

# An inverted textbook on thermodynamics: Part II

Graeme Ackland



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# **An inverted textbook on thermodynamics**

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

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

1<sup>st</sup> edition


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## 1 Some properties of materials

### 1. The magnitude of things

Rearranging the things cited, we find that.

- (a) Using  $E = mc^2$  for the rest mass of hydrogen, this gives  $9 \times 10^{16} J$
- (b) Daily energy consumption of the UK is  $3 \times 10^{15} J$
- (c) 1 atom of uranium, when fissioned, produces about 200MeV energy. 1kg of uranium-235, when fissioned, produces  $200 \times 1.6 \times 10^{-13} \times 6.022 \times 10^{26} / 235 = 82 \times 10^{12} J$
- (d) Deuterium fusion releases about 3.65MeV, depending on whether it makes tritium or helium. Per kg this is  $3.65 \times 1.6 \times 10^{-13} \times 6.022 \times 10^{26} / 4 = 88 \times 10^{12} J$
- (e) The binding energy of  $H_2$  is 4.52eV, and of H is 13.6eV, so to ionise everything requires  $(4.52 + 2 \times 13.6) \times 6.022 \times 10^{23} \times 1.602 \times 10^{-19} = 3 \times 10^9 J$
- (f) Zero point energy in hydrogen =  $\hbar\omega/2$  and  $4161 \text{ cm}^{-1} = 0.51\text{eV}$ , so  $50 \times 10^6 J$ .
- (g) Gravitational energy for tidal power  $mgh = 49 \times 10^6 J$
- (h) The energy density of coal is 24MJ/kg, so 1kg produces  $24 \times 10^6 J$
- (i) The gravitational potential energy of the sandwich is  $GMm/r$ ,  $12 \times 10^6 J$ .
- (j) A KFC doublicious chicken sandwich contains about  $2 \times 10^6 J$ . Source: KFC website.
- (k) The density of air is  $1.22 \text{ kg/m}^3$ , so the KE is  $61 \times 10^3 J$
- (l) Chicken sandwich is a hydrogen-bonded solid, so estimate the specific heat capacity to be similar to ice,  $2.1 \text{ kJ/kg/K}$ . If the sandwich weighs 0.2kg then the thermal energy to heat it 40K is  $17 \times 10^3 J$
- (m) The thermal energy of hydrogen molecules is  $\frac{3}{2}RT = 3.7 \times 10^3 J$
- (n) The kinetic energy of a railway sandwich is  $\frac{1}{2}mv^2 = 250 J$

So there are some 14 orders of magnitude between the kinetic and rest mass energy of a sandwich on a train. No physical quantity has ever been measured with that precision. There are almost enough calories in a chicken sandwich to put it into orbit.

Although the questions mix large and small things, the answers cover a much larger range of energies. From this we obtain some idea of the order of magnitude of things. Rest mass is by far the largest store of energy, followed by nuclear energy, atomic physics, chemical bonding, gravity and finally everyday kinetic energy. Each is separated by about 3 orders of magnitude.

### 2. Heating and metabolism

We will assume that all the energy used in metabolising is converted to heat in the air.

Amount of heat produced by the students:

$$E = n \times P \times t = 6.48 \times 10^7 J$$

Assume that this all goes to heating the air

$$E = Mc\Delta T$$

mass of air, volume times density, is  $M = 1200 \text{ kg}$ , heat capacity is mass times specific heat capacity:  $C = 1200 \times 1000 = 1.2 \times 10^6 \text{ J/K}$

$$\Delta T = E/mc = 54 K$$

Final temperature =  $20 + 54 = 74^\circ\text{C}$

That's hot! People generate a significant amount of heat, roughly equal to our energy intake, around 3000 "nutritional calories" or 12 million Joules per day.

You might also ask how stuffy it gets: typically people use about 25 litres of oxygen per hour so even 100 students make a small impact on the total oxygen content.

Obviously the sun is much bigger than a person, a more interesting comparison eliminates this effect. The mass of the sun is  $2 \times 10^{30}\text{kg}$ , so it produces energy  $1.93 \times 10^{-4}\text{Wkg}^{-1}$ . By contrast, a person is about 60kg, so metabolises  $1.4\text{Wkg}^{-1}$ . Per unit mass, you produce 10,000 times more heat than the sun!

3. **Thermal properties in food science** Strawberries are 88% water, and water has a high specific heat capacity so we assume this component will dominate. The specific heat capacity for strawberries is then

$$c_{\text{strawberries}} = 0.88 \times 4.2 \times 10^3 = 3696\text{J/kg/K}$$

- (a) Energy lost  $\Delta E = mc\Delta T = 38808\text{J}$   
 (b) "Respiration" assumes strawberries are emitting heat, so they will need more energy to cool, and this will take longer. We don't have quite enough information, so we need to make a sensible assumption about how long the process will take. A fridge uses a few tens of Watts (looked up on the internet), so 38808J will take about half an hour assuming reasonable efficiency of the fridge ( $30 \times 60$  seconds). Doing a sanity check, this sounds reasonable. So the heat produced by respiration is

$$q = 0.5 \times 0.21 \times 30 \times 60 = 189\text{J}$$

This is tiny compared with (a), so the effect can be safely neglected. Errors in the half-hour assumption do not change this conclusion.

- (c) Strawberries are mainly available in summer, and since this question comes from Edinburgh we'll take  $25^\circ\text{C}$  to be room temperature. From (a) we need to produce 38808J to heat back up, and since they are thermally insulated the only source is from respiration which takes:

$$\text{time} = 38808/0.5/0.21 = 3.7 \times 10^5\text{s}$$

which is over four days, consistent with our conclusion in (b) that respiration is generally a minor effect compared with heat flow.

- (d) Assume the respiration (105mW) is related to the breakdown of the strawberries, and loss of nutritional value (700kJ). This amount of energy is given off in heat in  $(700 \times 10^3/0.105)$  seconds, which is about 83 days. Assuming that 10% turned-to-mush is unacceptable for human consumption, this gives a lifetime of just over a week.

#### 4. Phase Change: latent heat

To do this question we will make a strong assumption: that we can reach the answer by considering only the conservation of energy between initial and final states. This is justified because the insulated container allows no heat to enter or leave (and no work to be done).

- a) We must consider whether cooling the water  $0^\circ\text{C}$  would release sufficient energy to provide the latent heat of melting the ice.

The latent heat required to melt the ice is given by

$$\Delta E^L = 334 \times 0.03 = 10.02\text{kJ}$$



The available heat in the warm water as it cools to  $0^\circ\text{C}$  is

$$\Delta E = 4.2 \times 0.2 \times (20 - 0) = 16.8\text{kJ}$$

So there is more heat available than needed to melt the ice, and all the ice will melt. There is 6.78kJ of excess heat remaining, so the final temperature is

$$T = 0 + \frac{16.8 - 10.02}{4.2 \times (0.2 + 0.03)} = 7^\circ\text{C}$$

Notice that if  $\Delta E - \Delta E^L < 0$  then this equation gives a water temperature below zero. This is unphysical: the criterion for the equation to be valid is that all the ice melts. We could blindly use the equation, then if the temperature turns out to be positive it proves the assumption was OK.

Also notice that the mathematical steps do not respect any physical process. They imply first cooling the original water to  $0^\circ\text{C}$ , and putting the energy “somewhere”, then taking some of the energy to melt the ice, and finally using the remaining energy to heat all the water.

The system has moved towards equilibrium. There is nothing in the calculation which tells us this: we used our physical intuition to say that heat should flow from the hotter body to the cooler body and the final state should be at the same temperature throughout. Later, we can replace this intuition with the Second Law of Thermodynamics.

### 5. Gravity and heat

Assume that all the gravitational energy is converted into heat energy.

$$mgh = mc\Delta T$$

Thus

$$\Delta T = gh/c = \frac{9.8 \times 50}{4200} = 0.12\text{K}$$

Of course, not all the gravitational energy is turned into heat. Sound is produced. Erosion occurs by breaking of chemical bonds. Spray and falling water exchange heat with the atmosphere and absorb heat from the sun.

Although most of the water in the Niagara River is diverted from the falls to generate hydro electric power, this does not change the conclusion regarding temperature: the volume of water does not appear in the calculation.

In 1847 Joule attempted to demonstrate the mechanical equivalent of heat by measuring the temperature differences in a waterfall (Cascade de Sallanches, near Chamonix). He failed.

### 6. The ideal gas law

Using a 0 subscript to define that standard  $P_0, T_0$  are 273K, 101325Pa, for one mole of ideal gas we have  $V_0 = 2.2414 \times 10^{-2}\text{m}^3, n=1$ .

Our actual sample has  $T = 298\text{K}, n = 1, P = P_0$  and,

$$R = \frac{P_0 V_0}{n T_0} = \frac{P V}{n T}$$

whence

$$\frac{V_0}{V} = \frac{T_0}{T}$$

$$V = \frac{298}{273} 2.2414 \times 10^{-2} = 2.447 \times 10^{-2}\text{m}^3$$

The ideal gas expands when heated.

The ideal gas features highly in thermodynamics, and surprisingly turns out to be a good model for many things, including dilute solutions and cavity radiation. But it fails at low temperature, due to interatomic forces and quantum mechanics. For that reason, chemists use “standard temperature and pressure” as a reference state, rather than “zero”.

### 7. Molecular ideal gas

For an ideal gas  $PV=nRT$ , where  $n$  is the number of *molecules*, not atoms. So

$$n = \frac{PV}{RT} = \frac{1.2 \times 101325 \times 82 \times 10^{-6}}{8.3 \times 300} = 0.004 \text{ mol}$$

$O_2$  is a diatomic molecule, and has a molecular weight of 32, which is the number of grammes per mole, so converting to SI units.

$$m = 0.004 \times 32 \times 10^{-3} = 1.28 \times 10^{-4} \text{ kg}$$

For  $O_3$ , the molecular weight is 48, so the sample mass would have been  $1.92 \times 10^{-4} \text{ kg}$ . Note that if the ozone decomposed into  $O_2$  (at constant volume and temperature) then the pressure would increase by 50%.

In classical physics, every atom at equilibrium has the same amount of energy. This is called “equipartition”. Some of this goes into molecular vibrations, which leaves less available for moving the whole molecule to bang against the container walls, the microscopic process which causes pressure. This is why a gas of atoms arranged as  $O_3$  molecules has lower pressure than the same atoms as  $O_2$  - more of the energy is in bonds which do not contribute to the pressure. (n.b. in a solid the pressure *does* include the energy needed to compress the bonds.)

### 8. Melting, heating and boiling

The heat is supplied at a constant rate of 1kW, so the time taken in seconds will be equal to the number of kJ of energy required, so,

- a) Heat ice:  $mc_P\Delta T = 1 \times 1.94 \times 4 \Rightarrow 7.8$  seconds
- b) Melt ice:  $ml_{melt} = 1 \times 334 \Rightarrow 334$  seconds
- c) Heat water  $mc_P\Delta T = 1 \times 4.2 \times 100 \Rightarrow 420$  seconds
- d) Boil water  $ml_{vap} = 1 \times 2256 \Rightarrow 2256$  seconds
- e) Heat steam  $mc_P\Delta T = 1 \times 10 \times 2.04 \Rightarrow 20.4$  seconds

Melting involves structural rearrangements, breaking some bonds to change a rigid structure to a fluid one.

Boiling requires much more energy as all bonds between molecules must be broken.

Heating adds thermal energy to individual molecules, including vibration in ice, motion of molecules in water and steam, and vibrations of the atoms in the molecule itself.

Comparing boiling with melting, we see that about  $1/8^{th}$  of the bonds are broken in melting, and this is enough to allow the water molecules to move about over time. In liquid water, bonds are continually breaking and reforming, sometimes between different molecules.

### 9. Conduction of Heat

Strictly, this question is outside the realms of thermodynamics, as the heat conduction equation cannot be derived from the Laws of Thermodynamics.

a) Consider the system at time  $t$  where  $T(t) < T_0$ . In a small interval of time  $\Delta t$ , the heat transfer into the system is

$$\Delta Q = \frac{KA(T_0 - T(t))}{L} \Delta t$$

New temperature is then

$$T(t + \Delta t) = T(t) + \frac{KA(T_0 - T(t))}{mcL} \Delta t$$

so that

$$mc\Delta T = \frac{KA(T_0 - T(t))}{L}\Delta t$$

assumptions being that  $\Delta T \ll T$ , heat is only lost through area A, the heat source has a homogeneous temperature throughout.

b) In the limit of small  $\Delta t$ , can convert to derivatives...

$$\frac{dT}{dt} = \frac{KA[T_0 - T(t)]}{mcL}$$

$$\int_1^2 \frac{dT}{T - T_0} = -\frac{KA}{mcL} \int dt$$

$$\ln \left[ \frac{T_2 - T_0}{T_1 - T_0} \right] = -\frac{KA}{mcL} (t_2 - t_1)$$

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

Sanity check: as  $t_2 - t_1 \rightarrow \infty$ ,  $T_2 \rightarrow T_0$ . eventually, the object reaches the temperature of the heat source reservoir.

c) Aluminium 39.53°C, 60°C;

Porcelain 35.04°C 54.4°C;

Rubber 35.004°C 38.48°C;

Wool 35.001°C; 36.2°C.

Aluminium insulation is a bad idea.

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## 2 Temperature scales, work, equations of state

### 1. Temperature scales: influence of thermal properties

The scales will not necessarily give the same answers.

In order for alcohol and mercury thermometers to agree at all points the thermal expansion must change in the same way with temperature, because the “thermometer” reading is related to the thermal expansivity of the material. If the thermal expansions were *constant* with temperature then if they match at 0 °C and 100 °C they will agree with each other and with the Celsius scale at all temperatures. The actual value of the thermal expansion does not matter.

If thermal expansion varies *linearly* with temperature, they will agree with one another, but not with the Celsius scale.

If the thermal expansions varies *nonlinearly* with temperature, the thermometers will not agree, unless there is some freakish cancellation of errors.

Note that the thermal expansion applies to both the mercury/alcohol *and* the materials making up the thermometer. And further if the pressure of the mercury/alcohol changes then the bulk moduli must also be considered.

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

Roger’s “Resistance temperature” ( $T_R$ ) is defined relative to the ice temperature 273.15K

$$T_R = kR = kR_o(1 + \alpha T + \beta T^2)$$

where  $T = T_{ideal} - 273.15K$ . This guarantees that the scales match at the ice temperature. We need to find the constant  $k$  so that the scales match at the triple point ( $T = 0.01$ ):

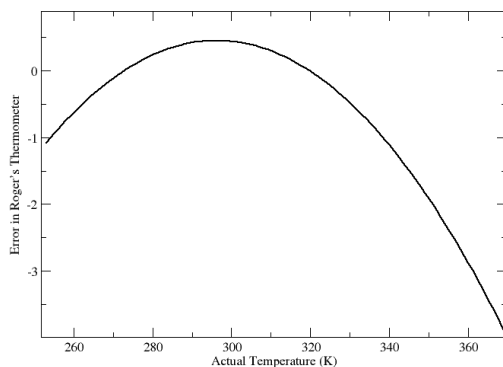
$$T_R^{TP} = T_{ideal}^{TP} = kR_o(1 + \alpha \times 10^{-2} + \beta \times 10^{-4}) = 273.16K$$

$$k = \frac{273.16}{R_o(1 + \alpha \times 10^{-2} + \beta \times 10^{-4})}$$

Now use this value of  $k$

$$T_R^{70^\circ C} = kR(70^\circ C) = T_R^{TP} \frac{(1 + \alpha \times 70 + \beta \times 70^2)}{1 + \alpha \times 10^{-2} + \beta \times 10^{-4}} = 341.79K$$

A couple of lines of code will give you the discrepancy at all temperatures.



The maths is easy, but the physics is quite subtle. Practical thermometers must use some physical object to measure temperature. The notion that nature has some absolute scale for temperature is the Zeroeth Law of Thermodynamics.

Linguistically, the plural of Kelvin is Kelvins, while for Celsius it is degrees Celsius.

### 3. Work Done in various processes

- (a) Ice has lower density than water at 0°C, so the volume decreases on melting. Assume pressure to be constant, Work = -PdV

$$W = - \int_{ice}^{water} PdV = -P_{atm} \times (M/\rho_{water} - M/\rho_{ice}) = -1.01 \times 10^5 \times [(10/916) - (10/1000)] = 92.6J$$

This is positive, which means work is done on the system - the pressure favours melting.

If the volume of a system expands, it has to do work on the atmosphere to push it back. Here the opposite is true, the atmosphere presses on the system and does work as it contracts.

Strictly, latent heat depends on whether we have constant pressure or constant volume melting. They differ by the work done, as calculated above. However, this energy is tiny compared to the latent heat (3340 kJ) so the two latent heats are essentially the same.

