An inverted textbook on thermodynamics: Part I

Graeme Ackland

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Graeme J Ackland

An inverted textbook on thermodynamics

Part I: A series of thermodynamics questions with extensive worked solutions

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An inverted textbook on thermodynamics: Part I: A series of thermodynamics questions with extensive worked solutions
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Part II

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Foreword

Thermodynamics is the study of flows of heat and its relation to materials. From two simple premises: that energy is conserved and that systems move towards equilibrium and a handful of definitions an incredible insight into the workings of engines and the properties of materials can be gained.

There are many comprehensive Thermodynamics textbooks. This is not one of them, rather this book will guide you through the subject by way of problem-solving. The intention is that you will tackle each problem with reference to external material, solve the problem, if necessary with reference to the worked solution, then formally review what you have done. This final stage is missing in traditional courses.

Each section offers a few key definitions, but they are not sufficient to start the problem. Thus it will be useful to use this book in conjunction with one of the many a standard textbooks, or online lecture notes.

The problems are pitched at the level of undergraduate thermodynamics courses worldwide, and indeed have been thoroughly tested on undergraduates at the University of Edinburgh. Each problem is designed to illustrate a particular point. The solutions are comprehensive, and at the end of each solution a discussion of the physical meaning of the calculation is given. The solutions are intended to help you to understand the subject, not simply to check that you got the right answer.

Most thermodynamics problems involves changing some quantity while holding another fixed, and seeing how a third quantity is affected. These words describe a *partial differential*, and this book assumes a knowledge of calculus sufficient to understand partial differentiation. It also assumes familiarity with the ideal gas law, and physical properties such as compressibility, thermal expansion etc.

Thermodynamics is often taught alongside statistical mechanics, and it is a commonly assumed that thermodynamics is simply the macroscopic consequence of statistical mechanics and quantum mechanics. In fact, thermodynamics allows one to correctly describe the real world using much less severe assumptions than are required obtain equivalent descriptions from microscopic principles. The Second Law is a particular case, being the only law of nature describing the self-evident time-irreversibility of the real world.

The book covers the two broad application areas of thermodynamics: heat engines and materials.

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1 Some properties of materials

Learning Outcomes

One of the most important skills in physics is to know which effects are large and therefore important, and which are small and therefore negligible. In this section some simple properties of materials are reviewed: Heat capacity, latent heat, conservation of energy, compressibility, the ideal gas and heat conduction.

Key definitions

Heat capacity $\frac{dQ}{dT}$ "The amount of heat required to raise a material's temperature"
Latent heat l "The amount of heat required to change the phase of a material"
Compressibility $\frac{1}{V}\frac{dV}{dP}$ "The fractional compression when pressure is applied"
Ideal gas any material defined by the equation of state $PV = nRT$. This form of the equation applies to total volume V and number of moles n. It is also sometimes written $Pv = RT$ (v being the volume per mole) or $PV = Nk_bT$ (N being the number of molecules)

Notes

We shall see later that none of the definitions above are fully defined. Strictly we should state which thermodynamic variables are held constant in the process described: the differentials become partial differentials.

Care must be taken with units, especially whether we are dealing with extensive properties which depend on the amount of material. We may deal with specific quantities per *mole*, *kg*, or *atom* which can be found in databooks (e.g. density, specific heat capacity) or with properties of the sample at hand (e.g. volume, mass, heat capacity). Any choice is valid, but you must ensure you are being consistent.

Questions

Use the following values where necessary in the questions:

latent heat of fusion (melting) of ice = 334 kJ kg^{-1}
latent heat of vaporization of water = 2256 kJ kg^{-1}
specific heat capacity of ice = 1.94 kJ kg^{-1} K^{-1}
specific heat capacity of water = 4.2 kJ kg^{-1} K^{-1}
specific heat capacity of steam = 2.04 kJ kg^{-1} K^{-1}

1. Place the following quantities of energy in order (use the internet)

   1/ The daily energy consumption of the UK

   2/ The binding energy of all the electrons in one kg of hydrogen molecules.

   3/ The rest mass energy of one kg of hydrogen molecules.

   4/ The zero point energy of one kg of hydrogen molecules (vibrational frequency 4161cm^{-1}).

   5/ The energy released when one kg of deuterium molecules fuse to create one kg of helium.

   6/ The thermal energy of one kg of hydrogen molecules at 300K.

   7/ The calorific value of a cold chicken sandwich at 280K.

   8/ The additional thermal energy of a cold chicken sandwich at 320K.

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9/ The energy required to remove the chicken sandwich from the earth's gravitational field.

10/ The kinetic energy of the chicken sandwich on a train at 50m/s.

11/ 1kg of coal, when burnt.

12/ 1kg of uranium-235, when fissioned

13/ 1000 cubic metres of air moving at 10m/s

14/ 1000 cubic metres of water, raised by 5m

2. **Heating and metabolism**

   A class of 180 students sits in a lecture theatre for one hour, each student metabolising at 100 W. The lecture theatre is a cubic room twenty metres long on each side and 2.5 metres high. The specific heat capacity of air at constant volume is 1 kJ kg^{-1} K^{-1}. The density of air is about 1.2 kg m^{-3}. The initial temperature was 20°C. The ventilation is poor, the air conditioning is broken and the walls are well insulated. What is the room temperature at the end of the lecture?

   Compare this to the rate of heat production of the sun, which produces 3.86×10^{26}W.

3. **Thermal properties in food**

   A 500-gram box of strawberries is cooled in a refrigerator, from an initial temperature of 25 °C down to the fridge temperature of 4 °C.

   (a) *Estimate* how much heat is removed from the strawberries during the cooling, explaining your reasoning. *Hint: Strawberries have a water content of about 88%. For this and subsequent problems, some of the data given at the start of this section may be useful.*

   (b) Fruits and vegetables actually respire continuously whilst in storage, taking in oxygen and converting it to carbon dioxide. In the case of strawberries take the heat produced by this reaction to be about 210 mW kg^{-1}. How does your estimate of heat removed change if respiration is taken into account? *Hint: You need to make a sensible assumption about timescales.*

   (c) The strawberries are now removed from the fridge and put into a polystyrene (i.e. thermally insulating) container in the kitchen. How long will it take for the strawberries to reach room temperature?

   (d) The nutritional value of 100g of strawberries is 33kcal (140kJ). Use this and the respiration rate to estimate the lifetime of strawberries.

4. **Phase changes: latent heat.**
   An ice cube of mass 0.03 kg at 0°C is added to 0.2 kg of water at 20°C in an insulated container. (a) Does all the ice melt? (b) What is the final temperature of the drink?
   Comment: The ice does all melt, but specify carefully the criterion which must be satisfied.

5. **Conservation of energy: gravity and heat**
   In 1845 James Prescott Joule suggested that the water at the bottom of a waterfall should be warmer than at the top. In particular, for Niagara Falls (a height of about 50 m) the temperature difference would be approximately 0.12 °C.

   How would you go about calculating this number?

   How do you know this must be an overestimate?

   Unlike in 1845 most of the water nowadays is diverted through hydroelectric power schemes. How does this affect Joule's prediction?

6. **The ideal gas law**
   The ideal gas is defined by its *equation of state*, which relates the variables pressure P, temperature T and volume V:

$$PV = nRT$$

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Here n is the number of moles of the gas sample, and R is the gas constant. Calculate the volume occupied by a sample of ideal gas at atmospheric pressure and a temperature of 25°C, given that its volume under *standard temperature and pressure* is $V_m = 2.2414 \times 10^{-2} m^3$.

n.b. Standard temperature and pressure means $T = 0°\text{C}$, $P = 1atm = 101325Pa$.

7. **Another 'ideal' gas** You are told that at a pressure of 1.2 atm and temperature of $T = 300K$, n moles of oxygen occupy a volume of $82cm^3$. Calculate n and the *mass* of the oxygen sample, assuming that under these conditions the gas behaves ideally. How would the answer change if the sample was *ozone* (O_3)?

8. **Melting, heating and boiling.** A 1 kg sample of ice at an initial temperature of −4°C is heated at constant pressure in an insulated container, heat being supplied at a constant rate of 1 kJ s^{-1}, until the sample is steam at 110°C. Using the data given below, sketch the temperature as a function of time. Discuss the differences in the times taken for melting, heating, and boiling.

9. **Conduction of heat (an idealised hot water bottle).** A certain heat source (a *heat reservoir* or *thermal reservoir*), is always at temperature T_0. Heat is transferred from it through a slab of thickness L to an object which is initially at a temperature $T_1 < T_0$. The object, which is otherwise thermally insulated from its surroundings, has a mass $m = 0.5$ kg and a specific heat capacity $c = 4 \times 10^3$ J kg^{-1} K^{-1}. Heat is conducted through the slab at a rate (in J s^{-1}) specified by the formula $KA((T_0 - T)/L)$, where K is the thermal conductivity of the slab, A is the area of the slab through which heat is transferred and T is the instantaneous temperature of the object.

