

PHY2201 - Statistical Physics

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1 The Normalisation condition

If we have a probability function of

$$F(E) = Ae^{\frac{-E}{T}}$$

then the normalisation conditions states that:

$$\begin{aligned}\int_0^\infty F(E)dE &= 1 \\ \therefore \left[-TAe^{\frac{-E}{T}}\right]_0^{\infty} &= 1 \\ \therefore 0 + TA &= 1 \therefore A = \frac{1}{T}\end{aligned}$$

This is an exponential graph that rapidly decreases and plateaus near zero.

One useful equation is:

$$\int_0^\infty x^n e^{-x} dx = n!$$

2 First Law of Thermodynamics

$$\Delta U = Q - W \quad (1)$$

Where ΔU is the change in internal energy of the system (related to temperature), Q is the heat provided to the system and W is the work done **by** the system.

Note this may sometimes be written as $\Delta U = Q + W$ when W is defined as the work done **on** the system.

The differential forms:

$$dU = dQ - dW \quad (2)$$

$$dU = dQ - PdV \quad (3)$$

Remember that:

$$dU = C_V dT$$

Note that Portnoi takes the n in to the C_V term.

The d symbols mean the differentials are not exact and so they **are** dependent on the path taken. The First Law basically states the conservation of energy in thermodynamic systems and the differential form states that the change in internal energy is path-independent.

We can derive that $W = \int PdV$ as follows, we know that $W = \int F \cdot dL$ but $F = PA$ and $dL = dx$ therefore $W = \int PA dx = \int PdV$.

2.1 Exact Differentials

If a differential is exact then it does not depend on the path taken. So in the first law of thermodynamics, U is an exact differential meanwhile Q and W are not.

$$dG = \left(\frac{\partial G(x, y)}{\partial x} \right) dx + \left(\frac{\partial G(x, y)}{\partial y} \right) dy$$

So $A(x, y)dx + B(x, y)dy = dF$ is an exact differential only if:

$$\left(\frac{\partial B(x, y)}{\partial x} \right) = \left(\frac{\partial A(x, y)}{\partial y} \right)$$

2.2 The Derivation of the Adiabatic condition for a Van der Waal's gas

First Law: $\delta Q = dU + PdV$

For an ideal gas: Equation of state: $P = NkT$, $P = \frac{nRT}{V}$. Adiabatic condition: $PV^\gamma = k$

Van der Waal's equation of state: $P = \frac{RT}{V-B} - \frac{A}{V^2}$
 so $(P + \frac{A}{V^2}) = \frac{RT}{V-B}$, so $RT = (P + \frac{A}{V^2})(V - B)$.

Internal energy for Van der Waal's gas: $U = c_V T - \frac{A}{V}$

Adiabatic so $\delta Q = 0$, $\therefore \frac{\partial U}{\partial T} dT + \frac{\partial U}{\partial V} dV + PdV = 0$

$\therefore c_V dT + \frac{A}{V^2} dV + PdV = 0 = c_V dT + (\frac{A}{V^2} + P) dV$

$\therefore c_V dT = -(\frac{A}{V^2} + P) dV$, but from Van der Waal's equation of state: $\frac{A}{V^2} + P = \frac{RT}{V-B}$

$\therefore c_V dT = \frac{-RT}{V-B} dV \therefore \frac{c_V}{R} \frac{dT}{T} = \frac{-dV}{V-B}$

$\therefore \frac{c_V}{R} \ln(T) = -\ln(V-B) + c_1 \therefore \ln\left(T^{\frac{c_V}{R}}\right) + \ln(V-B) = c_1$

$\therefore \ln\left(T^{\frac{c_V}{R}}(V-B)\right) = c_1$, letting $e^{c_1} = c_2$, $\therefore (RT)^{\frac{c_V}{R}}(V-B) = c_2 R^{\frac{c_V}{R}} = c_3$

$\therefore (P + \frac{A}{V^2})^{\frac{c_V}{R}}(V-B)^{\frac{c_V}{R}}(V-B) = c_3 \therefore (P + \frac{A}{V^2})^{\frac{c_V}{R}}(V-B)^{\frac{c_V}{R}+1} = c_3$

$\therefore (P + \frac{A}{V^2})(V-B)^{\frac{R}{c_V}+1} = \text{const.} \therefore (P + \frac{A}{V^2})(V-B)^\gamma = \text{const. where } \gamma = \frac{R}{c_V} + 1$

Note that the ideal gas adiabatic condition is returned when $A=0$, $B=0$.