- (b) Make the analogy to obtain an expression for work done in stretching,  $dW = FdL$ . Check dimensions: Force  $\times$  length = Energy. Consider the sign: doing work *on* a gas would compress it, hence  $-PdV$  doing work *on* a wire would extend it, hence  $+FdL$ .

$$W = \int FdL = F(L_2 - L_1)$$

The tension in the wire in  $F=mg=20N$ , and the length change is 0.0001m, so the work is 0.002J.

For the thermal expansion, we write the temperature change in terms of two variables:

$$dT = \left( \frac{\partial T}{\partial L} \right)_F dL + \left( \frac{\partial T}{\partial F} \right)_F dF$$

At constant force,  $dF = 0$ , and we are given that the linear thermal expansion is:

$$\beta = \frac{1}{L} \left( \frac{\partial L}{\partial T} \right)_F = 16.6 \times 10^{-6}$$

So we can write:

$$\int dT = \int \frac{dL}{\beta L}$$

$$\Delta T = \ln(1.001)/16.6 \times 10^{-6} = 60K$$

The required temperature change is fairly substantial  $0.001/16.6 \times 10^{-6} = 60K$ .

n.b. given that the length change is small, you can get the same answer using:  $\ln(\frac{\Delta L}{L}) \approx \frac{\Delta L}{L}$ . The hidden assumption here, that linear thermal expansion coefficient is at constant force (or tension). Does the mass matter?

The heat capacity of copper is 390J/kg/K, density 8960 kg/m<sup>3</sup>. Supposing the wire cross section is 1 mm<sup>2</sup>, then the mass is  $9 \times 10^{-4}$  and the heat supplied is 21J, far in excess of the work done lifting the mass. So in these conditions the linear thermal expansion coefficient is independent of the tension.

- (c) The electrical work is  $V^2t/R = (36 \times 10)/(4.2 \times 10^{-3})$ , a fairly hefty 86kJ. Enough to melt the wire. What we are doing here is, essentially, creating a short-circuit and blowing a fuse.

This question illustrates that mechanical work in condensed phases is typically small in comparison to the thermal energy at room temperature. So much so that reference quantities like “latent heat”, “Young’s modulus”, “resistivity”, even “heat capacity” for solids are usually quoted without stating whether they are constant volume or constant pressure.

#### 4. Calculating Properties from the equation of state, and vice versa

- (a) First, we show that measurable material properties can be calculated if we know the equation of state.

For properties of the ideal gas, we proceed by differentiating the equation of state  $PV=nRT$ .  
Definitions: isothermal compressibility  $\kappa = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T$ ; isobaric expansivity  $\beta = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P$

Notice that these are log derivatives  $\kappa = - \left( \frac{\partial \ln V}{\partial P} \right)_T$ ;  $\beta = \left( \frac{\partial \ln V}{\partial T} \right)_P$ . Ultimately this is because we are interested in fractional change in volume, not absolute change.

We rearrange the equation of state to make  $V = nRT/P$  and evaluate the differentials, then use the equation of state again to simplify the final expression.

$$\beta = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P = \frac{1}{V} \frac{nR}{P} = \frac{1}{T}$$

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

By definition, the bulk modulus is the reciprocal of the compressibility, so  $B = 1/\kappa = P$ .

The question illustrates the central role of the equation of state for determining material properties. The myriad of measurable physical properties are not independent, they can all be calculated from the equation of state.

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- (b) Now we don't know the equation of state: we must work it out from materials properties. So we reverse the process in the previous section, integrating instead of differentiating. So for this substance,

$$\left(\frac{\partial V}{\partial P}\right)_T = -a$$

$$\int dV_T = \int -adP_T = V = -aP + f(T)$$

Where  $f(T)$  is some as-yet unknown function of  $T$  only.

$$\left(\frac{\partial V}{\partial T}\right)_P = 2bT$$

$$\int dV_T = \int 2bdP_T = V = bT^2 + g(P)$$

Where  $g(P)$  is some as-yet unknown function of  $P$  only.

Now we match the two results to obtain

$$bT^2 + g(P) = -aP + f(T)$$

$$bT^2 - f(T) = -aP - g(P) = \text{constant}$$

This must be constant, since  $T$  and  $P$  are independent. So

$$V = bT^2 - aP + \text{constant}$$

Notice that knowing the properties doesn't fully specify the equation of state. In this case, the undetermined constant of integration is the volume at zero temperature and pressure.

- (c) Finally, we show that some materials properties can be calculated directly from others.

*Remember  $C_P - C_V = R$  and  $PV = RT$  for one mole 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  $PV = nRT$ .

$$R = \frac{PV}{T} = \frac{V\beta}{\kappa} = \frac{VT\beta^2}{\kappa}$$

In fact, this is a general result for any material. The difference in heat capacities is the extra work needed to expand the material in the constant pressure process. This work depends on how much expansion we get,  $\beta$ , and how resistant the materials is to expansion.

This illustrates that thermodynamic properties are not independent. It is sometimes possible to work out a hard-to-measure quantity by measuring other material properties.

Notice also that the compressibility and expansivity are independent of the amount of substance.

## 5. Temperature scales: based on water

Using  $\rho = A + BT + CT^2 + DT^3$ .

We are trying to fit the isobar for water to a cubic equation. We could directly set up four equations in four unknowns, but there is a simpler way to proceed. The equation is quartic, so we can define the zero of temperature for mathematical convenience. Once the parameters are determined, their values for other choices of the temperature are just linearly shifted.

If we define a temperature scale where  $T=0$  equates to the maximum density, then it follows immediately that  $A=1000\text{kg/m}^3$  and  $B=0$

Now the low temperature data point is at  $T=-44$ , the high temperature one is at  $T=96$ , so we have two simultaneous equations:

$$960 = 1000 + 44^2C - 44^3D$$

$$960 = 1000 + 96^2C + 96^3D$$

From which we obtain:  $C=-0.0125$   $D=0.000044$ . this is true for the temperature scale with zero at  $+4^\circ\text{C}$ . If we wanted to use  $T$  in Kelvins then the equation of state would still be quartic:

$\rho = A + B(T - 277) + C(T - 277)^2 + D(T - 277)^3$ , but the power series in  $T$  Kelvin would have coefficients  $A_K = A - 277B + 277^2C - 277^3D$  etc.

for the present calculation, retain the scale with zero at the maximum density.

In the thermometer, the water column rises by 1%, but the diameter is unchanged. So the volume expansion (or density decrease) required is 1%, to  $990\text{ kg/m}^3$

$$-10 = -0.0125T^2 + 0.00044T^3 \Rightarrow T = -27, +30$$

Converting back to Celsius, this gives two solutions,  $-23^\circ\text{C}$  or  $+34^\circ\text{C}$ . A sketch of the isobar will confirm this is reasonable.

Even assuming the water can be prevented from freezing, density of water is a terrible choice for a thermometric property because a single value for the density does not uniquely define the temperature.

## 6. Joule's experiment

(a) Assume that the Gravitational Potential Energy ( $mgh = 20 \cdot 10 \cdot 2 = 400\text{J}$ ) is converted to heat:  $mc\Delta T = mgh$ .

$$\Delta T = gh/c = 10 \cdot 2 / 4200 = 0.047\text{K}$$

(b) Some energy is still in kinetic.  $\text{KE} = \frac{1}{2}mv^2 = \frac{20 \times 0.1^2}{2} = 0.1\text{J}$ . But only one part in 4000, or 0.025%

This calculation follows the demonstration by Joule that potential energy could be converted to work, and then to heat. In the actual experiment great care has to be taken to avoid or compensate for heat loss, and there was some scepticism about Joule's claim to be able to measure temperature to the required accuracy.



### 3 Work and heat, the First Law

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

In an expansion,  $dV > 0$ , so positive work is done *by* the system, negative work is done *on* the system. It is best to think about the sign of the work, rather than try to memorise equations with or without minus signs.

The internal energy of an ideal gas depends only on the temperature, so it can't change in any isothermal process. As a consequence, in parts (a) and (b), if work is done, and equivalent amount of heat must be added.

(a) Start by writing the general expression for volume:

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

notice that the first term is zero for isothermal process ( $dT = 0$ ). then using the ideal gas equation

$$dV = \left(\frac{\partial V}{\partial P}\right)_T dP = -\frac{nRT}{P^2} dP$$

So that

$$dW = -PdV = \frac{nRT}{P} dP$$

(b) Gas expands isothermally ( $T = T_0$ ) from initial pressure  $P_0$ .  $P_0V_0 = nRT_0 = nRT = PV$ . since  $V = 2V_0$ , then  $P = P_0/2$ . Now using the result from (a)

$$W = - \int PdV = \int \frac{nRT}{P} dP = nRT [\ln P]_{P_0}^{P_0/2} = nRT \ln \frac{1}{2} = -nRT \ln 2$$

Notice that there are *three* minus signs here - one from the definition of work, one from differentiation, and one from the logarithm.

(c) Following the same logic, this time for isobaric process ( $dP = 0$ )

$$dV(T, P) = \left(\frac{\partial V}{\partial T}\right)_P dT = \frac{nR}{P} dT$$

$$W = - \int PdV = -nR \int dT = -nR\Delta T$$

You need to be careful about the definition of work. There is nothing in nature to define its sign, indeed chemists and engineers tend to use opposite definitions because chemists are interested in what happens to the material, whereas engineers are interested in the work the engine does.

#### 2. Work, heat, PV diagrams

Every material has an equation of state, which can be written as  $T(P, V)$ . Thus a point on a PV diagram is sufficient to give all the information about a particular sample of known mass at equilibrium. Any process is then fully represented by a line on a PV diagram. We could instead use PT or VT diagrams, but PV proves most convenient because of the direct link to work:  $\int PdV$ .

(a) The First Law tells us that the change in internal energy comprises the heat put into the system (+80J) minus the work done by the system:  $80 - 30 = 50J = \Delta U = U_B - U_A$

(b) U is a state variable, so its change is independent of the path taken:  $\Delta U_{ACB} = \Delta U_{ADB} = \Delta U_{AB} = 50J$ . Since the work done on the ADB path is only  $W_{ADB} = 10J$ , the balancing heat must be 60J.

(c) Again, for a state variable on the reverse stroke,  $\Delta U_{BA} = -\Delta U_{AB} = -50J$ . Now the work is done *on* the system, the sign is also changed, so the heat going into the system must be  $-50 - 20 = -70J$ . Of course, negative heat going into the system means positive heat given out.

(d)  $\Delta U_{AD} = 40J$ , so  $\Delta U_{BD} = \Delta U_{AB} - \Delta U_{AD} = 10J$

For the work:  $W_{ADB} = W_{AD} + W_{DB} = -10J$ . but since BD is a constant volume process, no work can be done, so  $W_{DB} = 0$  and  $W_{AD} = -10J$  From which the heat inputs can be seen to be divided  $Q_{AD} = 50J$ ,  $Q_{DB} = 10J$ .

The question illustrates that there are different ways to get from one state to another, involving different amounts of work and heat input. However, for a given start and end point, the *sum* of work and heat is independent of the process. This is a concept on which many thermodynamics calculations are based - to determine the properties of the final state of a sample, we can consider *any* path to get there, including irreversible one. Samples at thermodynamic equilibrium have no memory. The inverse is also true, anything with a memory cannot be at thermodynamic equilibrium.

### 3. Free expansion of van der Waals gas

In a free expansion, no work is done on the surroundings, and no heat flows into the system. Consequently, according to the First Law, the internal energy  $U$  must remain constant.

Given that

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

which represents the free expansion coefficient for T changing with V. We can get the temperature by integrating from the initial state (1) to the final state (2)...

$$\int_{T_1}^{T_2} dT = \int_{V_1}^{V_2} -\frac{an^2}{C_V V^2} dV$$

$$T_2 - T_1 = \Delta T = -\frac{an^2}{C_V} \left[\frac{-1}{V}\right]_{V_1}^{V_2} = \frac{an^2}{C_V} \left(\frac{1}{V_2} - \frac{1}{V_1}\right)$$

We know  $V_1$ , but it's not easy to extract  $V_2$ . But we do know that a gas (state 2) is a *lot* less dense than a liquid (state 1), so we will assume that it is big enough that  $\left(\frac{1}{V_2} - \frac{1}{V_1}\right) \approx -\frac{1}{V_1}$

Now, based on this assumption, The initial pressure comes from the van der Waals equation:

$$P_1 = \frac{n_1 RT_1}{V_1 - n_1 b} - \frac{n_1^2 a}{V_1^2} = 2.49 \times 10^7 \text{ Nm}^{-2}$$

compared with one atmosphere ( $P - 2 = 1.01 \times 10^5 \text{ Nm}^{-2}$ ) we see that  $P_1 \gg P_2$ . For a gas, this implies that our approximation to neglect  $\frac{1}{V_2}$  will cause less than 1% error. So finally

$$\Delta T \approx -\frac{an^2}{C_v V_1} = -2.29K$$

Recall that the constant  $a$  represents binding between atoms in the VdW gas. When you expand a VdW gas, this binding gets weaker. That energy has to come from somewhere, and in a free expansion the only possible source is the thermal energy.

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

The observation can be written mathematically as:

$$\left(\frac{\partial T}{\partial V}\right)_U = 0$$

we can use the reciprocity relation

$$\left(\frac{\partial T}{\partial V}\right)_U \left(\frac{\partial U}{\partial T}\right)_V \left(\frac{\partial V}{\partial U}\right)_T = -1$$

to give.

$$-\left(\frac{\partial T}{\partial V}\right)_U = \left(\frac{\partial T}{\partial U}\right)_V \left(\frac{\partial U}{\partial V}\right)_T = 0$$

so that the experiments imply that one of those partial derivatives must be zero for this gas.

Now  $\left(\frac{\partial U}{\partial T}\right)_V = C_v$ , and we know that heat capacities must be finite, so the measurement implies that...

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

i.e. if we expand the gas at constant T, the internal energy doesn't increase:  $U$  is independent of volume  $U = U(T)$  only. Remembering the model of the ideal gas as hard, elastic particles, it is reasonable that their only energy is kinetic energy, i.e. temperature.

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

## 5. Adiabatic processes

For an adiabatic process,  $dQ = 0$  so the first law is  $dU = -PdV$ , or using the ideal gas specific heat  $C_v dT = -(PdV)$ . The differential form for  $n$  moles of the ideal gas equation gives  $PdV + VdP = nRdT$ . We are looking for the relationship between  $P$  and  $V$ , so we combine the equations to eliminate  $dT$ :

$$dT = \frac{PdV + VdP}{R} = -\frac{P}{nC_V} dV$$

Rearranging:

$$\frac{dP}{P} = -\frac{nR + C_v}{C_v} \frac{dV}{V} = -\gamma \frac{dV}{V}$$

Where we used the fact that  $nR = C_P - C_V$  and defining  $\gamma = C_P/C_V$ .

(n.b. you can do this by considering one mole of ideal gas, in which case  $n = 1$  and  $C_v = c_V$ )

Thus  $\ln(PV^\gamma)$  is constant, and so is  $PV^\gamma$ .

$\gamma$  is a ratio of specific heats, so it has no units. The units of  $c$  depend on  $\gamma$ . e.g. for monatomic ideal gas  $\gamma = 5/3$  and  $c$  has units  $Jm^2$ , for a diatomic gas it is  $Jm^4$ . Notice that although  $\gamma$  is fractional, the units always have integer dimensions.

It is very important to define a sign convention with respect to work done.

$W = -PdV$  as the work done *on* the gas. (think: positive work means negative dV, energy needed to push a piston to compress the gas)

$W = +PdV$  as the work done *by* the gas. (think: positive work means positive dV, energy from the gas pushes a piston out)

Here we are interested in work done *by* the gas, so

$$W = \int_{V_1}^{V_2} PdV$$

For adiabatic processes, we know that  $PV^\gamma$  is constant. Calling the constant “c” and eliminating P.

$$W = c \int_{V_1}^{V_2} V^{-\gamma} dV = c \left[ \frac{V^{1-\gamma}}{1-\gamma} \right]_{V_1}^{V_2} = \frac{c}{1-\gamma} (V_2^{1-\gamma} - V_1^{1-\gamma})$$

now noting that  $c = P_1 V_1^\gamma = P_2 V_2^\gamma$  we obtain

$$W = \frac{P_1 V_1 - P_2 V_2}{1-\gamma}$$

Sanity checking, if  $P_1 V_1 = P_2 V_2$  (i.e.  $T_1 = T_2$ ) then no work is done, which seems sensible since internal energy  $U(T)$  is unchanged and adiabatic means no heat is exchanged either.