   (a) Show that provided certain assumptions are made,

   $$KA((T_0 - T)/L)\Delta t = mc\Delta T$$

   where the temperature of the object changes from T to $T + \Delta T$ during the time interval Δt. (For simplicity, treat the arrangement as a 1-dimensional system with the x-axis perpendicular to the slab.)

   (b) Show that for small Δt, and hence small ΔT, the above equation can be rearranged and integrated to give

   $$T_2 - T_1 = (T_0 - T_1)\left(1 - \exp\left(-\frac{KA(t_2 - t_1)}{Lmc}\right)\right)$$

   T_2 and T_1 are the temperatures of the object at the end, $t = t_2$, and the beginning, $t = t_1$, respectively, of the process described.

   (c) Put $A = 100$ cm^2 and $L = 1$ cm. Calculate the value of $T_2 - T_1$ for $t_2 - t_1$ equal to (a) 2 s and (b) 2000 s (about half-an-hour) for $T_0 = 60°\text{C}$ and $T_1 = 35°\text{C}$ for the following slab materials: whose thermal conductivities are given in the table.

   aluminium ($K = 200$ W m^{-1} K^{-1}) porcelain ($K = 1.5$ W m^{-1} K^{-1}) rubber ($K = 0.15$ W m^{-1} K^{-1}) wool ($K = 0.05$ W m^{-1} K^{-1}) air ($K = 0.025$ W m^{-1} K^{-1})

   Comment: The mathematical analysis incorporates a step which is quite common in problems in thermodynamics. If the temperature of part of a composite system changes from T_i to T_f, work done and/or heat flow during the process can often be calculated most quickly by considering intermediate stages in which the temperature changes from T to $T + dT$, setting up the appropriate equations and integrating them.

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2 Temperature scales, work, equations of state

Learning Outcomes

In this section we introduce the concepts of Temperature and Work. We also introduce the notion of system in thermal equilibrium, and the idea that all the equilibrium properties of a specific material can be obtained from a single “Equation of State”.

Key definitions

Temperature in thermodynamics provides a scale where the direction of heat flow is from the hotter to the colder region.

Temperature scales are defined with respect to a thermometric property and two reference temperatures.

Kelvin scale The Kelvin scale is defined using absolute zero and the triple point of water (273.16K).

In thermodynamics, temperature is defined from the efficiency of a Carnot engine. In statistical mechanics, and in the *ideal gas*, temperature is the average kinetic energy of constituent particles. In *quantum mechanics* it determines the probability that a quantum state is occupied. These are all equivalent and define the Kelvin scale.

Work is a catch-all term for energy other than thermal energy. Mechanical work is defined by $W = -\int PdV$. The sign depends on whether you are considering work done *on* a system or *by* a system. It is essential to define which choice you are using.

Equation of State defines a specific material, relating its pressure, volume and temperature. The equation of state does not define the absolute values of energy or entropy.

Equilibrium Thermodynamic Equilibrium is a condition where there are no macroscopic flows of work, heat or particles.

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Questions

1. **Temperature scales: influence of thermal properties**
   An alcohol and a mercury thermometer are constructed so that they agree at temperatures of 0 °C and 100 °C, and each scale (i.e. column of alcohol or mercury) is marked with 100 equal divisions between these two 'fixed points'. Will the two scales necessarily give the same reading at all temperatures between the fixed points? Explain your reasoning. What conditions are necessary for the two scales to agree completely? What conditions are needed for the thermometers to agree and *also* give readings in Celsius.

2. **Temperature scales: based on electrical resistance**

   Idiosyncratic Roger invents a temperature scale using as his thermometric property the resistance $R(T)$ of a special wire. He decides to calibrate his scale using the ice temperature (273.15K) and the triple point of water (273.16K). His wire has resistance R_0 at the ice point temperature, which he defines as $T_R = 273.15$. It has resistance $R_0 + \Delta R$ at the triple point, which he defines as $T_R = 273.16$. He then defines other temperatures by $T_R = 273.15 + 0.01(R - R_0)/\Delta R$, which he determines by measuring the resistance R.

   Unbeknownst to Roger, the resistance of his wire is given by

   $$R = R_0(1 + \alpha T + \beta T^2)$$

   where T is the temperature in degrees Celsius measured on the ideal gas scale. The constants α and β are 3.8×10^{-3} K^{-1} and -3.0×10^{-6} K^{-2} respectively. What temperature on Roger's resistance scale corresponds to a temperature of 70°C on the ideal gas scale?

3. **Work done in other processes**

   (a) **In melting**: Ice at 0°C and at a pressure 1 atm, has a density of 916 kg m^{-3}, while water under these conditions has a density 1000 kg m^{-3}. How much work is done when 10 kg of ice melts into water? Explain why this work is done "by the atmosphere" rather than "against the atmosphere". Is there a difference between latent heat of melting at constant pressure, and latent heat of melting at constant volume?

   (b) **On a wire**: Calculate the work done when a copper wire of length 10cm holding a 2kg weight extends by 0.1% due to reversible heating. Given the linear thermal expansion coefficient is $16.6 \times 10^{-6} K^{-1}$, estimate the required temperature change.

   (c) **In a wire**: Calculate the electrical work done when the wire is connected to a 6V battery for 10sec. (assume resistance=4.2mΩ)

4. **Calculating properties from the equation of state, and vice versa**

   (a) The isothermal compressibility κ and the isobaric volume expansivity β are given by:

   $$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \qquad \beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

   Using the equation of state, calculate the isobaric expansivity, β and isothermal compressibility, κ, of an ideal gas. Show that the bulk modulus for an ideal gas, $K = P$

   (b) A substance is found to have an isothermal bulk modulus $K = v/a$ and an isobaric expansivity $\beta = 2bT/v$ where a and b are constants and v is the molar volume. Show that the equation of state is $v - bT^2 + aP =$ a constant.

   [Hint: Integrate the expressions involving partial derivatives for κ and β, and merge/reconcile the outcomes.]

   (c) Show that for the ideal gas, the difference between the heat capacities at constant volume and constant pressure is actually given by:

   $$C_P - C_V = \frac{VT\beta^2}{\kappa}$$

   Remember $C_P - C_V = R$ and $PV = RT$ for one mole of an ideal gas.

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5. **Temperature scales: based on water**

   At atmospheric pressure, water has a density of 960kg/m^3 at 100^{o}C, the same as supercooled water at at -40^{o}C. The maximum density, 1000kg/m^3, is at 4^{o}C.

   If the equation approximating an isobar is $\rho = A + BT + CT^2 + DT^3$, evaluate the constants A-D. (*Hint - you are free to choose the zero of the temperature scale as you please*)

   A water thermometer comprises water in a glass tube of constant radius. At 4^{o}C, the column of water is 100mm high. At what temperature will it be 101mm high?

   Give reasons why mercury is used in preference to water in thermometers.

6. **Joule's experiment**

   In an experiment similar to Joule's paddle wheel experiment, a mass of 20 kg drops slowly through a distance of 2 m, driving the paddles immersed in 2 kg of water. Viscous dissipation generates heat in the water.

   (a) Ignoring heat losses, bearing friction, etc, calculate the rise in temperature of the water.

   (b) What would be the error in determining the mechanical equivalent of heat if the mass was still moving at 10 cm s^{-1} when it hits the ground?

   (The heat capacity of water is 4.2 kJ K^{-1}kg^{-1})


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3 Work and heat, the First Law

Learning Outcomes

This section introduces the First Law of Thermodynamics. There are many types of energy, and energy can be converted from one type to another, but is always conserved.

Key Points

The First Law is simply Conservation of Energy: $dU = \text{đ}Q + \text{đ}W$.
Heat and Work are *not* properties of a material or state variables. The heat flow or work done depends on all details of the process occuring.
A process takes a system from one thermodynamic state to another, normally due to interaction with its surroundings To fully specify a thermodynamics process, we must state what is changing *and* what is conserved. This will enable us to write the partial differential defining the process.
Joule coefficient describes adiabatic expansion, typically $\text{đ}W = 0$, $\text{đ}Q = 0$: $\mu_J = (\partial T/\partial P)_U$,
Joule-Kelvin coefficient describes isenthalpic expansion, typically from one pressure to another $\text{đ}W \neq 0$, $\text{đ}Q = 0$: $\mu_{JK} = (\partial T/\partial P)_H$,

Questions

1. **Work done in the expansion of an ideal gas**

   The volume of a given system containing n moles of a monatomic ideal gas is given by $V = V(P, T)$, where P is the pressure and T the temperature, and $PV = nRT$.

   (a) Obtain an expression in terms of the change in pressure, dP, for the incremental work done on the system, $\text{đ}W$ in an isothermal expansion.

   (b) The gas expands isothermally to twice its original volume. Using the formula for the incremental work on the system in terms of dP (previous part), obtain an expression for the total work done on the system.

   (c) Write down an expression in terms of the change of temperature, ΔT, for the work done on the system in an *isobaric* expansion.