2.3 Heat Reservoirs

For questions on the number of heat reservoirs required simply remember that:

Adiabatic : requires **no** reservoirs.

Isothermal : requires **one** reservoir.

Isobaric : requires **infinite** reservoirs.

If you have a combination of these processes then the number of reservoirs required is that of the highest number required by a constituent process.

3 The Second Law

The first law demonstrates that a perpetual motion machine is impossible (due to conservation of energy) but fails to explain:

- The ease of converting work to heat but not vice versa.
- Why systems naturally tend to a state of disorder rather than order.

- Why heat only flows **down** a temperature gradient

Second law explains these by stating that the net entropy of the universe can never decrease.

4 Reversible and Irreversible processes

Irreversible processes:

- Have finite changes in the state variables: $P_0 = P_{gas} + \Delta P \gg P_{gas}$
- Have dissipative forces such as friction:
 $P_0 = P_{gas} + P_{friction}$

All real processes are irreversible!

Reversible processes (idealised) have infinitesimally small changes in the state variables.

i.e. $P_0 = P_{gas} + \delta P \approx P_{gas}$ They:

- Have a well-defined locus on P-V (or equivalent) diagrams.
- All mechanical work is quasi-static and frictionless
- Variables of state change infinitely slowly so the system is **always** in equilibrium.
- Can be reversed so that the original system **and** surroundings are restored.

5 The Carnot Cycle

$$\Delta U = Q - W \text{ and } \Delta U_{cyc} = 0 \therefore W = Q$$

$$Q = Q_1 + Q_2 = Q_1 - |Q_2| \therefore W = Q_1 + Q_2 = Q_1 - |Q_2|$$

$$W = W_{1 \rightarrow 2} + W_{2 \rightarrow 3} + W_{3 \rightarrow 4} + W_{4 \rightarrow 1}$$

$$\eta = \frac{W}{Q_1} \text{ thermal efficiency of the engine}$$

Note that isobaric processes require infinite heat reservoirs, isothermal processes require one heat reservoir and adiabatic requires no heat reservoirs.

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

From experiment it is impossible to build a heat engine with perfect efficiency i.e. $\eta = 1$ And so, by extension, Q_2 can never equal 0, and so absolute zero is unattainable.

5.1 The Kelvin Formulation of the Second Law of Thermodynamics

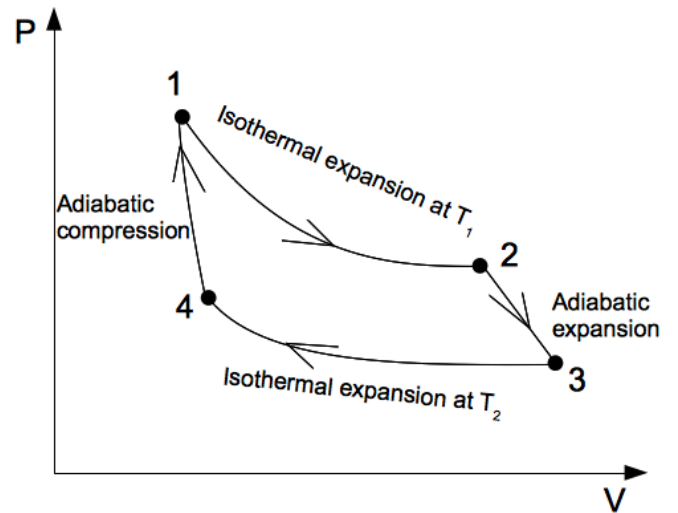
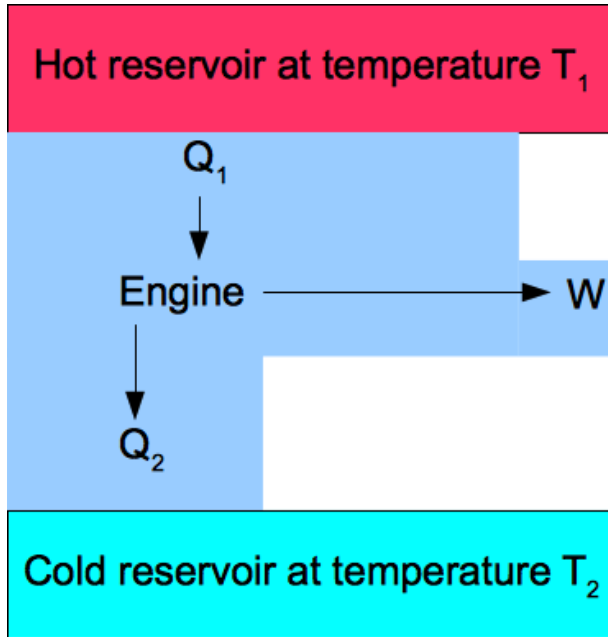
“No process is possible whose **sole** result is the extraction of heat from a single reservoir and the performance of an equivalent amount of work.” – Kelvin Formulation.