If  $\gamma = 1$  infinite work would be done. Of course, for an ideal gas  $\gamma = c_p/c_V$  is never 1, but it gets closer for a polyatomic ideal gas. Broadly what is happening in a polyatomic-molecular ideal gas is that much of the energy is tied up in molecular vibrations, and a smaller fraction in translations. Only the translations contribute to pressure, as the molecules bounce off the container walls. So for a given change in temperature, extra energy is released from molecular modes to do work.

### 6. Isobaric processes

From the First Law,  $\Delta U = \Delta W + \Delta Q$

$$\Delta Q = C_p \Delta T = C_p (T_2 - T_1)$$

$$\Delta W = -P \Delta V = -P_0 \Delta V = -P_0 (V_2 - V_1)$$

so that

$$\Delta U = U_2 - U_1 = C_p (T_2 - T_1) - P_0 (V_2 - V_1)$$



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This is completely general, now we consider the special case of an ideal gas. We can use the equation of state  $PV = nRT$  to eliminate temperature

$$U_2 - U_1 = \frac{C_P}{nR}(P_0V_2 - P_0V_1) - P_0(V_2 - V_1) = \left(\frac{C_P}{nR} - 1\right)P_0(V_2 - V_1)$$

We could plug and chug the numbers at this point, but we can go a bit further in the algebra with  $C_P - C_v = nR$  and  $\gamma = C_P/C_v$ . So that

$$\frac{C_P}{nR} - 1 = (\gamma - 1)^{-1}$$

so that

$$U_2 - U_1 = \frac{P_0(V_2 - V_1)}{\gamma - 1} = \frac{3}{2} \times 1.01 \times 10^5 \times (10 - 5) = 7.6 \times 10^5 J$$

Notice once again the pivotal role of  $\gamma - 1$ , which microscopically depends on the number of degrees of freedom per molecule  $\gamma = (m + 2)/m$ .

Also notice that the heat in an isobaric process goes to internal energy and work  $\Delta Q = \Delta(U + PV)$ . It can be convenient to define a state variable  $H = U + PV$  whose changes are equal to the heat supplied. This state variable is Enthalpy, and is used a lot in thermodynamic descriptions of isobaric processes. This is a recurrent theme in thermodynamics, although we can use *any* state variables to describe the system, choosing one which matches the boundary conditions makes things much easier.

## 7. Cooling in an adiabatic expansion

To derive the Joule-Kelvin expression, start with the triple product

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

We can now identify the specific heat at constant pressure  $C_P = \left(\frac{\partial H}{\partial T}\right)_P$ , and the given expression for  $\left(\frac{\partial H}{\partial P}\right)_T$ . Substituting these into the triple product gives:

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

where  $\beta$  is the thermal expansivity. You can check your working by noting that  $\left(\frac{\partial T}{\partial P}\right)_H$  is zero for an ideal gas.

To use this for the Joule-Kelvin cooling, we can always write  $T$  in terms of any two state variables, e.g.  $T(P, H)$ , from which

$$dT = \left(\frac{\partial T}{\partial P}\right)_H dP + \left(\frac{\partial T}{\partial H}\right)_P dH$$

By definition, for an isenthalpic process, we have  $dH = 0$ , so

$$dT = \left( \frac{\partial T}{\partial P} \right)_H dP$$

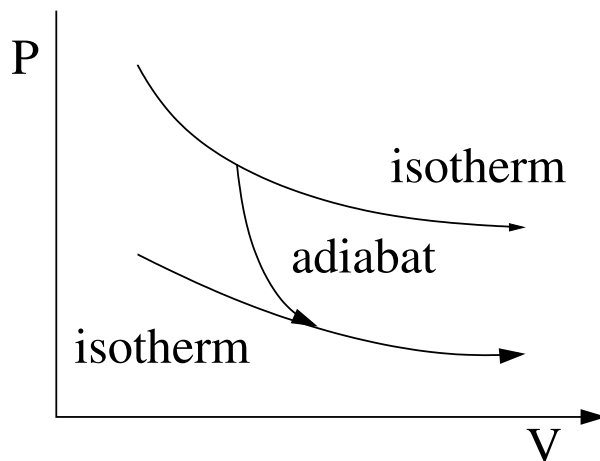
and provided the Joule-Kelvin coefficient  $\left( \frac{\partial T}{\partial P} \right)_H$  is independent of  $T$  we can separate variables and integrate.

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

We can anticipate that the adiabatic expansion produces more cooling than a throttling process. If we look at the PV diagram for an ideal gas, we see that adiabats  $P \propto V^{-\gamma}$  drop more steeply than isotherms  $P \propto V^{-1}$ , since  $\gamma > 1$ . This means that in an adiabatic expansion we drop from a higher temperature to a lower one. So if  $V_1 < V_2$  then  $T_1 > T_2$ , the gas cools as it expands adiabatically (no heat is exchanged, but work is done by the expanding gas, and the energy to do this work must come from lowering the internal energy).

For an ideal gas, internal energy depends on  $T$  only, so a Joule process (constant  $U$ ) follows an isotherm. The definition of Enthalpy is  $H = U + PV$ , and for an ideal gas the product  $PV$  is a function of temperature only, i.e.  $PV = nRT$ . Thus for an ideal gas the isenthalp is also an isotherm.

For a material “similar” to the ideal gas, we can assume that the isenthalp remains close to an isotherm.



To prove the inequality for any substance, consider the triple product for the relevant quantity in an adiabatic process:

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

Apply a Maxwell relation

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

Applying the definition of  $C_p$ , the second two terms become:

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

To see the difference in cooling between the isenthalpic and adiabatic expansion process, we look at:

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

so that

$$\begin{aligned} \Delta T_A - \Delta T_{JK} &= \int_{P_1}^{P_2} \left[ \frac{T}{C_P} \left( \frac{\partial V}{\partial T} \right)_P - \frac{T}{C_P} \left( \frac{\partial V}{\partial T} \right)_P + \frac{V}{C_P} \right] dP \\ &= \int_{P_1}^{P_2} \left[ \frac{V}{C_P} \right] dP \end{aligned}$$

and since  $P_2 < P_1$  in an expansion, while  $V$  and  $C_P$  are always positive, this integral must be negative. Both  $\Delta T_A$  and  $\Delta T_{JK}$  are negative on cooling, so the isenthalpic (Joule-Kelvin) throttling process produces a smaller cooling effect than the adiabatic process.

A final note: William Thomson became Lord Kelvin in 1892 (strictly, Baron Kelvin of Largs). Some people still haven't noticed and refer to isenthalpic expansion as the Joule-Thomson effect.

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## 4 Cycles and the Second Law

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

**Clausius** : It is impossible to construct a device that, operating in a cycle, produces no effect other than the transfer of heat from a colder to a hotter body.

**Kelvin-Planck** : It is impossible to construct a device that, operating in a cycle, produces no effect other than the extraction of heat from a single body at a uniform temperature and performs an equivalent amount of work.

Suppose that the Clausius statement of the Second Law of Thermodynamics is false: heat can flow spontaneously from a cold body to a hot body. Label the heat transferred by the Clausius-violating device  $Q_1$ . Now connect a separate standard heat engine to the two reservoirs, and adjust it so that it takes heat  $Q_1$  from the hot body (dumping heat  $Q_2$  to the cold body, and producing work  $W = Q_1 - Q_2$ ). Not net heat is taken from the hot body, so taken together, the Clausius-violating device + standard heat engine transforms heat  $Q_1 - Q_2$  from the cold reservoir directly into work. This violates the Kelvin-Planck statement of the Second Law.

This may also be proved by adjusting the standard engine to dump heat  $Q_1$  to the cold reservoir: now the heat come from the hot reservoir.

Notice that all the devices considered here obey the **First** Law of thermodynamics.

### 2. Efficiency of engines part 1

Efficiency of a heat engine, by definition, is  $\eta = (\text{work out})/(\text{heat in})$ . Here

$$\eta = \frac{W}{Q_1} = 1 - \frac{Q_2}{Q_1}$$

For the special case of a Carnot engine

$$\eta_c = 1 - \frac{T_2}{T_1}$$

To find which increases the efficiency more, we need to compare the change of increasing the hot temperature  $d\eta_c/dT_1$  with reducing the cold temperature  $-d\eta_c/dT_2$ . Notice that both of these quantities are positive.

$$\left(-\frac{\partial\eta_c}{\partial T_2}\right)_{T_1} = \frac{1}{T_1}$$

$$\left(\frac{\partial\eta_c}{\partial T_1}\right)_{T_2} = \frac{T_2}{T_1^2} = \left(-\frac{\partial\eta_c}{\partial T_2}\right)_{T_1} \times \frac{T_2}{T_1}$$

Since, by definition,  $T_1 > T_2$ , it follows that  $\left(-\frac{\partial\eta_c}{\partial T_2}\right)_{T_1} > \left(\frac{\partial\eta_c}{\partial T_1}\right)_{T_2}$ , so a decrease in the cold reservoir is more effective in increasing efficiency than an equivalent rise in the hot reservoir.

### 3. Efficiency of engines part 2

For the given system to maintain the cold reservoir at  $T_2$  no net heat should enter or leave it, hence the two  $Q_2$  flows with opposite sign.



From the first law, the work coming from the engine  $W_1 = Q_1 - Q_2$ , while the work going into running the fridge is  $W_a = Q_a - Q_2$ . For a compound device where the engine drives the fridge, the net work out is

$$W = W_1 - W_a = (Q_1 - Q_2) - (Q_a - Q_2) = Q_1 - Q_a$$

So the efficiency of the compound engine is work done divided by heat input.

$$\eta = \frac{W}{Q_1} = \frac{Q_1 - Q_a}{Q_1}$$

at best, with reversible Carnot engine and fridge, this would be,

$$\eta_c = \frac{T_1 - T_a}{T_1} = 1 - \frac{T_a}{T_1}$$

the same as if we ran the engine between the hot reservoir and the ambient one.

So maintaining the cold reservoir doesn't gain us anything. You can't beat the second law.

#### 4. Efficiency of engines part 3: The 'Otto cycle'

Process  $ab$  is an adiabatic compression of the air as the piston moves up, work being done on the system.

Process  $bc$  is a constant-volume heat transfer to the air from an external source while the piston is at the top. This process represents the ignition and explosion of the fuel-air mixture.

Process  $cd$  is an adiabatic expansion, the power stroke as the piston moves down doing work.

Process  $da$  completes the cycle by a constant-volume process which represents the exhaust.

By inspection  $T_d > T_a$  and  $T_b < T_c$  (convince yourself this is true)

For analysis, let's imagine everything is reversible, the working substance is one mole of an ideal gas, with internal energy  $\hat{c}RT$  ( $\hat{c} = 5/2$  for a diatomic gas, like air). Assume also it is not expelled and the heat for the "explosion" is actually supplied externally.

$ab$ , work is done on the system, no heat is exchanged, so work is equal to the change in internal energy

$$W_{ab} = \hat{c}R(T_b - T_a)$$

$bc$ : heat is added from some external source and the working substance pressure increases at constant volume.

$$Q_{bc} = \hat{c}R(T_c - T_b)$$

$cd$ : Work is done by the system as it expands, again equal to the internal energy change.

$$W_{cd} = \hat{c}R(T_c - T_d)$$

$da$ : heat is dumped from the system at low temperature

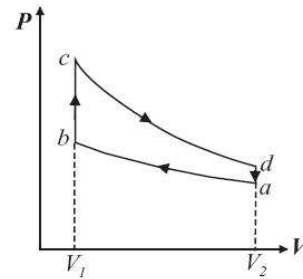
$$Q_{da} = \hat{c}R(T_d - T_a)$$

Net work done by the system is  $\hat{c}R(T_c - T_d) - \hat{c}R(T_b - T_a) = \hat{c}R(T_a + T_c - T_b - T_d)$

Note that this is per mole of gas - obviously the actual work done is proportional to the volume of the cylinder.

Remembering that the work done is given by  $\int PdV$  we can write the work done in the cycle as.

$$\int_a^b PdV + \int_b^c PdV + \int_c^d PdV + \int_d^a PdV$$



Deleting the bc and da segments for which  $dV$  is zero, and integrating ab in the opposite direct gives:

$$\int_c^d P dV - \int_d^a P dV$$

Remembering than an integral is just the area under a curve, we can recognise this quantity as *the area enclosed by the curve representing the cycle in the PV diagram*

Efficiency is defined as the ratio of heat input to work output. For the Otto cycle the work done is in the power stroke expansion (cd), less the work needed to recompress the gas (ab)  $W_{cd} + W_{ab}$ . The heat input occurs in the (bc) section.

Thus being careful about the signs of the work done *on* and *by* the system, the efficiency is

$$\frac{\text{work.done}}{\text{heat.in}} = \frac{\hat{c}R(T_c - T_b) - \hat{c}R(T_d - T_a)}{\hat{c}R(T_c - T_b)} = 1 - \frac{T_d - T_a}{T_c - T_b}$$

This is less than for a Carnot engine operating between  $T_c$  and  $T_a$ .

#### 5. Efficiency of engines part 4

The venture capitalists should consult a competent physicist. Who would check the laws of thermodynamics.

The first law requires conserving energy round a cycle:  $dQ + dW = 0$ , so

$$5000J = 3500 + 1500J$$

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So far so good...

The second law implies that the efficiency of the engine cannot be higher than the Carnot efficiency. The claimed efficiency is...

$$\eta = 1 - \frac{Q_{out}}{Q_{in}} = 1 - \frac{3500}{5000} = 0.3$$

While the Carnot efficiency for an engine running between those reservoirs is:

$$\eta_c = 1 - \frac{T_{cold}}{T_{hot}} = 1 - \frac{300}{400} = 0.25$$

So it is clear that this device is claimed to violate the laws of physics. The physicist will advise against investment.

*And the venture capitalists should try to find a "greater fool" and sell on the business*

## 6. Efficiency of Fridges

The "efficiency" of a fridge is defined by (heat removed from cold box)/(work in).

so for a Carnot fridge we have:

$$\eta = \frac{Q_2}{Q_1 - Q_2} = \frac{T_2}{T_1 - T_2}$$

If we take room temperature to be 293K, and the cool box 5K above freezing at 278K, then a Carnot fridge should have

$$\eta = \frac{278}{293 - 278} = 18.5$$

This is usually referred to as the "coefficient of performance", because an efficiency above 1 doesn't sound right. Note that cooling the ice box is a lot less efficient. Real fridges tend to have  $\eta \approx 5$ .

## 7. Efficiency of heat pumps

The electric heater simply supplies 20kW (i.e. 20kJ/s).

A Carnot heat pump operates with coefficient of performance  $Q_{in}/(Q_{in} - Q_{out}) = T_{in}/(T_{in} - T_{out})$ . In this case it would be 300/20=15, so in principle the heat pump could supply  $15 \times 20 = 300$  kW. In practice a coefficient of performance of around 4 is typical.

The heat pump really can outperform an electric heater. Although the electrical work can be converted 100% into heat, it is also possible to exploit the temperature difference to generate more energy.

## 8. Multipurpose device.

This device is acting as both a refrigerator and a heat pump, essentially putting the "waste heat" from the fridge to good use. Start by estimating the Carnot efficiency of such a device: a sensible assumption is needed for the temperatures, so lets take the temperatures as 275K (fridge) and 295K (living room). These are slightly different:

$$\eta_R^{max} = 275/(295 - 275) = 13.5$$

$$\eta_{HP}^{max} = 295/(295 - 275) = 14.5$$

Now look at the claimed efficiencies. For the refrigerator:

$$\eta_R = Q_C/W = 400/100 = 4$$

$$\eta_{HP} = Q_H/W = 1000/100 = 10$$

So we see that the claimed efficiencies are perfectly plausible.

There is an oddity here, since  $W + Q_C \neq Q_H$ . Does this mean that the device breaks the first law and the claim is invalid?

It doesn't. In any device there will be losses, and in this case the fridge isn't anywhere near the Carnot efficiency: probably heat is being extracted from the kitchen environment by cold pipes outside the fridge compartment. If the company had claimed  $\eta_R = 9$ , extracting 900W of heat from the fridge compartment, then all the energy would be accounted for. Since this is thermodynamically plausible, the more modest claim of  $\eta_R = 4$  certainly must be.

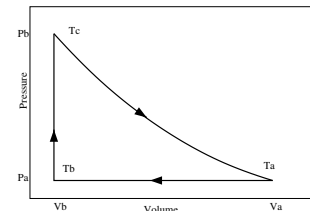
Don't worry if you got this wrong, almost everyone does! Coefficient of performance is a tricky concept: A fridge where the hot and cold baths had equal temperature would have infinite coefficient of performance. All that means is that no work is required to move heat across. If the "hot" bath has lower temperature than the "cold" one, the calculation gives a *negative* coefficient of performance. What that means is that heat will flow spontaneously in the direction required. If you open a window when its hot inside, then you are using an "air conditioner" with better than infinite coefficient of performance.