2. **Work, heat, PV diagrams**

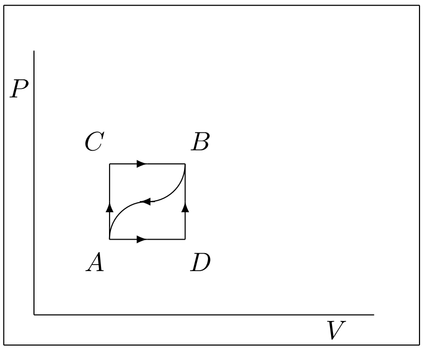
   A gas, contained in a cylinder fitted with a frictionless piston, is taken from the state A to the state B along the path ACB shown in the diagram. On this path, 80 J of heat flows into the system and the system **does** 30 J of work.

   (a) Using the First Law, write down the difference in internal energy between the states A and B.

   (b) How much heat flows into the system for the process represented by the path ADB if the work done by the system on this path is 10 J?

   (c) When the system returns from state B to state A along the **curved** path AB, the work done **on** the system is 20 J. What is the heat transfer?

   (d) If the internal energy of the system in state A is U_A while in the state D, $U_D = U_A + 40$ J, find the heat absorbed in the processes AD and DB.



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3. **Free expansion of a van der Waals gas**

   Assuming that helium obeys the van der Waals equation of state, determine the change in temperature when one kilomole of helium gas, initially at 20°C and with a volume of 0.12 m^3, undergoes a free expansion to a final pressure of one atmosphere. You should use the following expression:

   $$\left(\frac{\partial T}{\partial V}\right)_U = -\frac{a}{C_V}\left(\frac{n}{V}\right)^2$$

   For this gas the relevant parameters in the van der Waals equation of state are given by $a = 3.44 \times 10^3$ J m^3 kmol^{-2}; $b = 0.0234$ m^3 kmol^{-1}; and in this case $C_V/nR = 1.506$.
   (Hint: You may approximate. First show that the initial pressure is much higher than the final one. Then you may assume that the final volume is much larger than the initial volume.)
   Numerical answer: -2.3 K.

4. **Free expansion experiments and internal energy of ideal gas**

   In experiments on the free expansion of low-pressure (i.e. 'ideal') gases it was found that there was no measurable temperature change of the gas, i.e.

   $$\left(\frac{\partial T}{\partial V}\right)_{U,ideal} = 0$$

   Show that this observation means that the internal energy of the gas, U, must be a function of temperature T *only. Hint: you will need to use the* reciprocity *relation between partial derivatives:*

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

   In this case the relevant variables (x,y,z) are T, U, and V.

5. **Adiabatic processes**

   Use the First Law and the Ideal Gas equation to show that the pressure and volume of an ideal gas in an adiabatic expansion are related by $PV^\gamma = c$ where c and $\gamma = C_P/C_V$ are constants. Show that the work done by the gas in adiabatic expansion from (P_1, V_1) to (P_2, V_2) is

   $$W = \frac{P_1V_1 - P_2V_2}{\gamma - 1}$$

   Hint: Remember that $c_P - c_V = R$ for 1 mole of an ideal gas, and use the Ideal Gas equation in differential form RdT=PdV+VdP.

6. **Isobaric processes**

   Use the First Law to find the change in internal energy of a monatomic ideal gas in an isobaric expansion at 1 atm from a volume of 5 m^3 to a volume of 10 m^3. Show that this is independent of the number of moles of gas. γ for a monatomic ideal gas is 5/3.

7. **Cooling in the adiabatic expansion**

   By considering adiabats and isenthalps on an indicator diagram, *explain* why the adiabatic expansion produces more cooling than either a free expansion (Joule process) or a throttling (Joule-Kelvin) process for an ideal gas or similar material.

   Given that:

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

   use the triple product rule for partial differentials to derive the expression

   $$\mu_{JK} = \left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_P}\left(T\left(\frac{\partial V}{\partial T}\right)_P - V\right)$$

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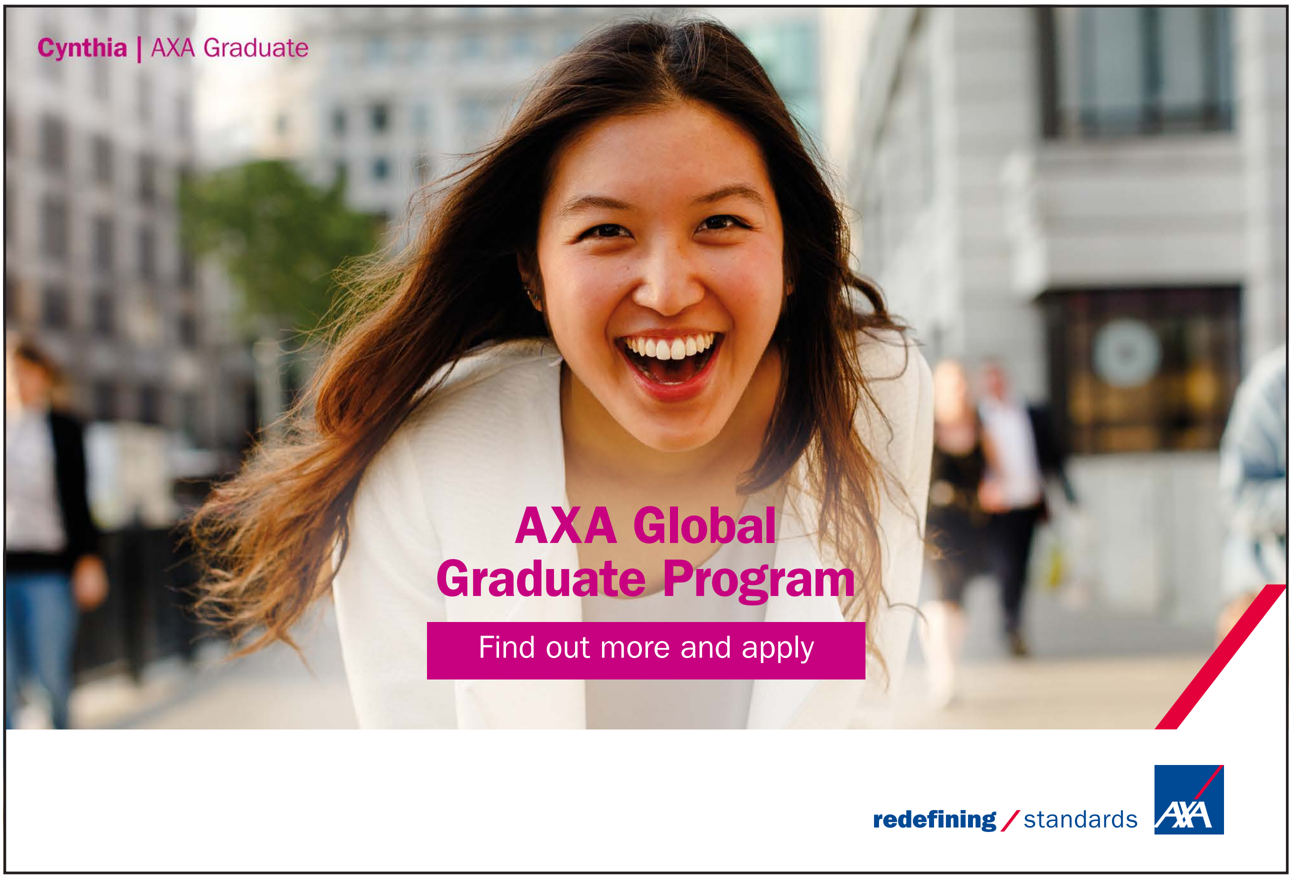
Show that over a range of T where μ_{JK} is independent of temperature, the cooling in a throttling (Joule-Kelvin) process with a pressure change from P_1 to P_2 is

$$\Delta T = \int_{P_1}^{P_2} \left(\frac{\partial T}{\partial P}\right)_H dP$$

In a similar way, show that the cooling in an adiabatic reversible expansion from a pressure P_1 to P_2 is

$$\Delta T = \int_{P_1}^{P_2} \left(\frac{\partial T}{\partial P}\right)_S dP$$

Hence *prove* that, for a given pressure change, the adiabatic expansion produces more cooling than a throttling process, i.e. that the difference in the integrands $(\partial T/\partial P)_S - (\partial T/\partial P)_H$ is positive.)



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4 Cycles and the Second Law

In this section some problems involving engines, refrigerators and heat pumps are investigated. The Second Law captures the idea that some processes are forbidden even though the First Law is obeyed. This means that some processes are irreversible, such that the arrow of time, as perceived in everyday life, is defined by the direction in which irreversible processes go.