5.2 Thermal Efficiency of the Carnot Cycle

$$\text{For } 2 \rightarrow 3 : T_1 V_2^{\gamma-1} = T_2 V_3^{\gamma-1}$$

$$\text{For } 4 \rightarrow 1 : T_1 V_1^{\gamma-1} = T_2 V_4^{\gamma-1}$$

$$\left(\frac{V_2}{V_1}\right)^{\gamma-1} = \left(\frac{V_3}{V_4}\right)^{\gamma-1}$$



$$\begin{aligned} \frac{V_2}{V_1} &= \frac{V_3}{V_4} \\ \frac{|Q_2|}{Q_1} &= \frac{T_2 \ln(V_3/V_4)}{T_1 \ln(V_2/V_1)} = \frac{T_2}{T_1} \\ \eta &= 1 - \frac{|Q_2|}{Q_1} = 1 - \frac{T_2}{T_1} \end{aligned} \quad (4)$$

Where $\eta < 1$.

No engine can be more efficient than a Carnot cycle operating between the same two temperatures. Note that since $\eta < 1$, then $T_1 \neq 0$ and so the Second Law means absolute zero can never be attained.

Refrigerators use work to extract heat from a colder reservoir and transfer it to a hotter reservoir. Whilst heat pumps use a heat gradient to produce work. Note that $Q_1 = Q_H$ is the amount of heat put *in* to the system, whilst $Q_2 = Q_C$ is the amount of heat *extracted* from the system.

$$\eta_R = \frac{|Q_2|}{|W|} \quad \text{Coefficient of performance} \quad (5)$$

$$\eta_{HP} = \frac{|Q_1|}{|W|} = 1 + \eta_R \quad \text{for heat pumps} \quad (6)$$

i.e. The coefficient of performance for refrigerators is the heat extracted per work put in, whilst for heat pumps it is the heat put in per the amount of work extracted.

Note that η_R and η_{HP} can be greater than 1.

Example question

“You are asked to design a refrigerated warehouse to maintain perishable food at a temperature of 5 C in an external environment of up to 30 C. The size of the warehouse means that the refrigeration plant must extract heat at a rate of 1000 KW. What value of electrical consumption would you suggest as a working minimum?”

$$\begin{aligned} W &= Q_H - Q_C \quad \therefore \frac{W}{Q_C} = \frac{Q_H}{Q_C} - 1 = \frac{T_H}{T_C} - 1 \\ \therefore W &= Q_C \cdot \left(\frac{T_H}{T_C} - 1 \right) = 1000 \cdot \left(\frac{303.15}{278.15} - 1 \right) = 89.9 \text{ kW} \end{aligned}$$

The Clausius Formulation of the Second Law of Thermodynamics

“No process is possible whose **sole** result is the removal of heat from a reservoir at one temperature and the absorption of an equal quantity of heat by a reservoir at a higher temperature.” – Clausius Formulation.

i.e. work is required for refrigeration.

6 Entropy

For the Carnot cycle:

$$\eta = 1 - \frac{|Q_2|}{Q_1} = 1 + \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1}$$
$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0 \quad \therefore \quad \sum_i \frac{Q_i}{T_i} = 0$$

Since any reversible cyclic process can be approximated by an infinite number of Carnot cycles. By summing $\frac{Q}{T}$ for each of them we obtain:

$$\sum_i \frac{Q_i^{(R)}}{T_i} = \oint_C \frac{\delta Q^{(R)}}{T} = 0 \text{ for any **reversible** cyclic process.}$$

This means that $\frac{\delta Q^{(R)}}{T}$ is an exact differential. For an infinitesimal **reversible** change: $dS = \frac{\delta Q^{(R)}}{T}$ therefore:

$$\delta Q^{(R)} = T dS$$

(where S is the entropy of the system).

Note that dS is an exact differential and so the entropy, S , is a function of state like the internal energy U .

The change in entropy ΔS between two states is determined solely by the initial and final equilibrium states and not by the path taken between them.

$$\Delta S = S_2 - S_1 = \int_{(1)}^{(2)} \frac{\delta Q^{(R)}}{T}$$

6.1 Entropy and irreversible processes

The reversible Carnot engine has a maximal thermal efficiency, equal to the efficiency of any other reversible heat engine.