### 9. Yet another cycle

Let there be  $n$  moles of gas in the system, such that the ideal gas law is  $PV=nRT$ .

The system has three states:

- (a)  $V_a, P_a, T_a$ , internal energy  $U = nRT_a = P_a V_a$
- (b)  $V_b, P_a, T_b$ , internal energy  $U = nRT_b = P_a V_b$
- (c)  $V_b, P_b, T_c$ , internal energy  $U = nRT_c = P_b V_b$



We will consider a sign convention using work done on and heat supplied to the working fluid of the system system.

(i) Work (positive) is done on the working fluid while compressing the system  $W_i = P_a(V_a - V_b)$ . The heat absorbed this constant pressure process is, by definition,  $Q_i = C_p(T_b - T_a)$ . This is negative - so the waste heat given up is  $Q_i = C_p(T_a - T_b)$

(ii) No work is done in this isovolumetric process, thus  $Q_{ii} = dU_{bc} = C_v(T_c - T_b)$ . This is the heat input to the cycle

(iii) No heat is exchanged in this adiabatic process, thus  $W_{iii} = dU_{ca} = C_v(T_a - T_c)$

The efficiency (work done)/(heat input) can be conveniently written as  $1 - (\text{waste heat})/(\text{heat in})$ . Here this is  $1 - Q_i/Q_{ii}$ . whence

$$\begin{aligned} \eta &= 1 - \frac{C_p(T_a - T_b)}{C_v(T_c - T_b)} \\ &= 1 - \gamma \frac{P_a(V_a - V_b)}{V_b(P_b - P_a)} \end{aligned}$$

At first glance, there is something odd about this expression: we expect that the efficiency is dependent only on temperature, and independent of the properties of the working substance, yet  $C_p$  and  $C_v$  appear in the expression. The resolution to this is that we cannot pick the pressures and volumes independently: given the two state points at  $V_b$ , the properties at  $V_a$  are completely determined by the adiabat.

### 10. Work and thermal equilibrium

We have a Carnot engine, but the temperature of the two reservoirs is not a constant. So consider an infinitesimal amount of work done while the temperature can be regarded as constant: from first law  $dW = dQ' - dQ''$

As heat is removed, the temperature of the heat bath drops (and vice versa), by  $dQ = C_P dT$ , where  $C_P$  is the heat capacity.

Now integrate over all temperatures as the heat baths approach equilibrium temperature  $T_f$ .

$$\int dW = -C_P \left( \int_{T_1}^{T_f} dT' + \int_{T_2}^{T_f} dT'' \right) = C_P(T_1 + T_2 - 2T_f)$$

This still tells us only that some heat was converted into work. To calculate  $T_f$  we must apply the Second Law.

For a Carnot engine, the entropy of the universe is conserved so that for each infinitesimal heat transfer, the increase in entropy of the low temperature reservoir equals the decrease in entropy of the high temperature reservoir.

$$\frac{dQ'}{T'} = \frac{dQ''}{T''}$$

Taking advantage of the fact that the heat capacities of the two bodies are identical, and being careful with signs:

$$\int_{T_1}^{T_f} \frac{dT'}{T'} = - \int_{T_2}^{T_f} \frac{dT''}{T''} = \ln \frac{T_1}{T_f} = \ln \frac{T_f}{T_2}$$

So  $T_f = \sqrt{T_1 T_2}$ , and the total work done is  $= C_P(T_1 + T_2 - 2\sqrt{T_1 T_2})$

This reflects the situation in any case where the amount of heat energy is finite: by doing work the engine returns the two bodies to equilibrium. Only by continually supplying energy can the reservoir temperatures be kept constant.

If the cold reservoir is large, then we can assume the temperature  $T'' = T_2 = T_f$ , however the heat capacities are no longer equal.

So the First Law gives:  $W = C_P(T_1 - T_2) - \int dQ''$

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and the Second Law gives:

$$C_P \int_{T_1}^{T_2} \frac{dT'}{T'} = - \int \frac{dQ''}{T_2}$$

$$Q'' = C_P T_2 \ln \frac{T_1}{T_2}$$

From which we deduce:

$$W = C_P T_1 - C_P T_2 \left(1 + \ln \frac{T_1}{T_2}\right)$$

If we plot these expressions, we see that no work is extracted if  $T_1 = T_2$ . Otherwise, the second expression is always larger than the first.

The second case is closer to the situation in a power station, where a finite source of heat is dumped to a cold reservoir. It illustrates the importance of having cold water, either direct from a river or via a cooling tower, for the cold reservoir. If the water in the “cold” reservoir is heated a bit, it can be used for district heating.

## 5 Entropy

### 1. Calculation of entropy change

The heat flow must be sufficient to change the water temperature by 20K, i.e.  $Q = 5 \times 20 \times 4.19 = 419 \text{ kJ}$ .

Entropy change is given by

$$\Delta S = \int_{start}^{finish} \frac{dQ}{T}$$

For the surroundings, the temperature is a constant, 278K, so  $\Delta S = Q/T = 419/278 = 1.507 \text{ kJK}^{-1}$ .

For the water, it's not so simple because the temperature changes. We use the fact that entropy is a state variable, so the difference in entropy of the water is independent of the path between the start and finish of the process.

So imagine a reversible slow heating process such that  $\dot{d}Q = mc_p dT$ ,

$$\Delta S = \int_{T_1}^{T_2} \frac{mc_p dT}{T} = mc_p \ln\left(\frac{T_2}{T_1}\right) = 5 \times 4.19 \ln(278/298) = -1.46 \text{ kJK}^{-1}$$

A very simple calculation, but a subtle assumption: we can calculate the entropy change in an irreversible process by considering an equivalent reversible process. We can do this because entropy is a state variable. Also, the heat  $Q$  flows out of the water which means that  $dQ$  should be negative: in the integral this appears because  $dT$  is negative in the cooling process.

Note also that entropy is *not* conserved. The increase in energy of the surroundings is equal to the loss of energy from the hot water, but the increase in entropy of the surroundings is bigger than the reduction in entropy of the water.

Finally, notice that in a process of *heating* water from 5°C to 25°C, the total entropy still goes up. The general function for the entropy change is  $f(x) = x - \ln(1+x)$ , based on  $x = \Delta T/T$ . This function is positive for any value of  $\Delta T > -T$ . It becomes infinite at  $x = -1$ , i.e. cooling to absolute zero would generate infinite entropy in the surroundings.

### 2. Variation on the same theme

The resistor is in a steady state, so it has constant temperature and internal energy. If we look at the resistor some time later, it is identical (still has electrons flowing through, so not strictly in equilibrium, but not changing in time. In fact, all its state variables are constant, so  $\Delta S_{resistor} = 0$ .

Electrical work is done by the current, and this is converted into heat by the resistor. All this heat goes into warming the water: entropy is continually being produced, if we consider 1 second.

Since the temperature is constant, the entropy can be easily found with the normal integral

$$\Delta S_{water} = \int \frac{dQ}{T} = \frac{2000J}{300K} = 6.7J/K$$

Hence the entropy increase in the universe is.

$$\Delta S_{total} = \Delta S_{water} + \Delta S_{resistor} = 6.7J/K/sec$$

All the electrical energy is converted to heat at 300K. So an electrical heater has a 100% efficiency ( $\eta = 1$ ). Don't be impressed: the electricity generation would have been less than 100% efficient, and a heat pump would have  $\eta > 1$ .

In reality, the temperature increases by a small amount, which would make the equation somewhat more complicated, but the entropy change must be bounded by all heat supplied at the input temperature  $Q/300$  and all heat supplied at the output temperature  $Q/(300 + \delta T)$ .

### 3. Entropy and ideal gases

Use central equation  $TdS = dU + PdV$  to write

$$dS = \frac{dU}{T} + \frac{PdV}{T} = \frac{dU}{T} + R \frac{dV}{V}$$

Now we use the fact that the energy of an ideal gas depends on its temperature only (the actual value of this energy varies between monatomic, diatomic gasses etc.)

So for a constant  $T$  process,  $U$  is constant and so  $dU = 0$  and

$$\Delta S = R \int_{V_1}^{V_2} \frac{dV}{V} \quad (1)$$

$$S_2 - S_1 = R \ln \left( \frac{V_2}{V_1} \right) \quad (2)$$

If we think of entropy as being the number of different ways of arranging the molecules, then it is intuitive that larger volume means larger entropy.

Using the definition of  $C_P$  in terms of entropy  $C_P(T, V) = T \left( \frac{\partial S}{\partial T} \right)_P$ , the pressure dependence of  $C_P(T, V)$  at constant  $T$  is given by

$$\left( \frac{\partial C_P}{\partial P} \right)_T = T \left( \frac{\partial^2 S}{\partial P_T \partial T_P} \right) \quad (3)$$

$$= T \left( \frac{\partial^2 S}{\partial T_P \partial P_T} \right) \quad (4)$$

$$= -T \left( \frac{\partial^2 V}{\partial T^2} \right)_P \quad (5)$$

$$(6)$$

where we used the fact that for a state variable, the second derivative is independent of the order of differentiation (commutative), and then used a Maxwell relation to eliminate  $S$ . So far this is just another example of a general relationship between materials properties.

For an Ideal Gas we use the equation of state.

$$\left(\frac{\partial^2 V}{\partial T^2}\right)_P = \left(\frac{\partial(R/P)}{\partial T}\right)_P = 0$$

Since R is always constant, and P is constant here.

#### 4. Entropy changes in the ideal gas

A slightly more complicated version of the previous question: again we use central equation  $TdS = dU + PdV$  to write

$$dS = \frac{dU}{T} + \frac{PdV}{T}$$

We would like to eliminate  $dU$ , which we can do by considering the first law  $dU = dQ - PdV$  and differentiating with respect to T.

$$\left(\frac{dU}{dT}\right)_V = \left(\frac{dQ}{dT}\right)_V - P \left(\frac{dV}{dT}\right)_V$$

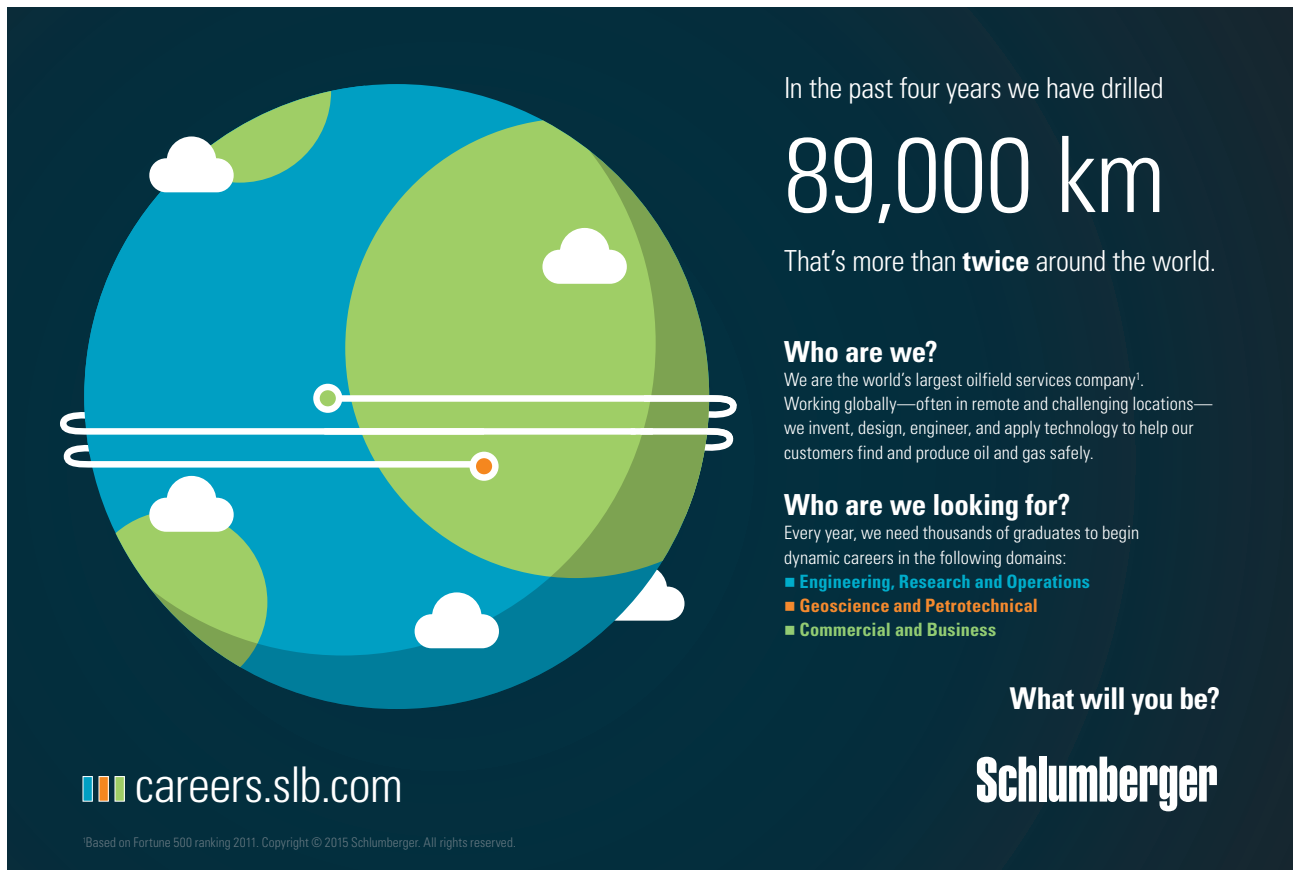
Now by definition the first term is

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

And trivially,  $\left(\frac{dV}{dT}\right)_V = 0$  since there is no change in volume at constant volume. Hence

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \Rightarrow dU(T, V) = C_V dT + 0$$

$$dS(T, V) = \frac{C_V dT}{T} + \frac{PdV}{T}$$



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So far this is all general for any material at constant volume.

In the specific case of the ideal gas (defined by  $PV = nRT$ ) we can use the first equation to create two integrals with single variables:

$$dS = C_V \frac{dT}{T} + nR \frac{dV}{V}$$

$$\Delta S = \int_{T_1}^{T_2} \frac{A + BT}{T} dT + nR \int_{V_1}^{V_2} \frac{dV}{V} \quad (7)$$

$$= A \ln \left( \frac{T_2}{T_1} \right) + B(T_2 - T_1) + nR \ln \left( \frac{V_2}{V_1} \right) \quad (8)$$

Now this should look worrying:  $\Delta S$  appears to diverge as  $T_1$  goes to zero. This is still true for  $B = 0$ , the normal ideal gas. Could an ideal gas really have an infinite (negative) entropy? In fact quantum mechanics comes to the rescue - classically  $T=0$  implies we know the precise velocity of the particle (zero) and  $V=0$  implies we know its position exactly. This violates the Uncertainty principle, so the idea of an ideal gas breaks down at  $T=0$ .

There is an expression called the Sackur-Tetrode equation which gives the ‘‘Entropy of an ideal gas’’, unfortunately it involves approximations which means that it breaks down at low temperatures.

### 5. Another look at the Carnot cycle

On a TS diagram, the Carnot cycle of isotherms and adiabat/isentropes is just a rectangle. Define this as being between  $T_2 > T_1$  and  $S_2 > S_1$

Heat is absorbed only in the isotherms, an amount  $dQ = TdS$ , so assuming the path runs clockwise (Carnot engine), the total heat absorbed is:

$$\int_{S_1}^{S_2} T_2 dS + \int_{S_2}^{S_1} T_1 dS = (T_2 - T_1)(S_2 - S_1)$$

Which is the area inside the cycle. So the net Heat absorbed is the area inside the cycle in a TS diagram, while the net Work is the area inside the cycle in a PV diagram. And of course they are equal to one another.

Mathematically, what we just did was a contour integral of  $dQ$  around the cycle. If we go the other way round the cycle we get negative heat in: a Carnot refrigerator.

### 6. Proving that booze increases randomness

The ice absorbs heat as it melts, but the water stays at  $0^\circ\text{C}$ . So the heat must be coming from the air. Consider first the ice, where everything is happening at  $0^\circ\text{C}$  and we are losing latent heat.

$$\Delta S_{ice} = \Delta Q_{ice}/T_{ice} = \frac{mL}{T_{ice}} = \frac{300 \times 334}{273} = 36.7 JK^{-1}$$

The entropy of the ice increases as it melts

Now consider the water. It stays conveniently at  $0^\circ\text{C}$  so no net heat is absorbed by it.  $\Delta Q_{water} = -\Delta Q_{ice} + \Delta Q_{air} = 0$  so  $\int dS = \int dQ/T = 0$

Finally consider the air

$$\Delta S_{air} = \Delta Q_{air}/T_{air} = -\frac{\Delta Q_{ice}}{T_{air}} = \frac{-300 \times 334}{293} = -34.2 JK^{-1}$$

The air loses heat and its entropy is reduced. In fact, it should cool down a tiny bit.