Key definitions

Heat engines move heat between reservoirs at different temperatures, either producing work (engines) or absorbing it (fridges and heat pumps). They are normally analysed in terms of energy per cycle.
Efficiency and Coefficient of Performance are measures of "What you get out" divided by "what you put in". The Carnot cycle defines the best possible values.
Engine efficiency: (work out) / (heat supplied) = W/Q_{hot}. Carnot Efficiency = $(T_{hot} - T_{cold})/T_{hot}$
Fridge efficiency: (heat extracted) / (work supplied) = Q_{cold}/W. Carnot Efficiency = $T_{cold}/(T_{hot} - T_{cold})$
Heat Pump efficiency: (heat delivered) / (work supplied) = Q_{hot}/W. Carnot Efficiency = $T_{hot}/(T_{hot} - T_{cold})$

1. **Statements of the Second Law of Thermodynamics**

   Show that if the Clausius statement of the Second Law of Thermodynamics is false, the Kelvin-Planck statement of the Second Law of Thermodynamics must be false also.

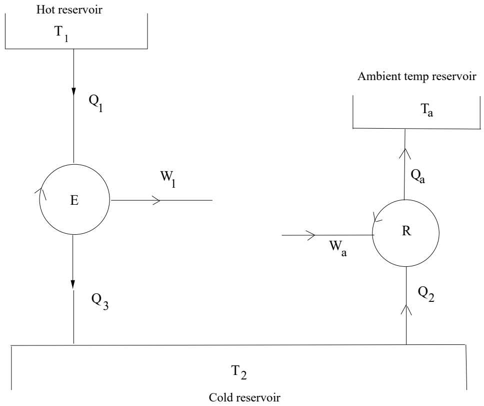
   Hint: Make a composite heat engine consisting of a Clausius-statement-breaking refrigerator which transfers an amount of heat Q_2 per cycle from a cold to a hot body together with an engine which delivers the same amount of heat, Q_2, per cycle to the cold body.

2. **Efficiency of engines part 1**

   Which gives the greater increase in the efficiency of a Carnot engine: increasing the temperature of the hot reservoir or lowering the temperature of the cold reservoir by the same amount?

3. **Efficiency of engines part 2**

   The maximum efficiency of a heat engine can be increased by reducing the temperature of the lower temperature reservoir. Consider the composite engine shown in the diagram opposite. Engine E operates between a high temperature T_1 and a body at T_2, lower than the ambient temperature. This lower temperature body is maintained at lower than ambient temperature by a refrigerator which extracts heat Q_2 from the lower temperature body and emits heat at the ambient temperature T_a. Show that the composite engine ER has a maximum efficiency equal to that of a single engine operating between the temperatures T_1 and T_a, in other words that nothing is gained by artificially cooling the lower temperature reservoir.



   For the composite engine use the usual formula for efficiency, in terms of the **net** *work done on the surroundings and the (heat) energy supplied at the* **highest** *temperature. Then exploit the relationships between heat flows and temperatures.*

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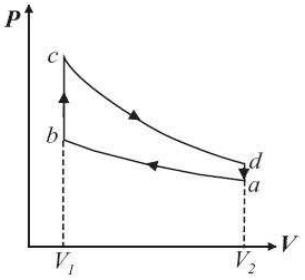
4. **Efficiency of engines, part 3**

   An ideal gas is taken through the reversible cycle (The Otto cycle) shown in the diagram where **ab** and **cd** are adiabatics. The temperature at a is T_a and so on.
   Briefly describe the working cycle identifing the processes during which heat flows in or out of the system. Give expressions for these heat flows in terms of an appropriate heat capacity. Give an expression for the net work output per cycle and identify this quantity on a sketch of the $P - V$ diagram.



   The 'Otto cycle' is an idealisation of the internal combustion engine. Which segments represent fuel compression, burning, and exhaust?

   Show that the efficency of the Otto cycle is

$$1 - \frac{T_d - T_a}{T_c - T_b}$$

5. **Efficiency of engines, part 4** An engineer applies to a venture capital company for money to market a new heat engine, which is claimed to extract 5000 J of heat from a reservoir at 400 K, reject 3500 J to a reservoir at 300 K, and do 1500 J of work per cycle on the surroundings. How should the venture capitalists go about studying details of the device.

6. **The best possible fridge** Using reasonable values for the temperatures inside and outside a domestic refrigerator, calculate its maximum possible efficiency.

7. **Domestic heating**

   A building is heated to 27^OC. How much heat per second could be supplied by

   (a) An electric heater, with power input 20kW

   (b) A heat pump connected to an adjacent river at 7°C, with power input 20kW.

8. **Multipurpose device.**

   A company markets a device which, it claims, can extract 400W heat from a fridge compartment *and* deliver 1kW heating to the living room using just 100W of electricity. Consider both First and Second Laws to determine whether the claim is thermodynamically plausible?

9. **Yet another cycle**

   An engine cycle using an ideal gas consists of the following steps
   (i) an isobaric compression from Volume V_a to V_b at pressure P_a
   (ii) an increase in pressure from P_a to P_b at a constant volume V_b
   (iii) an adiabatic expansion from (P_b, V_b) to the original state at (P_a, V_a)

   Sketch this cycle on a PV plot. Describe the steps where heat enters and leaves the system.

   What is the efficiency of a heat engine expressed in terms of the magnitudes of the heat inputs and outputs? Show that the efficiency of the cycle described above is

$$\eta = 1 - \frac{\gamma P_a}{V_b} \frac{V_a - V_b}{P_b - P_a}$$

   what is peculiar about this expression?

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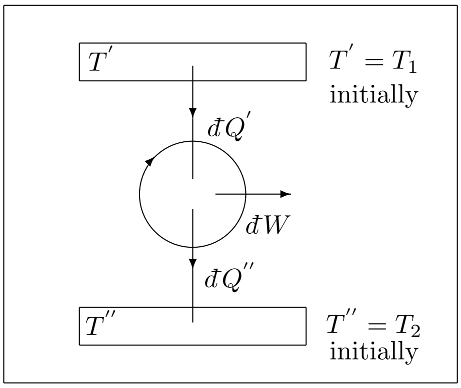
10. **Work extracted while approaching thermal equilibrium**

A small Carnot engine operates between two identical bodies each having a finite heat capacity C_P, initially at temperatures T_1 and T_2 respectively, as indicated in the diagram.

Heat flows from the higher temperature body to the lower temperature body until the two bodies eventually reach the same temperature, T_f. Calculate the total amount of work done by the Carnot engine before the temperatures of both bodies reach T_f.

How would the result differ if the cold reservoir was large enough that its temperature remains constant?



Hint: It is necessary to specify an intermediate stage between start (here the two temperatures T_1 and T_2) and finish (here the common temperature T_f). To avoid an ambiguous notation, use T' as the intermediate temperature for the body whose initial temperature was T_1; and T'' as the intermediate temperature for the body whose initial temperature was T_2. Then small temperature changes for an intermediate cycle can be represented – loosely – by dT' and dT'', and heat flows by $C_P dT'$ and $C_P dT''$. However, great care has to be taken when allocating/associating signs with these four quantities! An application of the general relationship between heat flows and temperatures, in this context, provides an equation which can be integrated between limits denoted by T_1, T_2 and T_f, as appropriate. The relationship between T_f, T_1 and T_2 turns out to be $T_f^2 = T_1 T_2$, which you should derive.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5 Entropy

We see that the concepts derived for heat engines are applicable to all materials. This requires the introduction of "entropy": the quantity which always increases in time, and thereby defines the arrow of time. It is also illustrated that the law of increasing entropy applies only on a universal scale. It i perfectly possible for a system to reduce its entropy, provided it increases the entropy of some other system.

Key definitions

Entropy change in a process $\int dS = \int \frac{dQ}{T}$ where T is the temperature at the point where the heat flows.

The Second Law can be restated that in any process the total entropy increases. This includes the entropy of the system *and* its surroundings.

Entropy is a state variable. If a system is taken around a thermodynamic cycle, its entropy returns to the original value. However, if the process is irreversible, the entropy of the surroundings will increase.

Equilibrium in isolated systed is defined by the state of maximum entropy.

The entropy change in a material during an irreversible process is *the same* as in a reversible process between the same endpoints. We can use an equivalent reversible process to calculate ΔS

The Central Equation, $dU = TdS - PdV$, describes the first and second laws of thermodynamics in terms of state variables.

Boltzmann's formula $\mathbf{S = k_B \ln W}$ relates macroscopic entropy to the number of microstates.

1. **Calculation of entropy change**

   5 kg of hot water at 25°C cools to the 5°C temperature of its surroundings. How much heat flows? What is the entropy change of the surroundings? What is the entropy change of the water? (c_P for water = 4.19×10^3 J kg^{-1} K^{-1}.)

2. **Variation on the same theme**

   An electric current of 10 A flows through a resistor of 20 ohms which is kept at 27°C by being immersed in running water. What is the entropy change per second of the resistor, the water and the universe?

3. **Entropy and ideal gases**

   The internal energy of an ideal gas is all kinetic energy, and so it depends only on the temperature.

   Use this fact to derive an expression for the difference, $S_2 - S_1$, in the entropies S_1 and S_2 of one mole of an ideal gas at volumes V_1 and V_2 respectively, at the same temperature.

   Then show that for an ideal gas, C_P is independent of pressure P.