Comparing a reversible (R) and an irreversible (I) heat engine:

$$\eta_I = 1 + \frac{Q_2^{(I)}}{Q_1^{(I)}} \text{ and } \eta_R = 1 + \frac{Q_2^{(R)}}{Q_1^{(R)}} = 1 - \frac{T_2}{T_1}$$

$\eta_I < \eta_R$ (note that Q_2 is negative so $\eta < 1$)

So for irreversible processes:

$$\frac{Q_2^{(I)}}{Q_1^{(I)}} < -\frac{T_2}{T_1}$$
$$\therefore \frac{Q_2^{(I)}}{Q_1^{(I)}} + \frac{T_2}{T_1} < 0$$
$$\therefore \sum_i \frac{Q_i^{(I)}}{T_i} < 0 \quad \therefore \quad \oint_C \frac{\delta Q^{(I)}}{T} < 0$$

Compared to reversible processes:

$$\sum_i \frac{Q_i^{(R)}}{T_i} = 0 \quad \therefore \quad \oint_C \frac{\delta Q^{(R)}}{T} = 0$$

And so in general:

$$\oint_C \frac{\delta Q^{(R)}}{T} \leq 0 \quad (\text{where the equality only applies for reversible processes}).$$

In terms of entropy:

$$dS \geq \frac{\delta Q}{T} \quad \text{Clausius's inequality}$$

(where the equality only applies for reversible processes).

For a thermally isolated system (e.g. the Universe), $\delta Q = 0$ and so $dS \geq 0$ - the entropy can never decrease.

Note that entropy distinguishes between reversible and irreversible processes, helps determine the direction of natural processes and the equilibrium condition of a thermally isolated system (maximal entropy) and provides a natural direction to the time sequence of natural events.

When considering an example such as heating a water bath from a lower temperature T_1 to a higher temperature T_2 by placing it in warmer surroundings, the entropy change as always is given by $dS = \frac{\delta Q}{T}$ for the surroundings the temperature (assumed to be at the higher temperature, T_2) can be treated as a constant as the change will be minute and thus we obtain:

$$\Delta S_{\text{surroundings}} = \frac{1}{T_2} \int \bar{d}q = \frac{1}{T_2} \int_{T_1}^{T_2} C_v dT = \frac{1}{T_2} \int_{T_1}^{T_2} -C_v dT = \frac{-C_v(T_2 - T_1)}{T_2}$$

However, for the water bath its temperature is changing and thus it cannot be treated as a constant and must be included in the integral:

$$\Delta S_{\text{water}} = \int \frac{\bar{d}q}{T} = \int_{T_1}^{T_2} \frac{C_v dT}{T} = C_v \ln \left(\frac{T_2}{T_1} \right)$$

The total entropy change for the process is just given by

$$\Delta S = \Delta S_{\text{water}} + \Delta S_{\text{surroundings}} = C_v \left(\ln \left(\frac{T_2}{T_1} \right) - \frac{(T_2 - T_1)}{T_2} \right)$$

For a reversible process the change in entropy of the surroundings becomes

$$\Delta S_{\text{surroundings}} = -C_v \ln \left(\frac{T_2}{T_1} \right) \quad \therefore \quad \Delta S = 0$$

as reversible processes consist of infinitesimal changes and the entropy change for the reversible process must sum to zero.

6.2 Entropy and disorder

$dS \geq 0$ for a thermally isolated system, spontaneous processes proceed in the direction of increasing entropy.

E.g. Reversible (quasistatic) isothermal expansion of an ideal gas:

$$dU = 0 \quad \therefore \quad \delta Q = \delta W = PdV = nRT \frac{dV}{V}, \quad \frac{dV}{V} \propto \frac{\delta Q}{T} = dS$$

$\frac{dV}{V}$ is a measure of the increase in disorder, $\frac{dV}{V} \propto dS$

So this is why gases expand of their own accord.

$S = k \ln(\Omega)$ where Ω is the thermodynamic probability.

6.3 The Fundamental Thermodynamic Relationship (FTR)

$dU = \delta Q - \delta W$ (always), $\delta W = PdV$ (reversible), $\delta Q = TdS$ (reversible). So:

$$dU = TdS - PdV$$

Note that since all the variables are functions of state (exact differentials) this is true of all processes, not just reversible.