Overall the G and T increases the entropy of the universe by  $2.5 JK^{-1}$ .

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

Divide the universe into the system (the lead, Pb), surroundings (heat bath) and everything else. Assume that the heat bath is thermally isolated from everything else, so the only entropy changes are in the lead and the bath.

Dropping hot lead into water is a rapid, irreversible cooling process. However the change in entropy of the lead is the same in each case, because entropy is a state variable, and the lead begins and ends in an equilibrium state. So we can calculate it by considering a reversible route between the states, successive equilibria between a series of heat baths at infinitesimally different T. We know  $\Delta Q_{Pb} = C_P \Delta T$  so the entropy loss is

$$\Delta S_{Pb} = \int \frac{dQ}{T} = \int \frac{C_P dT}{T} = C_P \ln[100/200] = -1000 \cdot \ln 2 = -693 \text{ J/K}$$

(a) We conventionally make the assumption that the bath is “large” and maintains its temperature at a constant, call it  $T_B$ , so its entropy is increased via an isothermal process:

$$\Delta S_{bath} = \frac{\Delta Q}{T_B} = \frac{C_P}{T_B} \int dT = \frac{1000 \cdot (200 - 100)}{100} = 1000 \text{ J/K}$$

The overall entropy change of the universe is then  $(1000 - 693) = 307 \text{ J/K}$ .

(b) With two baths we use the same equations

$$\Delta S_{baths} = \frac{\Delta Q}{T_{B1}} + \frac{\Delta Q}{T_{B2}} = \frac{1000 \cdot (200 - 150)}{150} + \frac{1000 \cdot (150 - 100)}{100} = 833 \text{ J/K}$$

The overall entropy change of the universe is then  $(833 - 693) = 140 \text{ J/K}$ .

(c) In a reversible process the entropy of the universe is conserved.

The question illustrates that the entropy of the universe depends on the process, even though the entropy of the system does not. The reversible case required a series of heat baths out of equilibrium with each other. An alternative would be to use the heat transfer to drive a Carnot engine, in which case some of the heat would be converted into work. This gives an alternative view of work: energy which does not contribute to the entropy.

## 6 Thermodynamic Potentials

### 1. Heat Capacities

For the heat capacity at constant volume, from the First Law  $dU = dQ + dW$ , differentiate with respect to  $T$  at constant volume:

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

where work is  $-PdV$ , and  $dV$ , the change in volume, is obviously zero for a constant volume process ( $\frac{\partial V}{\partial T}_V = 0$ ).

Now using the Central Equation  $dU = TdS - PdV$ . Once again  $dV$  is zero for a constant volume process, so:

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

For the heat capacity at constant pressure, directly differentiating the First Law would give two terms.

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

More convenient is to first write the First Law in terms of enthalpy ( $H=U+PV$ ;  $dH = dQ+VdP$ ). Now for a constant pressure process,  $dP=0$ .

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

Finally, using the Central Equation,  $dU = TdS - PdV \Rightarrow dH = TdS + VdP$ . So

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

It is not essential to introduce enthalpy, but it makes the analysis of constant pressure processes much more straightforward.

### 2. Helmholtz function and pressure

Helmholtz free energy is  $F = U - TS$ , so using the central equation:

$$dF = dU - TdS - SdT = -PdV - SdT$$

Expanding  $F = F(V, T)$  we can write

$$dF = \left(\frac{\partial F}{\partial V}\right)_T dV + \left(\frac{\partial F}{\partial T}\right)_V dT$$

so we can equate

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

So far this is general. Now for this particular gas:

$$P = -\left(\frac{\partial}{\partial v}\right)_T \left[ -\frac{a}{v} - RT \ln(v-b) + f_0(T) \right] = -\frac{a}{v^2} + \frac{RT}{v-b}$$

Where  $f_0(T)$  is some constant of integration, which does not appear in the equation of state.

Notice that we can tackle these problems using either total free energy, entropy, volume etc. ( $F$ ,  $S$ ,  $V$ ), or specific quantities ( $f$ ,  $s$ ,  $v$ ). Pressure and Temperature are the same in each case.

### 3. Using Maxwell relations

By definition  $F = U - TS$ , so:  $dF = dU - TdS - SdT$ , which combined with the central equation  $dU = -PdV + TdS$ , gives

$$F = -PdV - SdT$$

So we can equate

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

We use the fact that for a state variable ( $F$ ) the order of differentiation does not matter. Considering second differentials gives:

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

Which leads to a Maxwell relation:

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

To get the volume dependence of  $c_v = T \frac{dS}{dT}_V$  we find:

$$\left(\frac{\partial c_v}{\partial V}\right)_T = T \left(\frac{\partial}{\partial V_T} \frac{\partial S}{\partial T_V}\right) = T \frac{\partial}{\partial T_V} \left(\frac{\partial S}{\partial V_T}\right) = T \left(\frac{\partial^2 P}{\partial T^2}\right)_V$$

Now we are given an expression relating the heat capacities

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

and by definition

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

Now from the central equation, and application of the Maxwell relation from above, gives

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

so that, using the cyclical relation

$$c_P - c_V = T \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P \tag{9}$$

$$= \frac{-T \left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial P}\right)_P \left(\frac{\partial V}{\partial P}\right)_T} \tag{10}$$

$$= \frac{-T \left[\left(\frac{\partial V}{\partial T}\right)_P\right]^2}{\left(\frac{\partial V}{\partial P}\right)_T} \tag{11}$$

$$= \frac{VT\beta^2}{K} \tag{12}$$

$$\tag{13}$$

Now look at ratios. By definition, the compressibilities,  $\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T$ ;  $\kappa_S = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_S$

$$\frac{c_P}{c_v} = \frac{\left(\frac{dQ}{dT}\right)_P}{\left(\frac{dQ}{dT}\right)_V} = \frac{T \left(\frac{\partial S}{\partial T}\right)_P}{T \left(\frac{\partial S}{\partial T}\right)_V} \quad (14)$$

we have  $\left(\frac{\partial S}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_S \left(\frac{\partial P}{\partial S}\right)_T = -1$  and  $\left(\frac{\partial S}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_S \left(\frac{\partial V}{\partial S}\right)_T = -1$ , so that

$$\frac{c_P}{c_v} = \frac{\left(\frac{\partial T}{\partial V}\right)_S \left(\frac{\partial V}{\partial S}\right)_T}{\left(\frac{\partial T}{\partial P}\right)_S \left(\frac{\partial P}{\partial S}\right)_T} = \frac{\left(\frac{\partial V}{\partial P}\right)_T}{\left(\frac{\partial V}{\partial P}\right)_S} = \frac{\kappa_T}{\kappa_S} \quad (15)$$

Using the results  $C_P - C_V = \frac{VT\beta^2}{\kappa_T}$  and  $\frac{C_P}{C_V} = \frac{\kappa_T}{\kappa_S}$ .

We can write

$$\kappa_T - \kappa_S = \kappa_T \left(1 - \frac{\kappa_S}{\kappa_T}\right) = \kappa_T \left(1 - \frac{C_V}{C_P}\right) = \frac{\kappa_T}{C_P} \left[\frac{VT\beta^2}{\kappa_T}\right] = \frac{VT\beta^2}{C_P}$$

This is all general. For the specific case of one mole of ideal gas:  $PV = RT$ ,  $P \left(\frac{\partial V}{\partial T}\right)_P = R$ ;  $\beta = 1/T$ ;  $K = 1/P$ ;  $P \left(\frac{\partial V}{\partial P}\right)_T = -V/P$ . So that

$$c_p - c_v = VT(1/T^2)P = PV/T = R$$

where we use the cyclic relation  $\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T = -1$

$$\kappa_T - \kappa_S = VT(1/T^2)/\frac{5}{2}R = 2V/5RT = 2P/5$$

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Notice that for a diatomic gas the result would be different:  $\kappa_T - \kappa_S = 2P/7$ , and for a giant molecule (or solid) the two compressibilities become essentially the same. Tables of compressibilities and other elastic constants for condensed phases seldom distinguish between isothermal or adiabatic.

#### 4. A block of metal.

“Adiabatic” means no heat flow  $dQ = 0$ , which in the reversible case implies  $dS = 0$ . Choosing variables  $S(T, P)$  lets us write

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP = 0$$

Using the Maxwell relation  $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P = -V\beta$  and the definition  $C_P = \left(\frac{\partial Q}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P$  it follows that

$$\int V\beta dP = \int \frac{C_P}{T} dT$$

Solving the integrals, assuming volume is constant

$$V\beta[P_2 - P_1] = c_P \ln \frac{T_2}{T_1}$$

whence

$$\ln \frac{T_2}{T_1} = \frac{V\beta}{c_P} [P_2 - P_1]$$

This question is of a classic type beloved of thermodynamicists: “what happens when you change  $x$  and  $y$ , holding  $z$  constant”. The technique is to expand one variable in the other two, eliminate the term in  $dz$ , then use the Maxwell relations and/or triple product along with definition of materials properties to get to measurable quantities. There are several ways to get the answer, so let's do it again:

Expand  $T(S, P)$ :

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

For an adiabatic process,  $dS = 0$ , so:

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

Triple product, then Maxwell relation

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

Identify materials properties:

$$dT = \frac{T}{C_P} V\beta dP$$

Rearrange to obtain the same integrals as before.

$$\int \frac{C_P}{T} dT = \frac{V}{\beta} dP$$

and the correct answer follows once again!

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

We are given the specific Gibbs Free Energy

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

Expanding  $g = g(T, P)$  we can write

$$dg = \left( \frac{\partial g}{\partial T} \right)_P dT + \left( \frac{\partial g}{\partial P} \right)_T dP$$

and by definition ( $g = u + Pv - Ts$ ) we also have  $dg = vdP - sdT$ , so that we can identify

$$\begin{aligned} V &= \left( \frac{\partial g}{\partial P} \right)_T \\ &= \frac{RT}{P} + B + CP + DP^2 \end{aligned}$$

which is the equation of state. The constant  $A$  simply sets the zero of energy, which can be chosen arbitrarily. Often one can measure the equation of state experimentally, or calculate the Gibbs function theoretically. It is useful to know that, given one, it is possible to obtain the other.

### 6. A harmonic material The equation of state is given by $P = A(v - b) + CT$

We are given the form of the equation of state, but not the parameters. To determine them, we must build a set of simultaneous equations, one from each of the given properties.

Taking the value of  $v$  and  $T$  at  $p=0$  we find Bulk modulus  $K_T = 10^{10} = -v_0 \left( \frac{\partial P}{\partial v} \right)_T = -10^{-3}A$ ; So  $A = -10^{13}$ .

Expansivity  $\beta = \frac{1}{v} \left( \frac{\partial v}{\partial T} \right)_P = \frac{1}{v} \left( \frac{\partial v}{\partial P} \right)_T \left( \frac{\partial P}{\partial T} \right)_v = 10^{-5}$ .

From which  $\beta K_T = 10^5 = \left( \frac{\partial P}{\partial T} \right)_v = C$

Now use the pressure:  $0 = A(10^{-3} - v_0) + 300C$ ;

Rearranging  $v_0 = 300C/A + 10^{-3} = 1.003 \times 10^{-3}$ .

Inspecting the equation of state, there is a non-infinite equilibrium volume at  $P = 0$ , even for high- $T$ . Something must be holding the material together - this is a condensed phase.

The problem is oversimplified in that the measured properties should be pressure and temperature dependent. However for small changes in  $T$  and  $P$  the linear equation of state should be reasonable.

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

We start with the empirical observations known as Joule's Law  $U = U(T)$  and Boyle's Law  $PV = f_1(T)$  where  $f_1$  is some unknown function.

Joule's Law implies that  $\left( \frac{dU}{dX} \right)_T = 0$  for any quantity  $X$ , so we start with the central equation  $dU = TdS - PdV$ , and differentiate by volume at constant  $T$ :

$$0 = \left( \frac{dU}{dV} \right)_T = T \left( \frac{dS}{dV} \right)_T - P$$

rearranging, and using a Maxwell relation gives a relationship for constant volume process.

$$\begin{aligned} P &= T \left( \frac{dS}{dV} \right)_T = T \left( \frac{dP}{dT} \right)_V \\ \frac{dP}{P} &= \frac{dT}{T} \end{aligned}$$

Integration gives

$$\ln P = \ln T + f_2(V)$$


$$P/T = f_3(V)$$

So  $P/f_3(V) = T$ , and Boyle's Law gives  $PV = f_1(T)$ . The only way to make these compatible is if  $f_3(V) = a_1/V$  and  $f_1(T) = a_2T$ , with undetermined constants  $a_i$ . So that

$$PV = a_1a_2T$$

and we can identify the constants with the gas constant:  $a_1a_2 = nR$ .

Once again, the equation of state can be deduced from experimental observations.

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## 7 Expansion Processes

### 1. Free expansion of the van der Waals gas

Free expansion conserves  $U$ , because there is no heat input and the expansion is done into a vacuum (i.e. zero pressure), so no work is done. Starting with the Central Equation  $dU = TdS - PdV$ , we get an expression for a volume derivative at constant  $T$ :

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

We are trying to obtain an expression for  $\left(\frac{\partial T}{\partial V}\right)_U$ , and we can get this quantity into the expression by using a cyclic relation  $\left(\frac{\partial U}{\partial V}\right)_T = -\left(\frac{\partial U}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_U$ ,

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

Using the definition of  $C_V = \left(\frac{\partial Q}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V$ , we get

$$-C_v \left(\frac{\partial T}{\partial V}\right)_U = T \left(\frac{\partial S}{\partial V}\right)_T - P$$

Entropy does not appear in the van der Waals equation, so we must eliminate  $S$ . This can be done using a Maxwell relation:  $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$ , so substituting and rearranging

$$\left(\frac{\partial T}{\partial V}\right)_U = -[T \left(\frac{\partial P}{\partial T}\right)_V - P]/C_V$$

So far this is completely general. Now consider the special case of the van der Waals gas:

$$P = \frac{RT}{V-b} - \frac{a}{V^2}; \quad \left(\frac{\partial P}{\partial T}\right)_V = \frac{RT}{V-b}$$

$$\left(\frac{\partial T}{\partial V}\right)_U = -[T \frac{R}{V-b} - \frac{RT}{V-b} + \frac{a}{V^2}]/C_V = \frac{-a}{C_V V^2}$$

Note that for an *ideal* gas  $a = 0$ , so the temperature doesn't change in a free expansion, however for a non-ideal gas the important term is  $a$ , which represents the interactions between atoms. The sign of the cooling/heating effect depends on whether the gas atoms attract/repel. This is because the internal energy is split between bonding (potential energy) and kinetic. If the potential energy is increased (longer bonds), while  $U$  is constant, then the kinetic energy must be reduced.

The van der Waals equation of state works well for Helium at room temperature, with  $a > 0$  and, so we see that helium cools when it undergoes a free expansion at room temperature

### 2. Joule-Kelvin coefficients

- (a) This is another piece of manipulation of partial derivatives. We will need to absorb  $H$  into the heat capacity, so, start by taking triple product

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

We also know from  $dH = TdS + VdP$ , that

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

and

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

where we used a Maxwell relation to eliminate the entropy. Now, using the definition of the coefficient of thermal expansion we have

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

(b) For an ideal gas,  $PV = nRT$  we have

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{V} \frac{nR}{P} = \frac{1}{T}$$

So that  $(\alpha T - 1) = 0$ , and hence  $\mu_{JK} = 0$ , so an ideal gas doesn't change temperature in an isenthalpic expansion.

(c) For the van der Waals gas, it is a bit fiddlier. To get the thermal expansion, it's easiest to write the equation of state in terms of  $T$ , using specific heats and volume:

$$RT = \left[P + \frac{a}{v^2}\right](v - b)$$

and then find:

$$R \left(\frac{\partial T}{\partial v}\right)_P = \left(P + \frac{a}{v^2}\right) - 2a(v - b)/v^3 = \frac{RT}{(v - b)} - \frac{2a(v - b)}{v^3}$$

Where we eliminated  $P$  so that the expression refers only to two variables  $(T, v)$  which can be taken as independent, so that:

$$\mu_{JK} = \frac{v}{c_P} \left( \frac{RT/v}{RT/(v - b) - 2a(v - b)/v^3} - 1 \right)$$

Remember that the specific heat  $c_P$  is not uniquely determined by the van der Waals equation. It depends on whether the gas is a monatomic, diatomic, etc. So we can do no better than leave it as  $c_P$ , and remember that it must be positive.

