- (iv) Express μ as a function of T, V, N .
- (v) Sketch P versus V for a fixed T and N . This is called isotherm. Sketch isotherms for T_1 and $T_2 > T_1$.
- (14) The fundamental equation of a substance is given by,

$$U = \left(\frac{\theta}{R}\right) \frac{S^2}{N} - \left(\frac{R\theta}{v_0^2}\right) \frac{V^2}{N}.$$

Show that,

$$\mu = -\frac{U}{N}.$$

Express μ as a function of T and P .

(Taken from the reference given in footnote (68) Problems 2.2-4, 2.2-5)

- (15) The fundamental equation of a substance is given by,

$$\left(\frac{v_0\theta}{R}\right) \frac{S^2}{V} \exp\left(\frac{S}{NR}\right).$$

Find the three equations of state.

(Taken from the reference given in footnote (68) Problem 2.2-6)

10.3 Problems Set - 3

- (19) N D Hari Dass, *The Principles of Thermodynamics*, Taylor and Francis (2014)p.16

The volumetric coefficient of thermal expansion is defined as

$$\gamma = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P.$$

The isothermal compressibility defined as

$$k_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T.$$

Show that the energy transacted by work, when temperature and pressure change, can be determined in terms of γ and k_T and is given by

$$dW = PV (k_T dP - \gamma dT).$$

In a constant volume (isochoric) process, show that

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{\gamma}{k_T}.$$

Verify this for an ideal gas.

- (20) You can increase the efficiency of a Carnot engine by raising the source temperature, T_1 or by lowering the sink temperature, T_2 . Assume it costs the same to change the temperature of the source or the sink, by the same amount. Which of the two options is cost effective for improving the efficiency of the Carnot engine.
- (21) H B Callen, *Thermodynamics*, Wiley (1960)p.71
A Carnot engine draws energy by heat from a source of boiling water delivers one joule or work and rejects energy by heat to ice cubes, melting them in the process. How much of energy it withdraws from the source by heat ? How many grams of ice it melts in the sink ? 80 calories of energy is required to melt one gram of ice.

10.4 Problems Set - 4

- (22) to be supplied
(23) to be supplied
(24) Consider an isolated system of N identical, indistinguishable⁷⁰ and non-interacting point particles, in two dimensions. Each particle is of mass m .

The particles are confined to an area A .

Let $\hat{\Omega}(E, A, N)$ denote the number of micro states of the (macroscopic) system with energy less than or equal to E .

- (i) Show that

$$\hat{\Omega}(E, A, N) = \frac{1}{h^{2N}} \frac{A^N}{N!} \frac{(2\pi m E)^N}{\Gamma(N+1)}$$

- (ii) Express S as a function of E , A , and N .
(iii) Derive expressions for the partial derivatives of S with respect to E , A and N and interpret these quantities.
(iv) Derive equipartition theorem.
(25) Consider an isolated system of N identical, indistinguishable, see footnote (70) and non-interacting point particles, in one dimensions. Each particle is of mass m .

The particles are confined to a length L .

Let $\hat{\Omega}(E, L, N)$ denote the number of micro states of the (macroscopic) system with energy less than or equal to E .

- (i) Show that

$$\hat{\Omega}(E, L, N) = \frac{1}{h^N} \frac{L^N}{N!} \frac{(2\pi m E)^{N/2}}{\Gamma(\frac{N}{2} + 1)}$$

- (ii) Express S as a function of E , L , and N .
(iii) Derive expressions for the partial derivatives of S with respect to E , L and N and interpret these quantities.

⁷⁰ as specified by Boltzmann, *i.e.* employ Boltzmann counting of micro states.

- (iv) Derive equipartition theorem.
 (26) The internal energy of a mono atomic van de Waal gas is given by

$$U(T, V, n) = \frac{3nRT}{2} - \frac{an}{V}.$$

In the above, n is the number of moles; "a" is a constant; R is the universal gas constant. The gas is allowed to expand adiabatically into a vacuum⁷¹ from a volume of V_1 to a volume of V_2 ($> V_1$). Let T_1 be the initial temperature of the gas. What is its final temperature ?

If a mono atomic ideal gas expands adiabatically into vacuum from a volume V_1 and temperature T_1 to a volume V_2 , what will be the final temperature ?

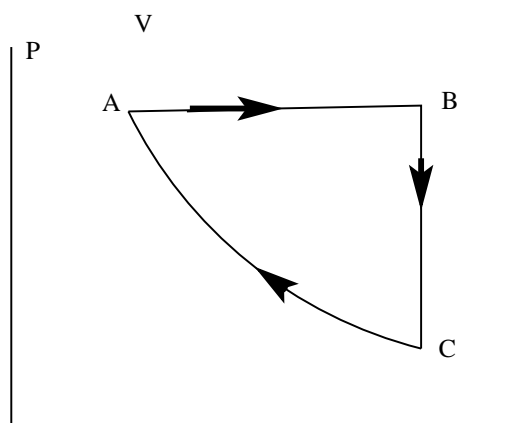
10.5 Problems Set - 5

- (27) Evelyn Guha, *Basic Thermodynamics*, Narosa (2000)p.77
 An ideal gas is taken through a cyclic process, which is represented on a $P - V$ plane, by a rectangle. Let P_1 and P_2 be the lower and higher pressures respectively. Let V_1 and V_2 be the lower and higher volumes respectively. (i) Calculate the work done per cycle. (ii) Indicate which parts of the cycle involve heat flow into the gas. (iii) Show that the efficiency of the engine is given by,

$$\eta = \frac{\gamma - 1}{\frac{\gamma P_2}{P_2 - P_1} + \frac{V_1}{V_2 - V_1}},$$

where $\gamma = C_P/C_V$ - the ratio of heat capacity at constant pressure to that at constant volume.