More generally: $dU = TdS - PdV + \sum_i X_i dx_i$ where $X_i dx_i = \begin{pmatrix} fdl \\ \sigma dA \\ \dots \end{pmatrix}$

From this we can prove why a system will expand spontaneously if able to, if there is no energy transfer. If there is no energy transfer then $dU = 0$ and so $TdS = PdV$ and $dS = \frac{PdV}{T}$ so:

$$\Delta S = \int_{\text{initial}}^{\text{final}} dS = \int_{V_1}^{V_1 + \Delta V} \frac{P}{T} dV$$

from $PV = nRT$ we see that $\frac{P}{T} = \frac{nR}{V}$, so:

$$\Delta S = \int_{V_1}^{V_1 + \Delta V} \frac{nR}{V} dV = nR \ln \frac{V_1 + \Delta V}{V_1}$$

And so an expansion means that $\Delta S > 0$, and so it will occur spontaneously.

7 Distribution functions

Discrete distributions

For discrete distributions, e.g. the number of students, n_i , achieving a particular mark s_i . Then the probability of a student receiving the i th mark is given by: $f_i = \frac{n_i}{N}$. Note that the sum of the probabilities must equal 1, i.e.

$$\sum_i f_i = \sum_i \frac{n_i}{N} = \frac{1}{N} \sum_i n_i = 1$$

This is the normalization condition. From this distribution equation many important characteristics can be determined:

$$\langle s \rangle = \frac{1}{N} \sum_i n_i s_i = \sum_i s_i f_i$$

$$\langle s^2 \rangle = \frac{1}{N} \sum_i s_i^2 n_i = \sum_i s_i^2 f_i$$

Note that $s_{\text{rms}} = \sqrt{\langle s^2 \rangle}$.

$$\langle g(s) \rangle = \frac{1}{N} \sum_i g(s_i) n_i = \sum_i g(s_i) f_i$$

Continuous distributions

For continuous distributions we must integrate instead of summing.

Let $f(h)$ be the probability density, e.g. the probability of someone having a height between h and $h + dh$. dN is the number of people with heights between h and $h + dh$:

$$dP = \frac{dN}{N} = f(h)dh$$

Note that the distribution must be normalized (since the person must have *some* height) and so:

$$\int f(h)dh = \int dP = 1$$

As with the discrete distributions, we can obtain many characteristics from the probability density:

$$\langle h \rangle = \int h f(h)dh$$

$$\langle h^2 \rangle = \int h^2 f(h)dh$$

$$\langle g(h) \rangle = \int g(h) f(h)dh$$

8 The Maxwell-Boltzmann Distribution

For the distribution of molecular speeds about the average, we expect:

- Mean $v_x = 0$ (no convection).
- The function is even.
- The number of molecules with $v_x \rightarrow \pm\infty$ is negligible.

Note that the first two points result from the fact there are the same number of molecules travelling left and right.

Let $f(v_x)$ be the velocity distribution function.

Then the probability that a molecule will have velocity between v_x and $v_x + dv_x$ is:

$$dP_{v_x} = \frac{dN}{N} = f(v_x)dv_x$$

And so the number of molecules with velocity between v_x and $v_x + dv_x$ is:

$$dN = N f(v_x)dv_x$$

Note that:

$$\int dN = \int_{-\infty}^{+\infty} N f(v_x)dv_x = N \int_{-\infty}^{+\infty} f(v_x)dv_x = N$$

And so as required by the normalization condition:

$$\int_{-\infty}^{+\infty} f(v_x)dv_x = 1$$

The Gaussian (normal) distribution meets all of the requirements. And so we let $f(v_x) = A e^{-B v_x^2}$. Note that A determines the height of the peak (and is specified in normalization) whilst B is inversely related to the width of the distribution.

8.1 Integrating the Gaussian

$$I = \int_{-\infty}^{+\infty} e^{-\alpha x^2} dx \quad \therefore \quad I^2 = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} e^{-\alpha(x^2+y^2)} dx dy$$

Substitute $r^2 = x^2 + y^2$ and translate the integral to 2D polars:

$$I^2 = \int_0^{2\pi} \int_{-\infty}^{+\infty} e^{-\alpha r^2} r dr d\phi \quad \therefore \quad I^2 = \frac{-1}{2} \cdot -1 \cdot \left[e^{-r^2} \right]_{-\infty}^{+\infty} \cdot 2\pi \cdot \frac{1}{\alpha}$$

$$\therefore I^2 = \frac{\pi}{\alpha} \quad \therefore \quad I = \sqrt{\frac{\pi}{\alpha}}$$

8.2 The Maxwell velocity distribution

Normalization:

$$\int_{-\infty}^{+\infty} f(v_x) dv_x = \int_{-\infty}^{+\infty} A e^{-B v_x^2} dv_x = 1$$