4. **General entropy changes in a ideal gas** The heat capacity of an ideal gas is not fully defined by the equation of state, it depends on details of the molecule. Consider the case of a near ideal gas with equation of state $PV = nRT$ and $c_v = A + BT$ where A and B are constants, and show that the change in entropy between state (V_1, T_1) and state (V_2, T_2) is

   $$\Delta S = A \ln(T_2/T_1) + B(T_2 - T_1) + R \ln(V_2/V_1)$$

   Hint: From the Central Equation, dS can be written as a sum of two terms, one involving dU and the other dV. A glance at the result sought shows that the term involving dU has to be re-cast as one involving dT before doing the integration to get ΔS.

5. **Another look at the Carnot cycle** Sketch a Carnot cycle, not on a PV diagram but on a TS diagram (i.e. temperature versus entropy). Show that the area within the closed path is equal to the heat absorbed per cycle provided that the path is traced out clockwise.

   Hint: consider what is happening on each 'leg' of the Carnot cycle, in terms of entropy and temperature.

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6. **Entropy change in a (simplified) gin and tonic**

   A cube of ice of mass 30 g melts in a glass of water at 0°C in a room at 20°C. The water is stirred slowly to keep its temperature at 0°C, but gently enough that the work done can be neglected. Calculate the changes in entropy of the ice, the water and the air in the room. (The latent heat of fusion of ice is 334 kJ kg^{-1}.)

7. **Entropy change, reversible and irreversible processes**

   A block of lead with heat capacity C_P=1000 J K^{-1} is cooled from T_1=200K to T_2=100K by:

   (a) plunging the block into a large bath of liquid at 100 K,

   (b) first plunging the block into a large bath at 150 K, equilibrating, then plunging into a second bath at 100 K.

   (c) a reversible process

   Calculate the entropy change of the universe in each case, and give an explanation for how the reversible process could be implemented in practice.

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6 Thermodynamic Potentials

Learning Outcomes

This section introduces the mathematical foundations of thermodynamics. We see that for a system with specific boundary conditions, the Second Law requirement that the entropy of the universe increases means that the thermodynamic potential (free energy) of the system is reduced by any process. The boundary conditions are accounted for by the appropriate definition of the free energy.

The four thermodynamic potentials have differential forms convenient for dealing with particular boundary conditions. Maxwell relations come from double-differentiating the potentials.

Key definitions

	Definition	Central Equation	Maxwell Relation
Internal Energy	U	$dU = TdS - PdV$	$(dT/dV)_S = -(dP/dS)_V$
Enthalpy	$H = U + PV$	$dH = TdS + VdP$	$(dT/dP)_S = (dV/dS)_P$
Helmholtz Free Energy	$F = U - TS$	$dF = -SdT - PdV$	$(dP/dT)_V = -(dS/dV)_T$
Gibbs Free Energy	$G = H - TS$	$dG = -SdT + VdP$	$(dV/dT)_P = (dS/dP)_T$

1. **Heat Capacities**

   The heat capacity is *defined* as the amount of heat required to raise the temperature of a body by 1K. From this, the First Law and the Central Equation, prove that:

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

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

2. **Helmholtz function and pressure**

   Write down the differential form of the Helmholtz function $F = U - TS$, and an expression for pressure in terms of F.

   The specific Helmholtz function of a particular gas is:

$$f = \frac{F}{n} = f_0(T) - \frac{a}{v} - RT\ln(v - b)$$

   where f_0 is a function of T only, while a and b are constants. Calculate the pressure of the gas, and hence its equation of state.

3. **Using Maxwell relations**

   The Helmholtz thermodynamic potential F is defined by $F = U - TS$. Use the Central equation ($dU = -PdV + TdS$) to derive the Maxwell relation associated with the Helmholtz potential.

   For any material, the difference between the heat capacities at constant pressure and volume is given by

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

   Using the Maxwell relation, show that

$$\left(\frac{\partial c_V}{\partial V}\right)_T = \left(\frac{\partial^2 P}{\partial T^2}\right)_V$$

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and that

$$C_P - C_V = \frac{VT\beta_P^2}{\kappa_T}$$

where β_P is the isobaric volume expansivity and κ_T is the isothermal compressibility.

Use a similar technique to prove that the difference between the isothermal and the adiabatic compressibilities is

$$\kappa_T - \kappa_S = \frac{TV\beta_P^2}{C_P}$$

Verify that $C_P - C_V = R$ and $\kappa_T - \kappa_S$ for a monatomic ideal gas.

4. **A block of metal.**

   A block of metal is subjected to an adiabatic and reversible increase of pressure from P_1 to P_2. Show that the initial and final temperatures T_1 and T_2 are related by

   $$\ln(T_2/T_1) = V\beta(P_2 - P_1)/C_P$$

   You may assume that the volume of the block stays approximately constant during the compression. *Hint: Think about entropy. What does reversible and adiabatic mean for entropy? Then try to obtain an expression involving T and P (the variables mentioned in the question...)*

5. **From Gibbs function to equation of state**

   A gas has molar Gibbs Free energy given by

   $$g = RT\ln P + A + BP + \frac{1}{2}CP^2 + \frac{1}{3}DP^3$$

   where A, B, C and D are constants. Find the equation of state (i.e. the relationship between P,V, and T) and explain why it is independent of A.

6. **A harmonic material**

   Suppose a material has an equation of state per kg given by

   $p = A(v - b) + CT$

   Given that at $P = 0$, T=300K: $v_0 = 10^{-3} m^3/kg$; $K_T = 10^{10}$Pa; $\beta = 10^{-5} K^{-1}$, determine the constants A, b, C? Is this a gas or a condensed phase?

7. **Deriving the ideal gas equation from experimental laws.**

   Use *Joule's Law* (the internal energy of an ideal gas depends only on temperature) and *Boyle's Law* (at constant temperature, the product of pressure and volume for a fixed amount of an ideal gas is a constant), to derive the form of the equation of state of the ideal gas.
   Hint: start with the Central Equation, and employ one of the Maxwell relations. Then integrate...

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7 Expansion Processes

Learning Outcomes

In this section we examine how materials behave on irreversible expansion. We see that this depends sensitively on the type of materials and the way that the expansion is done. It emphasizes how we can understand and do calculatons on irreversible processes using only equilibrium quantities.

Key definitions

Joule expansion means an irreversible free expansion into a vacuum. No work is done, nor does heat enter, so internal energy is conserved.

Joule-Kelvin expansion means an irreversible expansion into a low pressure region. Again, no heat enters, but work is done, so enthalpy is conserved.

Isothermal expansion means a reversible expansion, typically done slowly so that heat enters and work is done, so temperature is conserved.

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1. **Free expansion**

   Derive the expression for the Joule coefficient of the van der Waals equation of state.

   $$\left(\frac{\partial T}{\partial V}\right)_U = -\frac{a}{C_V}\left(\frac{n}{V}\right)^2$$

   Hint: this requires use of the cyclical relation, the Central Equation, and a Maxwell relation...

2. **Joule-Kelvin coefficients**

   (a) The Joule-Kelvin expansion is an isenthalpic process, in which the change in temperature is given: by

   $$\Delta T_{JK} = \int_{P_1}^{P_2}\left(\frac{\partial T}{\partial P}\right)_H dP$$

   Show that the Joule-Kelvin coefficient can be written in terms of the heat capacity and the coefficient of thermal expansion:

   $$\mu_{JK} = \left(\frac{\partial T}{\partial P}\right)_H = \frac{V}{C_P}(\alpha T - 1)$$

   (b) Show that the Joule-Kelvin coefficient is zero for an ideal gas.

   (c) Evaluate the Joule-Kelvin coefficient for a van der Waals gas with specific heat capacity c_P.

   (d) Show that, for a van der Waals gas, the line dividing positive and negative values of μ_{JK} (the "inversion curve") is given by:

   $$T_{in} = \frac{2a}{Rb}\left(\frac{v_{in} - b}{v_{in}}\right)^2$$

   Hint: The easiest way to get an expression for $(\partial v/\partial T)_P$ *from the van der Waals equation is to write it as* $T(P,V)$ *and find* $(\partial T/\partial v)_P$.

3. **Cooling in an adiabatic expansion**

   Draw two isotherms and an adiabat for an ideal gas on an indicator (PV) diagram, and hence show that an ideal gas always cools when undergoing a reversible adiabatic expansion. You do not need to do any detailed mathematics.

   Now show that the coefficient for cooling in an adiabatic expansion is:

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

   Hence explain why an adiabatic expansion produces more cooling than an isenthalpic process, with a similar pressure change.

4. Discuss why the isenthalpic Joule-Kelvin process is used in real refrigerator, rather than the adiabatic or Joule processes.

5. **Expanding through a phase transition**

   In a throttling process we normally write

   $$\Delta T_{JK} = \int\left(\frac{\partial T}{\partial P}\right)_H dP = \int \frac{V}{C_P}\left(\alpha T - 1\right) dP$$

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In an evaporator, the cooling substance goes from liquid to gas in an isenthalpic process. With reference to the equation above, explain why this is a good thing to do, and why it creates a problem applying the equation. What happens in practice is that the system remains at constant pressure and temperature, while extracting heat from the surroundings to overcome latent heat and allow it to evaporate.