- (28) An ideal gas goes through a quasi static reversible cyclic process $A \rightarrow B \rightarrow C \rightarrow A$ as shown below, on a pressure-volume phase plane.

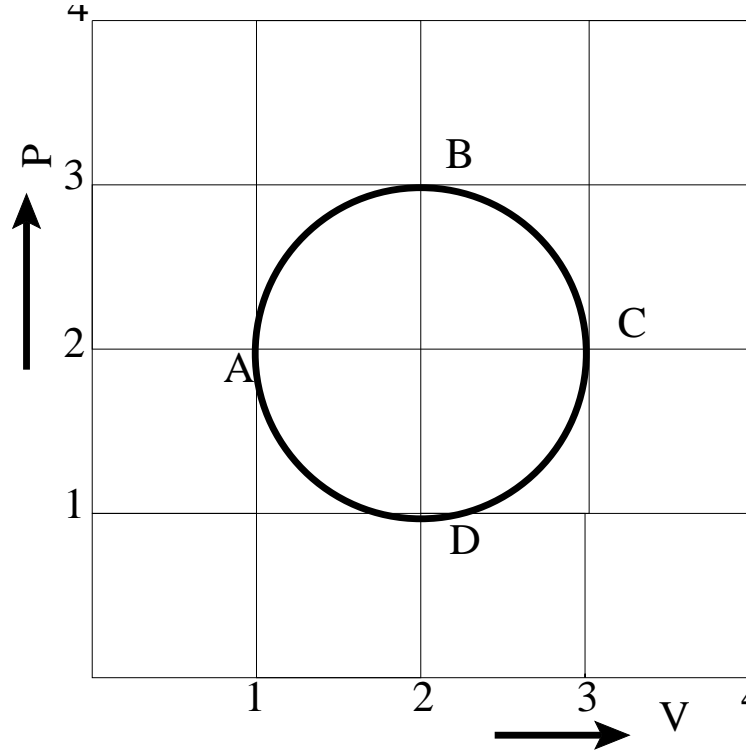


⁷¹ when a gas expands into a vacuum, no work is done. Note : Work is done only when there is movement against an opposing force. When a gas expands into a vacuum, there is no force that opposes the expansion. Hence no work is done.

The segment $C \rightarrow A$ is a reversible adiabat. Let $V(A) = v_1$; $V(B) = V(C) = V_2$; $P(C) = P_1$; $P(A) = P(B) = P_2$. $\gamma = C_P/C_V$ - the ratio of heat capacity at constant pressure to that at constant volume. (i) Show that the efficiency of the engine is $\eta = 1 - \frac{1}{\gamma} \left[\frac{1 - (P_1/P_2)}{1 - (V_1/V_2)} \right]$ (ii) Let $S(A) = 0$; find $S(B)$ and $S(C)$

- (29) Evelyn Guha, *Basic Thermodynamics*, Narosa (2000)p.59 worked example 3

One mole of an ideal gas is taken through a quasi static reversible cycle which when plotted on a Pressure-Volume phase plane is a circle traversed clock-wise, $A \rightarrow B \rightarrow C \rightarrow D \rightarrow A$, see figure below.



The area of a square in the figure is $\Delta V \times \Delta P = [10^{-3} \text{ (m}^3)] \times [10^5 \text{ (pa)}]$. Show that (i) net work done in one cycle is 314 j (ii) $U(C) - U(A) = 600$ j; (iii) heat absorbed by the gas during the process $A \rightarrow B \rightarrow C$ - upper hemisphere traversed clock-wise, is 100 j.

- (30) $G(T, P) = R T \ln(P/P_0) - A T P$, is the Gibbs free energy of a system, where R , A and P_0 are constants. Derive an expression for entropy as a function of pressure.
- (31) Start with fundamental relation expressing entropy as a function of energy, volume and the number of particles : $S \equiv S(U, V, N)$.
- (i) Express the partial derivatives

$$\left(\frac{\partial S}{\partial U} \right)_{V, N}, \left(\frac{\partial S}{\partial V} \right)_{U, N}, \text{ and } \left(\frac{\partial S}{\partial N} \right)_{U, V},$$

in terms of T , P , and μ .

(ii) Show that $\left(\frac{\partial S}{\partial U}\right)_{V,N} \times \left(\frac{\partial U}{\partial V}\right)_{S,N} \times \left(\frac{\partial V}{\partial S}\right)_{U,N} = -1$.

(iii) Show that

$$\left(\frac{\partial}{\partial V} \left(\frac{\mu}{T}\right)\right)_{U,N} + \left(\frac{\partial}{\partial N} \left(\frac{P}{T}\right)\right)_{U,N} = 0.$$

(iv) For an ideal gas show that

$$\left(\frac{\partial}{\partial V} \left(\frac{\mu}{T}\right)\right)_{U,N} = -\frac{k_B}{V}.$$

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