Using that $\int_{-\infty}^{+\infty} e^{-\alpha x^2} = \sqrt{\frac{\pi}{\alpha}}$:

$$\therefore 1 = A \sqrt{\frac{\pi}{B}} \quad \therefore A = \sqrt{\frac{B}{\pi}}$$

Physical meaning of B Calculate $\langle v_x^2 \rangle$:

$$\langle v_x^2 \rangle = \int_{-\infty}^{+\infty} v_x^2 f(v_x) dv_x = \sqrt{\frac{B}{\pi}} \int_{-\infty}^{+\infty} v_x^2 e^{-B v_x^2} dv_x$$

Using the fact that:

$$\int_{-\infty}^{+\infty} x^2 e^{-\beta x^2} dx = \frac{1}{2} \sqrt{\frac{\pi}{\beta^3}}$$

We obtain:

$$\langle v_x^2 \rangle = \sqrt{\frac{B}{\pi}} \cdot \frac{1}{2} \sqrt{\frac{\pi}{B^3}} = \frac{1}{2B}$$

From the *Equipartition Theorem* we know that:

$$\langle E_x \rangle = \frac{1}{2} m \langle v_x^2 \rangle = \frac{1}{2} kT$$

and so using this with the previous equation:

$$\frac{m}{4B} = \frac{kT}{2} \quad \therefore B = \frac{m}{2kT} \quad \text{note } B \propto \frac{1}{T}$$

For the distribution function we have:

$$f(v_x) = A e^{-B v_x^2} = \left(\frac{m}{2\pi kT} \right)^{\frac{1}{2}} e^{-\frac{m v_x^2}{2kT}}$$

8.3 In 3 dimensions

The probability a molecule will have a velocity between v_x and $v_x + dv_x$, v_y and $v_y + dv_y$, v_z and $v_z + dv_z$:

$$dP_{v_x, v_y, v_z} = \frac{dN}{N} = f(v_x) dv_x f(v_y) dv_y f(v_z) dv_z = f(v_x) f(v_y) f(v_z) dv_x dv_y dv_z$$

$$dP_{v_x, v_y, v_z} = \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} e^{-\frac{m(v_x^2 + v_y^2 + v_z^2)}{2kT}} dv_x dv_y dv_z$$

$$dP_{v_x, v_y, v_z} = \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} e^{-\frac{m(v^2)}{2kT}} dv_x dv_y dv_z$$

$$dP_{v_x, v_y, v_z} = f_1(v) dv_x dv_y dv_z$$

8.4 The Maxwell-Boltzmann speed distribution function

What is the probability of a molecule having a **speed** between v and $v + dv$. (Recall that $v^2 = v_x^2 + v_y^2 + v_z^2$):

$$dP_{v_x, v_y, v_z} = f_1(v) dv_x dv_y dv_z$$

Making this a volume for a shell:

$$\begin{aligned} dP_v &= f_1(v) 4\pi v^2 dv \\ dP_v &= 4\pi \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} v^2 e^{-\frac{mv^2}{2kT}} dv \\ \therefore f(\mathbf{v}) &= 4\pi \left(\frac{\mathbf{m}}{2\pi \mathbf{kT}} \right)^{\frac{3}{2}} \mathbf{v}^2 e^{-\frac{m\mathbf{v}^2}{2kT}} dv \end{aligned}$$

Note that $4\pi \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}}$ is the normalization constant, v^2 is the density of state which depends on the dimensionality of the space (it is a linear relation for 2D and a constant for 1D), $e^{-\frac{mv^2}{2kT}}$ is the most important part, the Boltzmann factor, which contains the energy $\frac{mv^2}{2}$ divided by kT .

Note that if this is applied to only 2 dimensions then it is simply an area rather than a volume and so we have a factor of $2\pi v$ instead of $4\pi v^2$.

8.4.1 Effect of temperature

$$f(v) = 4\pi \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} v^2 e^{-\frac{mv^2}{2kT}} dv$$

As T increases the distribution becomes wider and flatter (and the peak frequency lowers), and the peak speed shifts right towards higher speeds.

8.4.2 Useful Integrals and Integration Techniques

We have derived above by converting its square into polars that

$$\int_{-\infty}^{\infty} e^{-\alpha x^2} dx = \sqrt{\frac{\pi}{\alpha}}$$

If we then wish to solve $\int_{-\infty}^{\infty} x^2 e^{-\alpha x^2} dx$ we simply notice that if we integrate the function with respect to α we obtain $\int_{-\infty}^{\infty} -e^{-\alpha x^2} dx$ and so we may write

$$\int_{-\infty}^{\infty} x^2 e^{-\alpha x^2} dx = -\frac{d}{d\alpha} \int_{-\infty}^{\infty} e^{-\alpha x^2} dx = -\frac{d\sqrt{\frac{\pi}{\alpha}}}{d\alpha} = \frac{1}{2} \sqrt{\frac{\pi}{\alpha^3}}$$

This trick can be used for any even powers of x as you simply use higher order derivatives of α , note that as both functions (the x^2 and the $e^{-\alpha x^2}$) are even if we instead wish to integrate between 0 and positive infinity rather than between negative infinity and infinity we simply have to divide our result by 2.