(d) The inversion curve is where  $\mu_{JK} = \left(\frac{\partial T}{\partial P}\right)_H = 0$ , i.e. when the effect of a Joule-Kelvin expansion changes from cooling to heating. Therefore, from setting the bracket to zero in the expression for  $\mu_{JK}$ , the inversion curve is specified by:

$$\frac{RT_{IN}}{v_{IN}} = RT_{IN}/(v_{IN} - b) - 2a(v_{IN} - b)/v_{IN}^3$$

which after some tidying up gives an equation for the inversion line

$$RT_{IN} = \frac{2a(v_{IN} - b)^2}{bv_{IN}^2}$$

Sketching the curve shows that the highest value for  $T_{IN} = 2a/b$  comes at the high- $v$  asymptote. Above this temperature, Joule-Kelvin expansion of an ideal gas always results in heating. To obtain this formally, we need to differentiate to find the turning point:

$$\frac{dT_{IN}}{dv_{IN}} = \frac{2a}{Rv_{IN}^3}(v_{IN} - b) = 0$$

Mathematically, this implies a turning point when  $v_{IN} = b$ . Plugging this back into the equation for the inversion temperature gives a value for zero. This is a minimum of the function, although  $v < b$  is unphysical as it implies that the volume available for the substance is less than the volume of the component atoms.

Now for some mathematical legerdemain. Rearranging the inversion line equation and square rooting gives

$$\sqrt{\frac{RbT_{IN}}{2a}} = \frac{(v_{IN} - b)}{v_{IN}}$$

from which

$$v_{IN} = \frac{2ab}{2a - RbT_{IN}}$$

which we can substitute back into the van der Waals equation to get an expression for the “inversion curve” in PT space:

$$P \frac{8a}{27b^2} = 9 - 12 \left( \sqrt{\frac{8aT}{27Rb}} - \sqrt{3} \right)^2$$

This gives a maximum inversion *pressure* at  $T = \frac{81Rb}{8a}$ . Above this pressure, the Joule-Kelvin process always results in heating.



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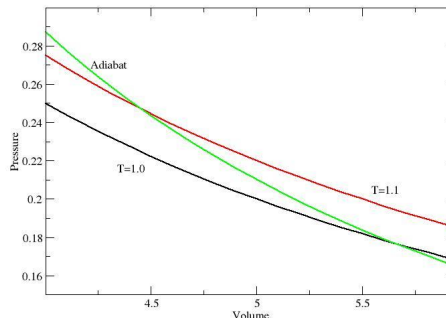
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### 3. Cooling in an adiabatic expansion

Figure shows curves  $P=1/V$ ,  $P=1.1/V$ ,  $PV^{7/5}$  representing two isotherms and an adiabat (with  $nR=1$ ). It can readily be seen that between the isotherms the adiabat has the larger slope. The temperature at any point along the adiabat is that of the isotherm passing through that point. Hence expanding the ideal gas adiabatically takes it from one isotherm to another corresponding to lower temperature.



For the adiabatic expansion process we are interested in the change in temperature when pressure is reduced at constant entropy (no heat exchanged)  $(\frac{\partial T}{\partial P})_S$ .

To get this into a manageable form, we eliminate  $S$  using the triple product, then a Maxwell relation, then the definitions of  $C_P$  and  $\beta$ :

$$\left(\frac{\partial T}{\partial P}\right)_S = -\left(\frac{\partial S}{\partial P}\right)_T \left(\frac{\partial T}{\partial S}\right)_P = \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial S}\right)_P = \left(\frac{\partial V}{\partial T}\right)_P \frac{T}{C_P} = \frac{TV\beta}{C_P}$$

So the adiabatic expansion always produces cooling, and the cooling is always larger than for the isenthalpic process:  $(\frac{\partial T}{\partial P})_H = \frac{TV\beta - V}{C_P}$ .

For completeness, the coefficient for the Joule process:

$$\mu_J = \left(\frac{\partial T}{\partial V}\right)_U = -\left(\frac{\partial T}{\partial U}\right)_V \left(\frac{\partial U}{\partial V}\right)_T = \frac{1}{C_v} \left[ T \left(\frac{\partial S}{\partial V}\right)_T - P \right] = \frac{TK\beta}{C_v}$$

has different dimensions, so cannot be directly compared.

- The Joule-Kelvin process involves a continuous flow of gas which can be achieved in is cyclic process. By contrast, the Joule process involves a one-off expansion into a vacuum and cannot easily be used for continuous cooling. Neither process is reversible, so they cannot be used in a Carnot refrigerator. The adiabatic expansion process lowers the temperature of the working fluid by more than the Joule-Kelvin process, but since it doesn't extract heat from the environment it is not useful in refrigeration.

### 5. Expanding through a Phase Transition

To maximise  $\mu_{JK}$  we want a very large value of  $(\frac{\partial V}{\partial T})_P$ . In a boiling phase transition, the volume changes discontinuously at the transition:  $\alpha$  is infinite, as is  $C_P$ . So the equation implies integrating over a divergent function.

### 6. Gibbs Helmholtz Equation

From the definition  $dG = Vdp - SdT$ , we have  $(\frac{\partial G}{\partial T})_p = -S$ .

Now consider the quantity:

$$\left(\frac{\partial G/T}{\partial T}\right)_p = \frac{1}{T} \left(\frac{\partial G}{\partial T}\right)_p - \frac{G}{T^2} = -\frac{(G + TS)}{T^2} = -\frac{H}{T^2}$$

Which in integral form can be written

$$\int d(G/T) = -\int \frac{H}{T^2} dT$$

doing the integral gives...

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

and rearranging

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

We now apply this equation to two different phases of the same material. Let state 1 be atmospheric pressure and 300K, state 2 atmospheric pressure and 400K. We are told that 300K is the melting point, so here the gibbs free energies are equal:  $G_1^l = G_1^s = G_1$ , and the free energy difference  $G^l - G^s$  is zero.

At 400K:

$$\Delta G_2 = G_2^l - G_2^s = -T_2 \int_{T_1}^{T_2} \frac{H_l - H_s}{T^2} dT$$

Calling the volumes  $V_l$  and  $V_s$  we have

$$\int_{T_1}^{T_2} \frac{H_l}{T^2} dT = [U_l + PV_l](1/T_1 - 1/T_2) + A_l \ln(T_2/T_1)$$

$$\int_{T_1}^{T_2} \frac{H_s}{T^2} dT = [U_s + PV_s](1/T_1 - 1/T_2) + A_s \ln(T_2/T_1)$$

So that at  $T_2$

$$\Delta G = -(T_2/T_1 - 1)[U_l - U_s + P(V_l - V_s)] - (A_l - A_s)T_2 \ln(T_2/T_1)$$

(sanity check:  $\Delta G = 0$  for  $T_2 = T_1$ )

The first term refers to the enthalpy difference between the phases. We can expect the constant  $[U_l - U_s + P(V_l - V_s)]$  will be positive, since the solid has lower enthalpy than the liquid. We can also expect  $(A_l - A_s)$  to be positive: these quantities are heat capacities, and we expect the liquid to be higher. Taken together,  $\Delta G$  is negative for  $T_2 > T_1$  and positive for  $T_1 > T_2$  - the stable phase of the material is liquid above the melting point and solid below.

As  $T \rightarrow 0$  the free energy difference tends to the enthalpy difference, as it should. However, with the given expression the heat capacities remain finite, in violation of the Third Law.

Notice that we do not have enough information to calculate the actual values of  $G$ , just the free energy difference

In analytic thermodynamics, the Gibbs-Helmholtz equation tends to look like just rearranging symbols. In fact, it is incredibly useful in Monte Carlo and Molecular Dynamics calculations which are the mainstay of computational physics. Given a set of atomic positions and velocities, it is easy to calculate the enthalpy directly from the Hamiltonian. However, there is no way to obtain the Gibbs free energy, or anything involving entropy. To understand why, remember that the entropy represents all the possible ways the atoms could be arranged to give the same macroscopic phase. Knowing what a typical state looks like tells us nothing about how many there are. The Gibbs-Helmholtz equation gives us a way to determine the changes in entropy (number of states), simply by measuring changes in enthalpy (energy of states).

Notice that it does not allow us to determine the value of  $G$ , only values for changes,  $\Delta G$ .

### 7. Critical point

The van der Waals gas has  $P = RT/(v - b) + a/v^2$ .

Considering turning points with  $\frac{\partial P}{\partial V} = 0$  we find that there are three cases for an isotherm

$T > T_c$ : no turning point on the isotherm with  $\frac{\partial P}{\partial V} = 0$ .

$T < T_c$ : one maximum point on the isotherm with  $\frac{\partial P}{\partial V} = 0$  and  $\frac{\partial^2 P}{\partial V^2} < 0$ .

$T = T_c$ : one inflection point on the isotherm with  $\frac{\partial P}{\partial V} = 0$  and  $\frac{\partial^2 P}{\partial V^2} = 0$ .

there is also an unphysical region with  $v \ll b$  where either the pressure or temperature must be negative. This region has an unphysical negative bulk modulus.

With  $T < T_c$ , for given external pressure and temperature, there are two possible volumes. What actually happens here is that if the external condition fixes the volume, we get a coexistence between the two phases, in the right proportions to fill the volume available. Alternately, if the external pressure and temperature are fixed, any infinitesimal difference from the values on the phase boundary causes the material to transition into the relevant phase.

To find  $T_c$  we require both of the first and second differential of pressure to be zero. For a van der Waals gas,

$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$$

$$\left(\frac{\partial P}{\partial V}\right)_T = \frac{nRT}{(V - nb)^2} + \frac{2an^2}{V^3} = 0$$

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_T = \frac{2nRT}{(V - nb)^3} - \frac{6an^2}{V^4} = 0$$

Eliminate T from the above:

$$\frac{nRT}{(V - nb)^3} = \frac{3an^2}{V^4} = \frac{3}{2V} \frac{an^2}{V^3} = \frac{3}{2V} \frac{nRT}{(V - nb)^2}$$

From the first and fourth expression  $2V = 3(V - nb)$ ;  $V_c = 3nb$ .

Remembering the idea that  $b$  is the volume of the atom, this is when "The atoms take up one third of the volume".

By substitution, we can find  $T_c$

$$T_c = \frac{2an^2}{V_c^3} \frac{(V_c - nb)^2}{nr} = \frac{2an^2}{27b^3n^3} \frac{4n^2b^2}{nR} = \frac{8a}{27bR}$$

and finally

$$\begin{aligned} P_c &= \frac{nR(8a/27bR)}{3nb - nb} - \frac{an^2}{(3nb)^2} \\ &= \frac{4a}{27b^2} - \frac{a}{9b^2} \\ &= \frac{a}{27b^2} \end{aligned}$$

Sometimes, it is convenient to treat the van der Waals gas using dimensionless units such that the triple point lies at  $T_c = 1$ ,  $P_c = 1$ ,  $V_c = 1$ . This saves us having to carry round factors of  $R$ ,  $a$  and  $b$ , at the cost of not being able to check dimensions of our equations.

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## 8 Thermodynamics in other systems

### 1. A rubber band

a) Start with Central Equation  $dU = TdS - PdV$  from which, differentiating by V.

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

Use Maxwell relation  $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$  to get the required answer

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

b) For a wire, substitute P (pressure) with -F (force) and V (volume) for L (length). Note that increased pressure makes the volume smaller, while increased force makes the wire longer.

$$\left(\frac{\partial U}{\partial L}\right)_T = -T \left(\frac{\partial F}{\partial T}\right)_L + F$$

You might think the second term looks odd, normally force is just the derivative of the energy? What's happening here is the boundary conditions, we're not simply stretching the band, we're also allowing it to absorb/emit heat. The normal spring definition is recovered if we consider an adiabatic process on  $dU = TdS + FdL$  :

$$\left(\frac{\partial U}{\partial L}\right)_S = F$$

Remember that  $F$  is the force exerted *on* the band, not *by* it.

If we have an isothermal process, then rearranging the above:

$$F = \left(\frac{\partial U}{\partial L}\right)_T + T \left(\frac{\partial F}{\partial T}\right)_L$$

and using a Maxwell relation

$$F = \left(\frac{\partial U}{\partial L}\right)_T - T \left(\frac{\partial S}{\partial L}\right)_T = \left(\frac{\partial(U - TS)}{\partial L}\right)_T$$

We recover the result that the required force for an isothermal extension is the derivative of *Helmholtz free energy*, U-TS.

c) The equivalent of an equation of state for a wire is  $F = aT \left[ \frac{L}{L_0} - \left(\frac{L_0}{L}\right)^2 \right]$

From which we can calculate

$$\left(\frac{\partial U}{\partial L}\right)_T = -aT \left[ \frac{L}{L_0} - \left(\frac{L_0}{L}\right)^2 \right] + aT \left[ \frac{L}{L_0} - \left(\frac{L_0}{L}\right)^2 \right] = 0$$

i.e  $U(L, T) = U(T)$ : internal energy depends on temperature only. This works for this carefully chosen equation of state which has energy proportional to temperature.

This does not mean that we can stretch the wire at no cost. If we stretch the wire to length  $L$  isothermally, the relevant thermodynamic potential is the analogy of Helmholtz free energy.



d) Work done, again by analogy

$$\begin{aligned}
 W &= \int dW = \int_{L_1}^{L_2} F dL \\
 &= \int_{L_1}^{L_2} aT \left[ \frac{L}{L_0} - \left( \frac{L_0}{L} \right)^2 \right] dL \\
 &= aT \left[ \frac{L^2}{2L_0} + \left( \frac{L_0^2}{L} \right) \right]_{L_1}^{L_2} \\
 &= aT \left( \frac{L_2^2}{2L_0} - \frac{L_1^2}{2L_0} \right) + aTL_0^2 \left( \frac{1}{L_2} - \frac{1}{L_1} \right)
 \end{aligned}$$

Using the values  $L_0=1\text{m}$ ,  $L_1=1\text{m}$ ,  $L_2=2\text{m}$ ,  $a=1.3 \times 10^{-2} \text{NK}^{-1}$ ,  $T=300\text{K}$ .

$$W = (300) \cdot (0.013) (2 - 0.5) + (300) \cdot (0.013) (0.5 - 1) = 3.9\text{J}$$

Since  $U = U(T)$  only, and  $T$  is constant,  $U$  is constant, so from the first law  $dU = dQ + dW = 0$  the work done is equal to minus the heat input.

So heat input is  $-3.9\text{J}$ , alternately  $3.9\text{J}$  of heat is given off.

## 2. Adiabatic rubber band

Now consider the adiabatic case, where we don't give the wire time to warm up after stretching it. Adiabatic and reversible means  $dS = 0$ , so write an expression for the entropy.

$$dS = 0 = \left( \frac{\partial S}{\partial L} \right)_T dL + \left( \frac{\partial S}{\partial T} \right)_L dT$$

The relevant specific heat, at constant length, is  $c_L = T \left( \frac{\partial S}{\partial T} \right)_L$ , and we have a Maxwell relation:  $\left( \frac{\partial S}{\partial L} \right)_T = - \left( \frac{\partial F}{\partial T} \right)_L$

So we have a relation

$$\left( \frac{\partial F}{\partial T} \right)_L dL = \frac{c_L}{T} dT$$

We now integrate this equation

$$\begin{aligned}
 \int_{L_1}^{L_2} a \left[ \frac{L}{L_0} - \left( \frac{L_0}{L} \right)^2 \right] dL &= \int \frac{c_L}{T} dT \\
 a \left( \frac{L_2^2}{2L_0} - \frac{L_1^2}{2L_0} \right) + aL_0^2 \left( \frac{1}{L_2} - \frac{1}{L_1} \right) &= c_L \ln \frac{T_2}{T_1}
 \end{aligned}$$

Plugging in the numbers

$$c_L \ln \frac{T_2}{300} = 0.013 \cdot [1.5 - 0.5]$$

$$T_2 = 300 \exp(0.013/1.2) = 303.3\text{K}$$

Change in temperature is a  $3.3\text{K}$  increase.

### 3. Entropy of diamond

Given that  $c_P = 124(T/1860)^3$ .

To find entropy change, consider a reversible process involving small changes at constant volume:  
 $dS = c_v dT/T$

$$\begin{aligned}\Delta S &= \int_4^{300} 124 \left( \frac{T}{1860} \right)^3 \frac{dT}{T} \\ &= \frac{124}{1860^3} \left[ \frac{300^3}{3} - \frac{4^3}{3} \right] \\ &\approx 0.173 \text{ kJ/K/kg}\end{aligned}$$

For graphite, similarly

$$\frac{89}{1500^3} \left[ \frac{300^3}{3} - \frac{4^3}{3} \right] = 0.237 \text{ kJ/K/kg}$$

Thus graphite has higher entropy and is more stable at high temperatures. Since it is also the less denser phase, it means that  $\Delta s$  and  $\Delta v$  for the diamond-graphite transition have opposite signs, so the Clausius-Claperon slope is negative.