6. **Gibbs Helmholtz**

   A system is heated from temperature T_1 to T_2, show that

   $$G_2 = \frac{G_1 T_2}{T_1} - T_2 \int_{T_1}^{T_2} \frac{H}{T^2} dT$$

   If the interatomic forces are known, it is fairly simple to compute the internal energy of a system.

   Suppose a material at atmospheric pressure in its liquid phase has internal energy

   $$U = U_l(V) + A_l T$$

   and in its solid phase

   $$U = U_s(V) + A_s T$$

   Assume further that it has zero thermal expansion: $\left(\frac{dV}{dT}\right)_P = 0$ and melting point of 300K.

   Write down the gibbs free energy difference at 300K, and calculate its value at any other temperature T_2. Discuss each term in your final expression. By examining what happens at $T = 0$, prove that the given expressions for U are no longer valid in that limit.

7. **Critical point** At the critical point, where liquid and gas become indistinguishable, $(\partial P/\partial V)_T = 0$ and $(\partial^2 P/\partial V^2)_T = 0$. Sketch isotherms on a PV diagram showing these two conditions. Show that, for a van der Waals gas, the critical point is at:

   $$P_c = \frac{a}{27b^2}, \qquad V_c = 3nb, \qquad T_c = \frac{8a}{27Rb}$$

   For a van der Waals gas for which $a = 0.27$ N m^4 mole^{-2} and $b = 3.1 \times 10^{-5}$ m^3 mole^{-1} (approximately the values for carbon dioxide) calculate the values of P_c, V_c and T_c. Compare the value of the critical temperature T_c with the value of the Boyle temperature T_B and comment.

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8 Thermodynamics in other systems

Learning Outcomes

The laws of thermodynamics apply to any system in equilibrium. In general "Work" can be any form of non-heat energy: chemical, elastic, electromagnetic, gravitational.

Key definitions

Non-mechanical work which contributes to internal energy can be used in place of PdV. After a simple replacement of PdV with XdY the whole thermodynamic apparatus can be applied, where X and Y are the appropriate variables.

Equilibrium A system is in equilibrium if it minimises the Free Energy relevant to the boundary conditions.

The Second Law applies to all thermodynamic systems: in any allowed process, the entropy of the universe always increases.

1. **A rubber band**

   (a) Derive the so-called 'energy equation'

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

   for a simple substance. If the equation of state of the substance is known, the energy equation allows one to calculate the dependence of the internal energy on volume.

   Hint: Use the Maxwell relation derived from the Helmholtz function.

   (b) Write down the analogous result for rubber band, where work done is tension times extension. Why is it different from force being the differential of energy?

   (c) The equation of state of a rubber band is

   $$\mathcal{F} = aT\left(\frac{L}{L_0} - \left(\frac{L_0}{L}\right)^2\right)$$

   where a is a constant and L_0 is the unstretched length. For this band, show that U is a function of T only.

   (d) If $L_0 = 1$ metre and $a = 1.3 \times 10^{-2}$ N K^{-1}, calculate the work done on the band and the heat rejected when it is stretched isothermally and reversibly from 1 m to 2 m at $T = 300$ K.

2. **An adiabatic variation on the rubber band.**

   If the rubber band in the previous problem is stretched *adiabatically* and reversibly from 1 m to 2 m, by how much does its temperature rise? (Take the heat capacity to be $C_L = 1.2$ J K^{-1}.)

3. **Entropy of diamond**

   The low temperature specific heat of diamond varies with temperature as:

   $$c_p = 124\left(\frac{T}{\theta_D}\right)^3 \quad \text{kJ kg}^{-1}\ \text{K}^{-1}$$

   where the Debye temperature $\theta_D = 1860$ K. What is the entropy change of 1 g of diamond when it is heated at constant pressure from 4 K to 300 K?

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The Debye temperature of graphite is $\theta_D = 1500$ K, and

$$c_p = 89\left(\frac{T}{\theta_D}\right)^3 \quad \text{kJ kg}^{-1}\ \text{K}^{-1}$$

Given that diamond has higher density than graphite, discuss whether the phase boundary on a PT phase diagram has positive or negative slope.? Does the equation for specific heat satisfy the Third Law, that the change in entropy in any process becomes zero at 0K?

(The atomic weight of carbon is 12.)

4. **Planck's Law**

   The equation of state for radiation in a cavity is $P = U/3V$, where U(T) is the energy and V the volume. Use this with the Central Equation to show that the energy density varies as the fourth power of temperature.

   The total energy density must be the integral of the energy density over all frequencies:

$$u = \int u_\nu(\nu, T) g(\nu) d\nu$$

   where $g(\nu)$ is the probability distribution that a photon will have frequency ν

   Show that the Planck distribution of energy between wavelengths satisfies the requirement that the energy density varies as the fourth power of temperature. Show that the classical distribution with each mode having energy $k_B T$ gives divergent energy. What would the Boltzmann distribution give?

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5. **Photon Gas**

   (a) For a photon gas, the equation of state can be written $P = \frac{u(T)}{3}$ where $u(T)$ is the specific internal energy, which depends only on temperature. Show that the internal energy of a photon gas varies as the fourth power of temperature, $U = kVT^4$, where k is a constant.

   (b) An evacuated cylinder of volume $1m^3$ contains a photon gas confined by a piston. At what temperature would the cylinder need to be for the piston to move outward against atmospheric pressure (10^5Pa) ($k = 7.56 \times 10^{-16} J/m^3/K^4$)

   (c) Show that the Heat Capacity C_v of a photon gas obeys the Third Law, and evaluate the entropy of a photon gas, assuming that S=0 at T=0.

   (d) Show that the Gibbs Free Energy of a photon gas is zero and comment on the implication for creation and absorption of photons at a cavity wall.

   (e) Using the fact that $G = 0$, and *without* using the equation of state, prove that the pressure of a photon gas depends on temperature only.

6. **Temperature of the sun.**

   By assuming that both the earth and the sun are perfect black bodies that radiate equally in all directions use the Stefan Boltzmann law to estimate the temperature of the sun. (You will need Temperature of the earth $\approx 287K$, Radius of the sun $\approx 6.96 \times 10^8 m$, Distance from earth to sun (astronomical unit) $\approx 1.5 \times 10^{11} m$.

   Comment on the various assumptions you have made.

   Hint: Think of how much area the earth takes up relative to the total emission surface of the sun at the orbital distance. Assume there is a radiative equilibrium on the earth. Note the earth's radius cancels out during this calculation.

   Historical note: Stefan, lacking accurate knowledge of the relevant distances, performed this calculation by using a measure of the incident flux on earth. This was measured using huge reflecting mirrors and target objects!

7. **Black hole entropy**

   A black hole has only three independent variables, mass, charge and angular momentum. When a particle falls into a black hole, information (entropy) is "lost".

   It has been predicted that the entropy of a (non-rotating, uncharged) black hole depends on a single variable, such as its surface area (A) measured in Planck areas, $S = k_B A c^3 / 4G\hbar$. this is called the "Bekenstein-Hawking formula". Use it to calculate the temperature of a mini black hole of mass $M = 10^{12}$ kg, and a black hole the size of the sun $M = 2 \times 10^{30}$ kg.

   Hint: You will need to identify, and find values for, k_B, G, $\hbar$ and c. The radius of a black hole depends only on its mass $r = 2Gm/c^2$ (Schwartzchild radius), and its energy also depends only on the mass $U = mc^2$ The Central Equation of Thermodynamics lets you introduce T explicitly. The same equation suggests that the appropriate variables are U and V, so that **formally** *$S = S(U, V)$. Assume that S is a function of U only.*

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9 Phase transitions

Learning Outcomes

Real materials have "phases" which have well defined thermodynamic properties, even though atoms are moving around. In a phase transition, there is a discontinuous change in some thermodynamic property, so that the phases are distinctly diffeent from one another. Phases can coexist, with a sharp interface between them. The stable phase, or combination of phases, can always be calculated by minimising the appropriate thermodynamic potential of the system.

Key definitions

The stable phase is the one with lowest Gibbs Free energy.
The *order* of the phase transition is named for the lowest derivative of G is discontinuous.
In a single component system, with fixed P,T a single phase is present. With fixed V,T, phase coexistence is possible with Helmholtz free energy minimised.
Any transition with increasing pressure must go to a phase with lower specific volume (high density).
Any transition with increasing temperature must go to a phase with higher specific entropy.
The Clausius-Clapeyron equation relates the slope on a phase diagram to the discontinuity in entropy (or latent heat) and volume.
In some cases, the free energy of a system comprising two distinct regions of different phases may be lower than the free energy in either phase alone.

1. **Phases and Clausius-Clapeyron**

   (a) Sketch the P-T projection of the PVT surface for a simple substance and identify its main features.