We may use a somewhat similar trick which also involves substitution to integrate odd powers of x :

$$\begin{aligned} \int_0^{\infty} x^3 e^{-\alpha x^2} dx &= \int_0^{\infty} \frac{x^2}{2} e^{-\alpha x^2} dx^2 = \frac{1}{2} \int_0^{\infty} u e^{-u} du \\ &= \frac{1}{2} \frac{d}{d\alpha} \int_0^{\infty} e^{-\alpha u} du = \frac{1}{2} \cdot \frac{d}{d\alpha} \left[\frac{1}{\alpha} e^{-\alpha u} \right]_0^{\infty} \\ &= \frac{1}{2} \cdot \frac{d}{d\alpha} \left(\frac{-1}{\alpha} \right) = \frac{1}{2\alpha^2} \end{aligned}$$

8.4.3 Molecular speeds

Mean (average) speed:

$$\langle v \rangle = \int_0^{+\infty} v f(v) dv = 4\pi \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} \int_0^{+\infty} v^3 e^{\frac{-mv^2}{2kT}} dv$$

$$\therefore \langle \mathbf{v} \rangle = \sqrt{\frac{8kT}{\pi m}}$$

Root mean square (RMS) speed:

$$\langle v^2 \rangle = \int_0^{\infty} v^2 f(v) dv = 4\pi \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} \int_0^{\infty} v^4 e^{\frac{-mv^2}{2kT}} dv$$

$$\therefore v_{\text{rms}} = \sqrt{\langle v^2 \rangle} = \sqrt{\frac{3kT}{m}}$$

Note that this means $v_{\text{rms}}^2 = \frac{3kT}{m}$ and so $\frac{mv^2}{2} = \frac{3}{2}kT$ which is from the equipartition theorem.

Most probable speed:

In this case we want to differentiate the distribution. As this occurs at the maxima, i.e. $\frac{df(v)}{dv} = 0$:

$$\frac{df(v)}{dv} = 8\pi \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} v e^{\frac{-mv^2}{2kT}} - \frac{mv}{kT} \cdot 4\pi \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} v^2 e^{\frac{-mv^2}{2kT}} = 0$$

$$\therefore 2 = \frac{mv^2}{kT} \quad \therefore v_{\text{mp}} = \sqrt{\frac{2kT}{m}}$$

Note that:

$$v_{\text{mp}} < \langle v \rangle < v_{\text{rms}}$$

8.5 The Maxwell-Boltzmann Energy distribution function

The speed distribution function is:

$$dP_v = f(v)dv = 4\pi \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} v^2 e^{\frac{-mv^2}{2kT}} dv$$

By substituting $dE = mv dv$ and $v^2 = \frac{2E}{m}$, we can obtain the energy distribution function:

$$\mathbf{F}(\mathbf{E}) = \frac{2}{\sqrt{\pi}} (\mathbf{kT})^{-\frac{3}{2}} \mathbf{E}^{\frac{1}{2}} e^{\frac{-E}{kT}} d\mathbf{E}$$

Where $\frac{2}{\sqrt{\pi}} (kT)^{-\frac{3}{2}}$ is the normalization coefficient, $E^{\frac{1}{2}}$ is the density of state (and depends on the dimensionality), and $e^{\frac{-E}{kT}}$ is the Boltzmann factor.

In general the density of states factor may be written as $E^{\frac{d}{2}-1}$, where d is the number of dimensions. Note that in the 2D case there is no density of state for this function (i.e. it is a constant).