As  $T \rightarrow 0$   $C_P \rightarrow 0$ .  $C_P$  involves changes in entropy, so the Third Law is satisfied. There is no divergence in the integral at  $T=0$ .



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#### 4. Planck's Law

We are given that  $P = U/3V$ .

From the central equation  $dU = TdS - PdV$ ,

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

and using one of the Maxwell's relations,

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

Energy density is defined as  $u = U/V$ , and for the photon gas  $P = \frac{1}{3}u$ ,  $U = uV$  and  $u = u(T)$ , so we get

$$u = \frac{1}{3}T \frac{du}{dT} - \frac{1}{3}u$$

which implies that  $4 \frac{dT}{T} = \frac{du}{u}$ . Which integrates to  $4 \ln T + \ln \left(\frac{4\sigma}{c}\right) = \ln u$  with appropriately defined for some constant of integration.

$$u = \left(\frac{4\sigma}{c}\right) T^4$$

The Planck distribution law, for energy density of cavity radiation as a function of wavelength  $\lambda$ , and temperature  $T$  is:

$$u_\lambda(\lambda, T) \propto \frac{1}{\lambda^5} \left( \frac{1}{e^{hc/\lambda k_B T} - 1} \right)$$

To get the total energy density, we need to integrate this over all wavelengths:

$$u = \int_0^\infty u_\lambda(\lambda, T) d\lambda = \int_0^\infty \frac{2\pi c^2 h}{\lambda^5} \left( \frac{1}{e^{hc/\lambda k_B T} - 1} \right) d\lambda$$

If we make a substitution:

$x = hc/\lambda k_B T$  then this becomes

$$u = 2\pi c^2 h \int_\infty^0 \left( \frac{k_B T x}{hc} \right)^5 \frac{1}{e^x - 1} \left( \frac{-hc}{k_B T x^2} \right) dx$$

Rearranging to make clear the dedimensionalisation the integral

$$u = 2\pi c^2 h \int_\infty^0 \left( \frac{k_B T}{hc} \right)^4 \int_0^\infty \frac{x^3}{e^x - 1} dx$$

The integral is clearly bounded, so it is simply a number. You can solve it if you enjoy that sort of thing (its about  $2\pi$ ), but the physically important result, the  $T^4$  dependence, is thereby shown.

Had we used the Boltzmann energy distribution, the integral would have been

$$u = \int u_\lambda(\lambda, T) d\lambda = \int_0^\infty \frac{2\pi c^2 h}{\lambda^5} e^{-hc/\lambda k_B T} d\lambda$$

Which also gives a Stefan's law  $T^4$  result. It's only if we use classical equipartition that the integral becomes infinite

$$u = \int u_\lambda(\lambda, T) d\lambda \propto \int_0^\infty \lambda^{-4} d\lambda \rightarrow \infty$$

the so-called "ultraviolet catastrophe" since the integral blows up for short wavelengths.

### 5. Photon Gas

- (a) To obtain  $U(V,T)$  we will need to obtain a relationship between the internal energy, pressure, temperature and volume, then use the equation of state to eliminate the pressure. Start with the central equation

$$dU = TdS - PdV$$

Differentiate wrt  $V$  at constant  $T$

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

and use a Maxwell relation to eliminate  $S$

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

This is a general thermodynamic relation. We now apply it to the case of cavity radiation. Since specific internal energy  $u$  (energy density: energy per unit volume) depends only on  $T$ , the total internal energy depends on how big the cavity is, i.e. it is proportional to  $V$ :  
 $U = Vu(T)$

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

Using specific energy and volume, and  $P = \frac{u(T)}{3}$  we find:

$$\frac{T}{3}\left(\frac{\partial u}{\partial T}\right)_v = \frac{4u}{3}$$

Rearranging and integrating:

$$\int du/u = 4 \int dT/T$$

Integrating, and introducing a constant of integration  $\ln k$

$$\ln u = 4 \ln T + \ln k$$

Implies  $u = kT^4$  or  $U = kVT^4$ .

- (b) For a photon gas to have sufficient energy to move a piston:

$$P = 10^5 \text{ Pa} = u/3 = kT^4/3 \Rightarrow T = (3P/k)^{1/4} = 1.4 \times 10^5 \text{ K}$$

This is hotter than the sun, but considerably less than in a nuclear bomb. The blast from a nuclear weapon is primarily a shock wave of air compressed by black body radiation. Since the pressure rises with the fourth power of the temperature, it quickly becomes enormous.

- (c) Since the energy depends only on  $T$ , the heat capacity is  $\left(\frac{dU}{dT}\right)_V = 4kVT^3$ , or specific heat capacity  $4kT^3$ . The Third Law requires heat capacities to go to zero as  $T \rightarrow 0$ , which is obviously true for a  $T^3$  dependence.

The specific entropy can be obtained considering a constant volume heating process from  $T=0$ . Using the Central Equation

$$\begin{aligned} du &= Tds - Pdv \\ ds &= \frac{1}{T} \frac{dU}{dT} dT = \int 4kT^2 dT \\ s &= \frac{4kT^3}{3} = \frac{4u}{3T} \end{aligned}$$

- (d) The Gibbs Free energy is defined as  $G = U + PV - TS$ , whence

$$G = U + \frac{U}{3} - \frac{4U}{3} = 0$$

At equilibrium, only processes for which  $dG = 0$  can occur. Remarkably, creation and absorption of photons are both thermodynamically allowed because neither cause any change to the free energy.

- (e) We have derived  $G = 0$  from the equation of state. However, from observations of the spontaneous creation and absorption of photons, we could have used this as a starting point. Start with the definition

$$dG = VdP - SdT$$

since  $G$  is a constant (zero!) for the photon gas,  $dG$  must also be zero, so that:

$$VdP = SdT$$

Rearranging gives:  $dP = \frac{S}{V}dT$  Comparing this to the general expression for pressure as a function of  $T$  and some other variable  $X$

$$dP = \left(\frac{\partial P}{\partial T}\right)_X dT + \left(\frac{\partial P}{\partial X}\right)_T dX$$

We see that  $\left(\frac{\partial P}{\partial X}\right)_T = 0$ , i.e. pressure is independent of any variable other than  $T$ .

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6. **Temperature of the sun.** The total radiation from the sun is  $(4\pi R_S^2)\sigma T_S^4$ , with a similar equation for earth  $(4\pi R_E^2)\sigma T_E^4$ .

The fraction of the solar radiation hitting the earth is given by the area of the earth divided by a sphere the size of the earth's orbit ( $D$ ):

$$\frac{(\pi R_E^2)}{4\pi D^2}$$

At equilibrium, the radiation hitting earth is the same as that emitted:

$$(4\pi R_S^2)\sigma T_S^4 \frac{(\pi R_E^2)}{4\pi D^2} = (4\pi R_E^2)\sigma T_E^4$$

whence

$$\begin{aligned} T_S &= T_E \left[ \frac{4D^2}{R_S^2} \right]^{1/4} \\ &= 287 \sqrt{\frac{2 \cdot (1.5 \times 10^{11})}{(6.96 \times 10^8)}} \\ &= 5959K \end{aligned}$$

This assumes that the earth's radiation comes from the surface. In fact, the Greenhouse Effect means that much of the radiation comes from the (cooler and larger) upper atmosphere. It also neglects the contribution of radioactive decay in the Earth's core to warming the planet.

## 7. Black hole entropy

Start by writing the central equation as an expression for entropy

$$dS = \frac{dU}{T} + \frac{PdV}{T}$$

Remember that we can write any state variable as a function of any other two: this time we use  $S(U,V)$

$$dS = \left( \frac{\partial S}{\partial U} \right)_V dU + \left( \frac{\partial S}{\partial V} \right)_U dV$$

giving us  $\left( \frac{\partial S}{\partial U} \right)_V = \frac{1}{T}$ . So we need to calculate the relationship between  $S$  and  $U$ .

We are given that  $S = k_B A c^3 / 4G\hbar$ , and we know that  $A = 4\pi r^2$ ;  $r = 2Gm/c^2$  and  $U = mc^2$ , from which we find that  $S = \frac{4\pi k_B G}{\hbar c^5} U^2$ , so

$$\frac{dS}{dU} = \frac{1}{T} = \frac{8\pi k_B G}{\hbar c^5} U$$

A quick rearrangement gives

$$T = \frac{\hbar c^3}{8\pi k_B G M} = 1.2 \times 10^{11} K$$

Which is pretty hot, and so will evaporate very quickly. By contrast, a solar sized hole with  $m = 10^{30}$  has  $T = 6 \times 10^{-8} K$ .

In previous examples, we have been considering entropy in terms of atoms, however the Second Law applies to all processes, with increasing entropy determining what can and cannot happen. There are a number of difficulties with entropy in astrophysics, arising from the fact that a self-gravitating system is denser in the middle, and therefore doesn't meet the equilibrium criterion of homogeneity.

## 9 Phase transitions

### 1. Phases and Clausius-Clapeyron

- a) Sketch shows solid, liquid, gas, phase boundaries triple and critical points.  
b) In phases 1 and 2 at T,P coexistence, specific Gibbs functions are equal  $g_1 = g_2$ .

$$dg = vdP - sdT$$

at T, P.

$$s = - \left( \frac{\partial g}{\partial T} \right)_P ; \quad v = \left( \frac{\partial g}{\partial P} \right)_T ;$$

At another point infinitesimally further along the coexistence line (T+dT, P+dP), still have  $g_1 = g_2$  which we can get by Taylor expansion from (T,P):

$$\begin{aligned} g_1(T + dT, P + dP) &= g_2(T + dT, P + dP) \\ g_1(T, P) + \left( \frac{\partial g_1}{\partial P} \right)_T dP + \left( \frac{\partial g_1}{\partial T} \right)_P dT &= g_2(T, P) + \left( \frac{\partial g_2}{\partial P} \right)_T dP + \left( \frac{\partial g_2}{\partial T} \right)_P dT \\ -s_1 dT + v_1 dP &= -s_2 dT + v_2 dP \\ (s_2 - s_1) dT &= (v_2 - v_1) dP \\ \left( \frac{dP}{dT} \right)_{p.t.} &= \frac{(s_2 - s_1)}{(v_2 - v_1)} = \frac{l}{T(v_2 - v_1)} \end{aligned}$$

Which is the Clausius Clapeyron equation.

- c) For the pressure cooker example, we plug in numbers to get

$$\left( \frac{dP}{dT} \right)_{p.t.} \approx \frac{\Delta P}{\Delta T} = 3600 \text{ Pa/K}$$

therefore, for  $\Delta T = 30\text{K}$ ,  $\Delta P = 1.09 \times 10^5 \text{Pa}$ , so since we start at atmospheric pressure, the total pressure is

$$P = 1.09 \times 10^5 + 1.0 \times 10^5 \text{Pa} = 2.09 \times 10^5,$$

This is typical for a pressure cooker. ‘‘Cooking’’ is an irreversible process in which proteins are denatured - normally this means taking them from a non-equilibrium state to a lower free-energy state. Although we normally cook with temperature, it is also possible to use pressure alone to denature proteins.

### 2. Phase mixtures

Write the total mass of liquid and vapour as  $m = m_l + m_v$ . The mass is conserved in the vapourisation process.

Total volume =  $V = V_l + V_v = m_l v_l + m_v v_v$  where  $v_i$  are the specific volumes (inverse density). Also define the specific volume of the whole system

$$v = \frac{V}{m} = \frac{v_l m_l + v_v m_v}{m_l + m_v}$$

Rearranging this gives the ‘‘Lever rule’’

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

The name is by analogy with finding the balance point (pivot) of a bar with two weights hanging from it,  $m_l, m_v$  being the weights, and  $v - v_l, v_v - v$  the distances from the pivot.

The gibbs free energy of two phases in equilibrium is the same, and since neither T nor P change in the coexistence region, it remains constant.

Compressibility is defined by

$$\beta = \frac{1}{V} \frac{\partial V}{\partial P}$$

and so, since the slope of the graph is zero, substances are infinitely compressible in the coexistence region.

### 3. Solid-solid phase transitions

The question asks about the phase transition line for a first order transition, so we will apply the Clausius-Clapeyron equation. Assuming  $dP/dT = \Delta P/\Delta T$ :

$$\Delta T = \Delta P / \left( \frac{l}{T(v_2 - v_1)} \right) = 291 \times 99 \times 10^5 \times \left( \frac{1}{7333} - \frac{1}{5750} \right) / 18500 = -5.8K$$

Like water, the high temperature, metallic white tin phase is denser than the low temperature, insulating grey tin. Consequently high pressure favours denser the white tin phase, and the transition temperature drops.

### 4. Triple Point

a) At the triple point, the vapourisation and sublimation curves meet, so we must have  $\ln P = 0.04 - 6/T$  and  $\ln P = 0.03 - 4/T$

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Whence  $T_{tp} = 200K$  and by substitution:

$$P_{tp} = \exp(0.03 - 4/200) = \exp(0.01) = 1.01005$$

b) To get the latent heats, we use the Clausius-Clapeyron equation:

$$\left(\frac{dP_{pb}}{dT_{pb}}\right) = \frac{l}{T(v_2 - v_1)} \approx \frac{l}{Tv_2}$$

where the suffix  $pb$  reminds us that this is the derivative of the phase boundary line.

We now assume that the gas phase  $v_2$  can be taken to be an ideal gas. This lets us eliminate  $v_1 \ll v_2$ .

$$\frac{dP}{dT} \approx \frac{l}{Tv_2} \approx \frac{lP}{RT^2}$$

Integrating this:

$$\int \frac{dP}{P} = \int \frac{l}{RT^2} dT$$

$$\ln P = \frac{-l}{RT} + \text{const}$$

Which can be compared directly to the given equations for the sublimation and vapourisation curves to give  $l = 6R$  and  $l = 4R$  respectively.

c) Consider reversible changes in a loop around the critical point. The entropy change around the loop  $\Delta S = 0$ , since entropy is a state variable.

$$\Delta S = \sum \frac{\Delta Q}{T} = \sum \frac{l}{T} = \frac{l_{SV}}{T} + \frac{l_{VL}}{T} + \frac{l_{LS}}{T} = 0$$

For a loop close to the triple point, all temperatures are the same, so noting that e.g.  $l_{SV} = -l_{VS}$ , we get

$$l_{SL} = l_{SV} - l_{LV} = 2R$$

## 5. Impossible Phase diagram

(a) The stable phase minimises the Gibbs free energy,  $dG = -SdT + VdP$ , so at constant  $T$ , increased  $P$  will favour smaller volume. Hence the density increases in order  $\rho_1 < \rho_2 < \rho_3 < \rho_1$ . The compressibility of phase 1 must be large, since at low pressure it has the lowest density, and at high pressure the highest.

(b) For first order transitions, the densities are different. At the triple point, we have  $\rho_1 < \rho_2 < \rho_3 < \rho_1$  - phase 1 cannot have both highest and lowest density at the same  $(T,P)$ . Thus the diagram is impossible.

(c)  $Z = T - mP$ , which is a state variable. Consequently every point along the iso- $Z$  line has a different value of its conjugate variable,  $Y$  which will be some combination of  $s$  and  $v$ . Precisely what isn't important, all that matters is that this conjugate variable increases monotonically along the iso- $Z$  line and changes discontinuously at the phase boundary.

(d) At the triple point, since a first order transition implies the diagram implies that,  $Y_1 < Y_2 < Y_3 < Y < 1$  which is clearly impossible.

This is known as the  $180^\circ$  rule, and is an effective shortcut for detecting incorrect claims regarding phase diagrams. It does *not* prohibit a maximum in phase boundary (e.g. the left hand figure if phases 2 and 3 were actually the same phase). At the point of maximum temperature, the densities of the two phases must be the same. At high pressure, phase 1 has higher density, while at low pressure phase 2/3 is denser.

### 6. Pressure effect on melting ice

Another Clausius-Clapeyron question, and again assume the phase boundary to be a straight line, so that  $dP/dT = \Delta P/\Delta T$

$$\frac{\Delta P}{\Delta T} = \left( \frac{l}{T(v_2 - v_1)} \right) = \frac{333700}{273 \times \left( \frac{1}{1000} - \frac{1}{916} \right)} = -1.3 \times 10^7 \text{ Pa/K}$$

Now the applications

(a) Pressure at bottom of Glacier =  $\rho gh = 916 \times 9.8 \times 2000 = 1.79 \times 10^7 \text{ Pa}$

Change in melting point:  $1.79 \times 10^7 / -1.3 \times 10^7 = -1.38 \text{ K}$ .

So the melting point is  $-1.38^\circ$

at the given temperature,  $-1.5^\circ$  the ice is frozen.

note we *assumed* it was frozen by using the density of ice (916). that assumption is now validated. There a small curiosity that if we assumed the density of water, the pressure would have been higher and the conclusion would be that the bottom was liquid.