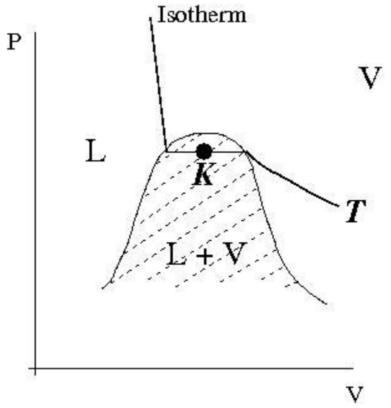
   (b) By using the fact that the specific Gibbs functions of coexisting phases are the same, derive the Clausius-Clapeyron equation

   $$\frac{dp}{dT} = \frac{l}{T(\nu_2 - \nu_1)}$$

   where ν_1 and ν_2 are the specific volumes of the two phases and l is the specific latent heat of the transition.

   (c) In a pressure cooker, food is cooked more quickly by raising the pressure so that water boils at a higher temperature. Estimate the pressure at which water boils at $130°C$. The density of water and steam at $100°C$ are 959 kg m^{-3} and 0.600 kg m^{-3} respectively, and the latent heat of vaporisation is 2257 kJ kg^{-1}. Take 1 atmosphere to be 10^5 N m^{-2}.

2. **Phase mixtures**



The figure shows an isotherm on the $P-V$ projection. At the point X the substance is a mixture of liquid and vapour. The total mass of substance is the sum of the liquid and vapour masses $m = m_l + m_v$. At coexistence v_l and v_v are the specific volumes of the liquid and vapour (per kg).
Write down an expression for the total volume at X.
Let the specific volume of the mixture at X be v. Show that :

$$m_l(v - v_l) = m_v(v_v - v)$$

Explain why this result, which gives the ratio m_v/m_l, is known as the 'lever rule'.
How does the Gibbs free energy change with volume in the coexistence region?
What is the compressibility of the substance at X.

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3. **Solid-solid phase transitions**

   Tin can exist in two forms (“allotropes”): Grey tin is the stable form at low temperatures and white tin the stable at high temperatures and pressures. There is a first-order transition between the two phases at 291 K and 1 atm. Given the latent heat for the transition (18.5×10^3 J kg^{-1}); and the densities 5.75×10^3 kg m^{-3} (grey) and 7.30×10^3 kg m^{-3} (white); estimate the change in this transition temperature if the pressure is increased to 100 atm?

   Hint: The grey tin to white tin transition is a phase transition, so use the Clausius Clapeyron equation. Try assuming the phase boundary is a straight line, putting $dP/dT = \Delta P/\Delta T$ even though $\Delta P = 99$ atm. Note also that the density change going from the low-temperature-stable grey tin to the high-temperature-stable white tin is an increase, like in ice-to-water – so anticipate dP/dT to be negative.

4. **Triple Point**

   The sublimation and the vaporization curves of a particular material are given by:

$$\ln P = 0.04 - 6/T \quad \text{sublimation}$$

$$\ln P = 0.03 - 4/T \quad \text{vaporization}$$

   where P is in atmospheres.


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(a) Find the temperature and pressure of the triple point.

(b) By assuming that the volume in the gas phase is much larger than for the solid or liquid, show that the latent heats are $4R$ and $6R$ per mole.

(c) By considering entropy around a cycle around the triple point in the PT phase diagram, show that

$$\frac{l_{SV}}{T_{TP}} - \frac{l_{SL}}{T_{TP}} - \frac{l_{LV}}{T_{TP}} = 0$$

and hence calculate the latent heat of fusion.

Hint: Consider a loop round the triple point in the PT phase diagram. As S is a state function,

$$\frac{l_{SV}}{T_{TP}} - \frac{l_{SL}}{T_{TP}} - \frac{l_{LV}}{T_{TP}} = 0$$

5. **Impossible Phase diagram**

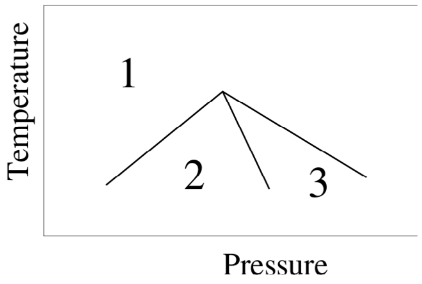
Consider the phase diagram shown below on the left, in which three proposed phases are separated by first order phase transitions. A diamond anvil cell experiment applies an isothermal pressure increase which traverses the three phases.

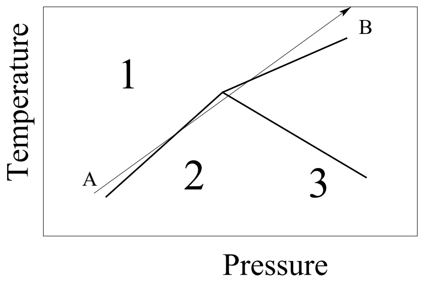
(a) List the phases 1-3 in order of density. Comment on the compressibilities.

(b) By considering isothermal pressure increase just below the triple point, show that this phase diagram is impossible.

(c) The diagram on the right represents a shock compression process, along the line AB, which has constant slope m. Define the quantity (call it Z) which conserved along this line. Is this quantity a state variable?

(d) By generalising parts (a) and (b) to consider Z and its conjugate variable, show that no sector of the phase diagram can have an angle greater than 180 degrees at the triple point. You do not need evaluate the conjugate variable.





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6. **Pressure effect on melting ice**

   Water has the unusual property that the solid phase (ice) can be melted by applying sufficently large pressure. Use the Clausius-Clapeyron equation to determine the additional pressure above atmospheric ΔP required to melt ice at temperature $-\Delta T$ below freezing (at $0^\circ C$). This value is in effect the slope of the phase boundary in the P-T representation. Comment on the sign of the value. Take l the latent heat of fusion to be $333.7 kJkg^{-1}$, and the densities of water and ice at $0^\circ C$ to be $\rho_w = 1000kgm^{-3}$ and $\rho_i = 916kgm^{-3}$.

   Assuming the slope of the phase boundary is constant away from the atmospheric melting point of water (which turns out to be a valid assumption), use your calculated value in the following situations.

   (a) Melting glaciers. The bottom surface of a $2000m$ thick glacier is at a temperature of $-1.5^\circ C$. Will the water here be liquid or ice? Use the density of ice given above.

   (b) Very cold water. The lowest temperature at which liquid water is stable is $-22^\circ C$. What pressure must be applied to keep the water from freezing? Express your answer in Pa and atm.

   (c) Ice skates. Do ice skates apply sufficent pressure on the surface of ice to melt it? You will have to make some assumptions regarding the area of skate in contact with the ice, the temperature and the weight of the skater

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10 Chemical Potential

Learning Outcomes

Particles move preferentially to regions of lower chemical potential. Although it is unusual, this may mean that they flow from regions of low concentration to high concentration, or from low pressure to high pressure. Living systems exploit this.

Key definitions

The chemical potential extends the Central Equation to consider adding particles. $dU = TdS - PdV + \mu dN$.
The Gibbs Duhem equation $\sum_i N_i d\mu_i = -SdT + VdP$
μ for a single species is the specific Gibbs Free energy.
Particles flow along gradients of the chemical potential: equilibrium is reached when the chemical potential for a given species is the same everywhere.
Dilute solutions of non-interacting solute can be treated as ideal gases.
Dalton's and Raoults "Laws" for Ideal solutions and gases The total pressure exerted by a mixture is equal to the sum of the partial pressures (Dalton) and the partial pressure is proportional to the mole fraction of that component.

1. **Chemical Potential: Nature's boundary condition**

   Show that the molar chemical potential for an ideal gas at temperature T is given by

   $$\mu = RT\ln(P/P_0) + \mu_0$$

   where $\mu_0 = \mu(T, P_0)$.

   Under standard temperature and pressure, dilute carbon dioxide has $\mu_0 = 394$kJ/mol in air and $\mu_0 = 386$kJ/mol. in water.

   If the atmosphere contains 0.04% CO_2, estimate the concentration of CO_2 dissolved in the ocean.

2. **Irn Bru**

   A 1.05l bottle of Irn Bru contains 1l of drink and is pressurised to 5atm with CO_2 gas.

   At this pressure, the CO_2 concentration in the drink is given by Henry's law C = 0.031 P_g where C is the concentration in moles/L, and P_g is the partial pressure of the gas (5.0 atm).

   What is the chemical potential of the CO_2 in this system relative to the gas at atmospheric pressure?

   The cap is briefly loosened, so that the gas comes fully into equilibrium with the atmosphere, but the dissolved CO_2 remains in solution. The bottle is then sealed.

   What are the chemical potentials of the CO_2 in the drink and the gas above?

   Now the bottle is shaken, such that the contents come into equilibrium. Describe what happens, and calculate the pressure inside the bottle now?

   Approximately how many times can this process be repeated before the drink goes flat?

3. **Chemical Potential Change in Mixing**

   A rigid, thermally isolated container holding 1mol of argon at 1atm, 300K is connected to an identical container holding 1mol of krypton at 1atm, 300K. No heat is added and no work is done on the system. Without calculation, explain what you expect to happen and the final equilibrium state. How do the pressure, temperature and entropy change?