(b) Using the given value of  $-22^\circ \text{C}$ , and assuming atmospheric pressure is negligible

$$\Delta P = (-1.3 \times 10^7) \times (-22) = 2.8 \times 10^8 \text{ Pa}$$

which is about 2860 atm., validating our assumption. Above this pressure the crystal structure of ice changes to an arrangement denser than water. (The “Ice Ih - ice III” transition)

(c) Skate has contact area of  $(0.3 \text{ m}) \times (0.001 \text{ m})$

assuming a 70kg skater, he exerts a force  $mg = 70 \times 9.8 \text{ N}$

$$\text{Increase in pressure is } \Delta P = \frac{F}{A} = \frac{70 \times 9.8}{0.3 \times 0.001} = 2.3 \times 10^6 \text{ Pa}$$

$$\text{So } \Delta T_m = \frac{2.3 \times 10^6}{1.3 \times 10^7} = -0.18 \text{ K}$$

This is too small to melt the ice in most cases. Even if we sharpen the blade to  $10^{-4} \text{ m}$ , the drop is only 1.8K. In fact, it’s almost impossible to find sensible parameters to back up the “skating works by pressure melting” story.

A salutary tale, all too often when a story is too good to check, even scientists don’t check. The concept is fine, but sometimes you just have to do the maths to show the application is wrong.

And how does skating work? There’s probably friction and surface chemistry involved. The Fourth Law will explain it all...

## 10 Chemical Potential

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

For a single component, the chemical potential is the specific Gibbs free energy, so start by considering changes in that:

$$dg = vdP - sdT$$

Considering a constant temperature process, we have  $dT = 0$  and

$$dg = d\mu = vdP = \frac{RT}{P}dP$$

Doing the integral from reference state labelled "0", we find:

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

Since the atmosphere is in contact with the ocean, the chemical potential of Carbon Dioxide is the same in each. Hence:

$$\mu_0^{atm} - \mu_0^{ocean} = RT \ln(p_i^{atm}/p_i^{ocean})$$

rearranging

$$p_i^{ocean} = p_i^{atm} \exp((\mu_0^{atm} - \mu_0^{ocean})/RT)$$

with atmospheric pressure at  $10^5$ Pa, the partial pressure of  $\text{CO}_2$  is 40Pa. Taking  $RT = 2500 \text{ J mol}^{-1}$ , and the given values for the chemical potential, we find that:

$$p_i^{ocean} = 40 \exp(-8000/2500) = 1.4 \text{ Pa}$$

Assuming that partial pressure is simply proportional to concentration, this implies that the concentration of  $\text{CO}_2$  in seawater is 0.0014% (14 parts per million).

The difference in  $\mu_0$  is due mainly to potential energy:  $\text{CO}_2$  in water disrupts the bonding network, increasing the potential energy of the solution by an amount proportional to the concentration of  $\text{CO}_2$ . It is proportional because at 14ppm, the  $\text{CO}_2$  molecules are far apart and so do not interact.

### 2. Iron Bru

Assuming that the chemical potentials come into equilibrium, both gas and drink have the same  $\text{CO}_2$  chemical potential. We can take this as the ideal gas value:

$$\mu = \mu_0 + RT \ln(P/P_0) = \mu_0 + 5RT$$

when the cap is removed, the  $\text{CO}_2$  partial pressure in the gas drops to its atmospheric value  $0.0004 \times P_0$ , so now in the gas

$$\mu = \mu_0 + RT \ln(0.0004) = \mu_0 - 7.824RT$$

The release of pressure is done quickly, so the  $\text{CO}_2$  in solution is the same as before. Gas and solution are out of equilibrium, so there is a significant difference in chemical potential between the two regions.  $\text{CO}_2$  will fizz out of solution when shaken. A first approximation would be to treat the large volume of liquid as an infinite reservoir, so that the  $\text{CO}_2$  would reach a partial pressure of 5atm (making 6atm in all). This amount of  $\text{CO}_2$  in gas would be

$$n = \frac{PV}{RT} = \frac{5 \times 10^5 \times 0.05 \times 10^{-3}}{8.314 \times 300}$$

which is 0.01 moles

We were told that originally there were 0.155 moles of  $\text{CO}_2$ , so the approximation that most of the  $\text{CO}_2$  remained in solution is a good one: the chemical potential in the drink will, in fact, have dropped by about 6%.

Repeated iterations will extract progressively less CO<sub>2</sub>, the concentration decreasing by a geometric series. We could calculate this, but since there is no numerical definition for “flat” it is sufficient to use the 6% value to estimate that after 10-20 iterations, most of the CO<sub>2</sub> will be lost.

The  $-7.824RT$  was never used. This is equivalent to neglecting the additional atmospheric CO<sub>2</sub> added to the bottle on each iteration. Notice also that if there were no CO<sub>2</sub> in the atmosphere, the chemical potential would be *minus infinity*: the gas is infinitely attractive to the first CO<sub>2</sub> molecules to arrive, or as Aristotle put it “Nature abhors a vacuum”. This infinity does not mean that the Gibbs free energy is infinite, because the free energy of any system is the chemical potential *times* the number of particles in the system. This product goes as  $n \ln n$ , which goes to zero as  $n \rightarrow 0$ .

### 3. Chemical Potential Change in Mixing

Once the containers are connected, we are out of equilibrium, and expect the gases to mix. Assume that both argon and krypton can be treated as ideal gases, which do not interact.

From the First Law, no work is done and no heat enters the system, so the internal energy cannot change. Since the internal energy of the ideal gas depends only on temperature, it is initially the same for each component. At equilibrium, the system has a single temperature, so we can deduce that the temperature cannot change.

The volume doubles for each gas, at constant temperature, so since we have an ideal gas, the partial pressure halves. However, since the two gases intermingle, the total pressure is unaffected.

The entropy change is given by

$$ds = \frac{c_V}{T} dT + \frac{R}{v} dv$$

where  $v$  is the specific volume. This is a quantity which changes by a factor of 2, hence for the argon:

$$dS = R \frac{\ln 2V}{V} = R \ln 2$$

and the entropy of the krypton changes similarly. So the total entropy change of the universe is  $2R \ln 2$ . The same value can be calculated from microscopic considerations, that each atom could be one the two types, so for  $2N_A$  molecules:

$$S = k_B \ln W = k_B \ln 2^{2N_A} = 2R \ln 2$$

where Avogadro’s number is  $N_A = R/k_B$ . Note that the thermodynamic derivation uses only macroscopic quantities, so is independent of the existence of atoms. The Gibbs free energy (chemical potential) for each species changes by:

$$\Delta g_i = \Delta u_i - \Delta(Ts_i) + \Delta(p_i v_i) = 0 - RT \ln 2 + 0$$

Notice that we use the partial pressure, which is halved as the volume doubles. No work is done in the mixing, so we should expect the  $p_i v_i$  term to make zero contribution to the change in free energy.

If the initial volumes were different, then the number of moles of the two gases would be:  $2N_K/(N_A + N_K)$  and  $2N_A/(N_A + N_K)$ ; the entropy changes of the two gases would be different, but still given by the same equation:

$$dS = \frac{2N_K R}{(N_A + N_K)} \ln \frac{(V_A + V_K)}{V_K} + \frac{2N_A R}{(N_A + N_K)} \ln \frac{V_A + V_K}{V_A}$$

In terms of mole fractions, this would be

$$dS = -2R(x_K \ln x_K + x_A \ln x_A)$$

Notice that if there is only one gas ( $x_K = 1; x_A = 0$ ) there is no entropy of mixing,  $dS = 0$ .

#### 4. Regular solution and solubility limits

This expression for the potential energy is proportional to the densities of each gas, so represents the average number of interactions between different types of atoms. This is similar to the  $a/v^2$  term in the van der Waals equation, but of opposite sign because they are repulsive.

In the isothermal process kinetic energy (temperature) is conserved. The potential energy rose by  $\frac{Z}{v_A v_K} = Zx_A x_K$ , so the internal energy increases by the same amount,

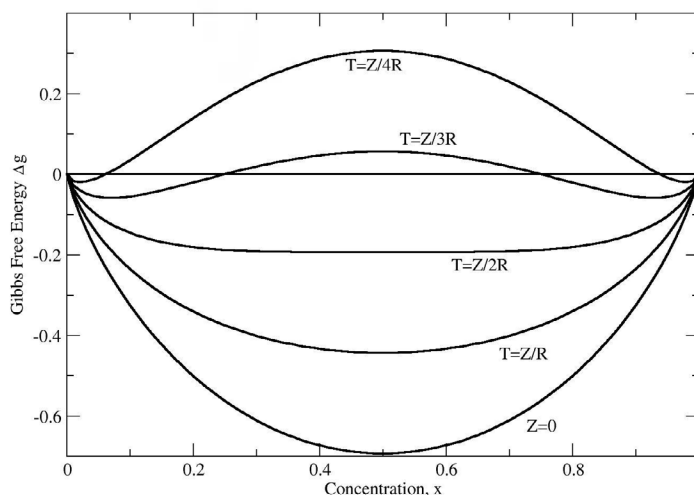
$$\Delta g = \Delta u + T\Delta s + \Delta P v$$

The change in entropy and  $Pv$  is the same as in the previous example (except the total is now 1 mole, so  $x_A + x_B = 1$ ), so we can write:

$$\Delta g = Zx_A x_B - RT(x_B \ln x_B + x_A \ln x_A)$$

The most stable structure is always the one which minimises  $\Delta g$ , i.e.

$$\frac{d\Delta g}{dx_A} = 0$$



For high temperatures, relative to the repulsion  $Z$ , the lowest Gibbs free energy can be read directly from the graph. For lower temperatures, there are *two* minima, and the lowest Gibbs free energy comes from a phase separation into A-rich and B-rich regions, the amount of each region being determined by the overall concentration via the lever rule.

Differentiating gives:

$$\frac{d\Delta g}{dx_A} = Z(1 - 2x_A) + RT \ln(x_A) - RT \ln(1 - x_A) = 0$$

which (via symbolic algebra package for  $Z=3RT$ ) has solutions at  $x=0.07, 0.5$  and  $0.93$ . The first and third are minima.

An approximate solution to the equation can be obtained by assuming that for small  $x_A$ :  $\ln(x_A) - \ln(1 - x_A) \approx \ln(x_A)$ ;  $(1 - 2x_A) \approx 1$ . Now

$$Z(1 - 2x_A) + RT \ln(x_A) = 0$$

or

$$x_A = \exp(-Z/RT)$$

This is always positive, so no matter how strongly the fluids repel, some solubility is always thermodynamically favoured. Notice also that solubility always increases with increasing temperature. There are limiting cases at  $x_A = 0, 1$ . These are not minima of the function but correspond to physical limits on concentration  $x_A$ . For an unphysical concentration, the equation for  $g$  gives a complex value.

*Aside:*  $x_A = \exp(-Z/RT)$  looks the same as the Boltzmann probability in statistical physics for finding a microstate with excess energy  $Z$ . But notice that the derivation from thermodynamics considered only macroscopic quantities.

The chemical potential in a mixture is given by the value of  $g$ . Substituting in the values at the turning points gives:

$$g_A = -0.058RT, +0.057RT, -0.058RT$$

The stable state is the one with minimum chemical potential.

By symmetry, the chemical potential of B will be the same as for A. Up to  $x=0.07$  this is a mixture of the two substances. For concentrations between 0.07 and 0.93, the lowest Gibbs free energy is obtained with a two-phase mixture of an A-rich and a B-rich fluid. Above  $x=0.93$  a single phase is obtained.  $x=0.07$  is the *solubility limit*.

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## 5. Supercool

Firstly, we calculate the  $\left(\frac{\partial\mu_L}{\partial X}\right)_T$ . Assume that we have an ideal solution at atmospheric pressure, then the partial pressure of water changes from  $P_0$  to  $P_0(1 - X)$ , and using the expression for an ideal solution, the chemical potential is reduced by

$$\mu(X, T) - \mu(0, T) = RT \ln(1 - X)$$

So that

$$\left(\frac{\partial\mu_L}{\partial X}\right)_T = \frac{-RT}{1 - X}$$

The general expression for a change in chemical potential at constant pressure is:

$$d\mu = \left(\frac{\partial\mu}{\partial T}\right)_{P, X} dT + \left(\frac{\partial\mu}{\partial X}\right)_{P, T} dX$$

Since  $d\mu = dg = -sdT + vdP$ , we can write

$$\left(\frac{\partial\mu}{\partial T}\right)_{P, X} = -s$$

and therefore

$$d\mu = -sdT - RTdX$$

On adding the salt, we must have the same change for liquid and ice  $d\mu_L = d\mu_I$ . Since  $dX = 0$  for the ice, equating the chemical potentials gives:

$$d\mu_l = -RTdX - s_l dT = d\mu_I = -s_I dT$$

The entropy difference is simply related to the latent heat by  $(s_I - s_l) = l/T$ , so we now have

$$\frac{dT}{dX} = -\frac{RT^2}{l} = -\frac{8.3 \times 273^2}{18000} = -33$$

so with a change  $\Delta X = 0.1$  we have a 3K drop in temperature.

In fact the temperature drop is bigger than this - the chemical bonding between water and salt lowers its chemical potential by more than the entropy of mixing. Notice that this drop in temperature is not due to a loss of energy (e.g. in an endothermic reaction). Some of the ice has melted and the latent heat absorbed in this process was extracted from the liquid.

## 6. Simplified Osmosis

Consider the two systems, inside and outside the cell. Since water molecules can pass through the cell wall, the chemical potential of water must be the same on both sides. Protein molecules cannot pass through the semipermeable membrane, so their chemical potential may be different.

Treating water and protein as ideal gases, the partial pressure of the water inside the cell is the same as the water pressure outside, 1atm. So the difference in pressure is just the partial pressure of the protein, which is 2% that of the water. Since the creature lives at the surface, the external pressure is 1atm, so the excess pressure is 0.02atm.

If we consider a hemisphere, then the net force due to excess pressure is balanced by the stress in the membrane.

$$\Delta P \times \pi r^2 = \sigma \times 2\pi r t$$

Rearranging to get stress, with diameter  $2r = 10^{-5}$ m and thickness  $10^{-8}$ m

$$\sigma = 0.02 \times 10^5 \times 10^{-5} / 10^{-8} = 2 \times 10^9 Pa$$

## 11 The Essential Mathematics:

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

The volume in an ideal gas is a function of two variables, e.g.  $V(T,P)$ . To fully evaluate the derivative, we need to know what quantity is being held constant. An isobaric expansion is different from an adiabatic one.

The ideal gas equation is  $PV = nRT$ , so the thermal expansion coefficient at constant  $P$  is

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

For the adiabatic expansion, we want to replace the explicit  $P$  by a constant, say  $K = PV^\gamma$ , so the ideal gas law is

$$KV^{1-\gamma} = nRT$$

and the adiabatic thermal expansion coefficient is:

$$\frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_K = \frac{1}{V} \left( \frac{nR}{K} \right)^{(1/(1-\gamma))} \frac{d(T^{1/(1-\gamma)})}{dT} = \frac{1}{(1-\gamma)T}$$

Which is actually negative! The two “thermal expansions” are different because they refer to different processes: in the first, familiar, case we describe an expansion due to heating without changing the pressure. The adiabatic case is a peculiar situation where we increase the temperature without supplying any heat. For an ideal gas, that means increasing the pressure and thus *reducing* to volume. Since  $\gamma > 1$  we see that  $\left(\frac{\partial V}{\partial T}\right)_P$  is positive, but  $\left(\frac{\partial V}{\partial T}\right)_K$  is negative for an ideal gas.

### 2. Exact differentials

Given  $X = PV^3 + aT$ , the constant  $a$  must have units of  $\text{Jm}^6/\text{K}$ . For an ideal gas  $PV = nRT$  so  $X = T(nRV^2 + a)$

$$\left( \frac{\partial X}{\partial T} \right)_V = nRV^2 + a$$

$$\frac{\partial}{\partial V} \left( \frac{\partial X}{\partial T} \right)_V = 2nRV$$

and

$$\left( \frac{\partial X}{\partial V} \right)_T = 2nRVT$$

$$\frac{\partial}{\partial T} \left( \frac{\partial X}{\partial V} \right)_T = 2nRV$$

The second derivative is the same, regardless of order of differentiation, hence  $X$  may be a state variable, although not a very useful one!

For Work, we can consider

$$\left( \frac{\partial W}{\partial P} \right)_V = 0$$

since no work is done at constant volume. However

$$\frac{\partial}{\partial P} \left( \frac{\partial W}{\partial V} \right)_P = \frac{\partial P}{\partial P} = 1$$

Thus the second differential  $\frac{\partial^2 W}{\partial P_V \partial V_P}$  does depend on order of integrations, and so work is not a state function.