   How would the result change if the initial amounts were different, in volumes V_A and V_K, still at the same initial T and P and still totalling 2 moles of atoms?

4. **Regular solution and solubility limits**

   A total of one mole of fluids, comprising two atomic types, A and B, are mixed at constant temperature. The fluids are ideal except that they repel one another, which adds a term to the internal energy $\frac{Z}{v_A v_B}$.

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Explain why this is a reasonable form for the interaction.

Calculate the change in Gibbs Free Energy when the two are mixed, with mole fractions x_A and $x_B = 1 - x_A$, and plot this as a function of x_A for various values of $\frac{RT}{Z}$

For Z=3RT what values of x_A minimise Δg? Calculate the chemical potential for species A at these values.

Describe the mixing process as x_A increases from 0 to 1.

5. **Supercool**

   Salt is added to a mixture of ice and water at 0^oC. Assuming that salt cannot dissolve in ice, what is the change in chemical potential of the water with salt concentration $X = 0.1$?

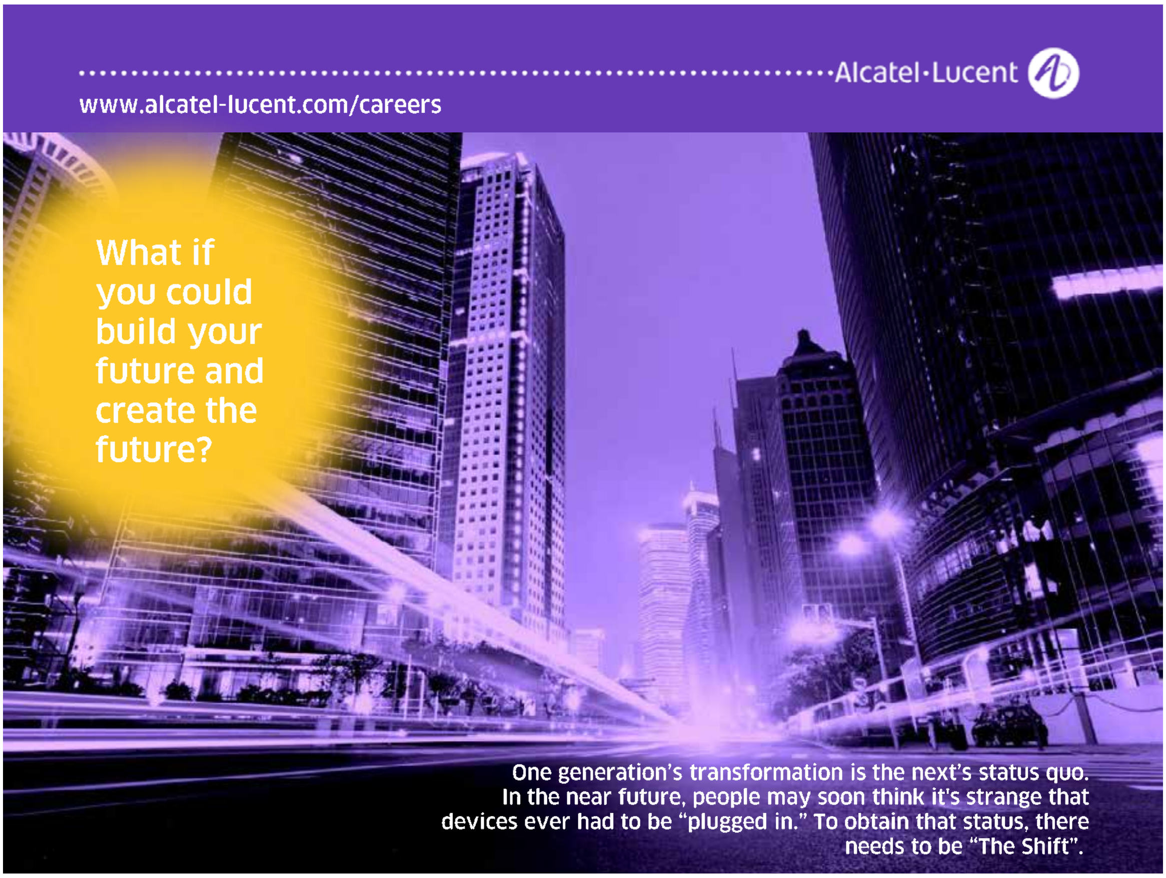
$$\left(\frac{\partial \mu_L}{\partial X}\right)_T$$

   What is the final temperature of the mixture? Assume that the partial pressure of each component in the brine is proportional to its concentration. Take the latent heat of fusion to be 18kJ/mol. For convenience, you can assume that for small changes in absolute temperature l/T^2 is temperature independent.

6. **Simplified Osmosis**

   A surface-dwelling single-celled, spherical marine creature contains protein molecules and water, and is separated from the sea by a semipermeable membrane through which water can pass, but not protein. Treating the protein as a monotonic ideal gas, and assuming there are 2% as many protein molecules as water molecules, calculate the total pressure inside the cell.

   If the membrane has diameter 10μm and thickness 10nm, then what is the stress in the membrane?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11 The Essential Mathematics

Learning Outcomes

In thermodynamics of fluids, any state variable can be written as a function of precisely two others, e.g. T(P,V). This function is differentiable, except at a phase transition.

The key pieces of maths needed for thermodynamics arise from the fact that thermodynamic quantities can be determined by two independent variables.

Key definitions

State Variables are properties of a material, independent of its detailed history. This means that integrals depend only on initial and final conditions, not the path.
Partial Differentials, such as

$$\left(\frac{\partial y}{\partial x}\right)_{z_1, z_2 \dots}$$

represent the change in one property (y) as another (x) is varied, while specifying one (or more) other properties (z_i) which are held constant.

Questions

1. **Partial differentials applied to an ideal gas**

   Explain why it is impossible to evaluate $\frac{dV}{dT}$ unambiguously for an ideal gas.

   The ideal gas equation can be written $PV = nRT$. For adiabatic processes, it is convenient to introduce a quantity $K = PV^\gamma$. Write the ideal gas equation in terms of V, T and K.

   Now evaluate the thermal expansion coefficients $\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$ and $\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_K$ and explain why they are different.

2. **Triple Product and Inverse Relation**

   These are two general mathematical relationships which are widely used in thermodynamics. When applied to thermodynamic quantities they often give relationships which are not physically obvious.

   Use the general relation

   $$dx = \left(\frac{dx}{dy}\right)_z dy + \left(\frac{dx}{dz}\right)_y dz$$

   to show that

   $$\left(\frac{dx}{dy}\right)_z \left(\frac{dy}{dz}\right)_x \left(\frac{dz}{dx}\right)_y = -1$$

   and that

   $$\left(\frac{dx}{dy}\right)_z = \frac{1}{\left(\frac{dy}{dx}\right)_z}$$

   Note that the first equation implies that x(y,z) depends on two independent variables.

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3. **Maxwell Relation**

   Maxwell's relations exploit the fact that thermodynamic variables do not depend on the history of the system. So if you start in state 1, change property x by dx, then change property y by dy, you get to the same state as if you changed y first, then x.

   Use the relation above, and the definition

$$dx = Ady + Bdz$$

   to show that

$$A = \left(\frac{dx}{dy}\right)_z$$

$$B = \left(\frac{dx}{dz}\right)_y$$

   and

$$\left(\frac{dA}{dz}\right)_y = \left(\frac{dB}{dy}\right)_z$$

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4. **Potentials, differential forms and Maxwell Relations**

   Use the definitions H=U+PV; F=U-TS; and G=H-TS to obtain the differential forms

   dU=TdS-PdV; dH=TdS+VdP; dF=-SdT-PdV; dG=TdS-VdP

   Now use the differential forms to derive the four Maxwell relations.

5. **Exact differentials**

   Explain why state variables must have exact differentials.

   Work is defined as $\int PdV$. Prove that work is not an exact differential, and therefore not a state function.

   A state variable X is defined as $PV^3 + aT$.

   What are the SI units of the constant a? Prove that for an ideal gas

   $$\frac{\partial}{\partial V}_T \left(\frac{\partial X}{\partial T}\right)_V = \frac{\partial}{\partial T}_V \left(\frac{\partial X}{\partial V}\right)_T$$

6. **Legendre transform**

   The Legendre transformation creates a new function of a transformed variable.

   $$f_L(X) = f - x.(\partial f/\partial x) \equiv f - X.x$$

   With $X = (\partial f/\partial x)$ By considering applying the Legendre transformation twice, prove that $f_L[f_L(f)] = f$.

   Hence explain why whatever information about a system is included in f, exactly the same information is included in f_L.

   By taking f to be internal energy and x to be volume or entropy show that the enthalpy and Helmholtz free energy are just Legendre transforms of the internal energy.

7. **Calculating Entropy**

   Entropy cannot generally be measured directly, however entropy chanes can be related to measurable quantities. Find three expressions for dS in terms of (dT & dV), (dT & dP) and (dP & dV),

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