8.6 Example of the Boltzmann factor

Consider a mass of isothermal ideal gas with temperature T . For a thin slab of gas at height z_0 , thickness δz and cross-sectional area A to not fall under gravity requires (from hydrostatic equilibrium):

$$p(z_0)A - p(z_0 + \delta z)A = \rho(z_0)A\delta z g$$

$$\therefore p(z_0) - p(z_0 + \delta z) = \rho(z_0)\delta z g$$

Expanding $p(z)$ in a Taylor series:

$$p(z_0 + \delta z) = p(z_0) + \left. \frac{dp(z)}{dz} \right|_{z_0} \delta z + \frac{1}{2!} \left. \frac{d^2 p(z)}{dz^2} \right|_{z_0} \delta z^2 + \frac{1}{3!} \left. \frac{d^3 p(z)}{dz^3} \right|_{z_0} \delta z^3 + \dots O(\delta z^4)$$

In the limit that the slab thickness $\delta z \rightarrow 0$,

$$p(z_0 + dz) - p(z_0) = \left. \frac{dp(z)}{dz} \right|_{z_0} dz$$

$$\text{Hence, } \rho(z_0)g dz = - \left. \frac{dp(z)}{dz} \right|_{z_0} dz, \quad \rho(z)g = - \frac{dp(z)}{dz}, \quad \therefore \frac{dp(z)}{dz} = -n(z)m_A g$$

Where m_A is the mass of one gas atom and n is the number density of gas atoms.

Ideal gas equation of state $pV = Nk_B T \rightarrow p = \frac{N}{V}k_B T = nk_B T$ hence:

$$k_B T \frac{dn(z)}{dz} = -n(z)m_A g \rightarrow \frac{dn(z)}{dz} = -\frac{m_A g}{k_B T} n(z)$$

$$\therefore n(z) = n(z=0) \cdot e^{-\frac{m_A g}{k_B T} z}$$

Hence $n(z)$, $\rho(z)$ and $p(z)$ all fall exponentially with height.

Here $m_A g z$ is the *gravitational potential energy* of a gas atom at height z . Since $n(z) \propto$ probability of finding a gas atom at height z , suggests that the probability of finding a gas atom in an 'energy level' of value $\varepsilon(z)$ is proportional to $e^{-\frac{\varepsilon(z)}{k_B T}}$ which is the **Boltzmann Factor**

The Boltzmann Factor is of universal validity, whenever an ensemble of classical particles are in equilibrium at temperature T , the probability of an energy level of value $\varepsilon(z)$ being "occupied" by a particle of the ensemble varies as the negative exponential of $\frac{\varepsilon(z)}{k_B T}$

9 Of Microstates and Macrostates

9.1 The fundamental postulates of Statistical Mechanics

An ensemble of identical yet distinguishable objects may be described completely by specifying its microstate. The microstate is the most detailed description that can be provided. For an ideal gas of N particles one must provide $6N$ co-ordinates as one requires the position and velocity of each particle (in 3D there are 3 velocity and 3 position co-ordinates). For the Boltzmann energy sharing example it involves specifying the energy level occupied by each individual system.

Physically we observe only the corresponding macrostates which are specified by quantities which may be macroscopically observed. A macrostate for an ideal gas is specified fully by a few observable quantities such as pressure, temperature, volume, entropy etc. For the example of Boltzmann energy sharing the macrostate is the occupancies of the various energy levels e.g. 6 particles in energy level 0 and one particle in energy level 7, without regard to which particles are in which energy levels.

If we observe an ensemble over time random perturbations ensure that all accessible microstates will occur with equal probability and thus the probability of any given macrostate occurring is simply the number of microstates corresponding to that macrostate divided by the total number of macrostates.

The macrostate with the highest probability of occurrence corresponds to the equilibrium state.

9.2 Boltzmann energy sharing

Let us assume we have seven identical and yet distinguishable objects (A,B,C,D,E,F,G) with quantized energy levels available to them ($\varepsilon_0, \varepsilon_1, \varepsilon_2, \varepsilon_3, \varepsilon_4, \varepsilon_5, \varepsilon_6, \varepsilon_7 \dots$). The system as a whole has a total energy of 7 which must be distributed amongst the objects.

One configuration would be to have A in level 7 and the rest in level 0, another configuration would be to have B in level 7 and the rest in level 0. Whilst these two microstates are distinct as A and B are different objects, they are the same macrostate as they both correspond to the energy distribution of the system of [6 0 0 0 0 0 1].

If we denote the number of systems in any given energy level ε_i as n_i , then Ω , the number of possible microstates corresponding to this macrostate is given by:

$$\Omega = \frac{N!}{\prod_{i=0}^{\infty} (n_i!)}$$

where N is the total number of objects (in real life this is just particles).

We also have the constraints $\sum_{i=0}^{\infty} n_i = N$ and $\sum_{i=0}^{\infty} n_i \cdot \varepsilon_i = U$ where N is the total energy of the system.

It can thus be calculated that for the above system the total number of microstates is 1716. However as the probability of a given macrostate is given by the number of microstates that lead to it divided by the total possible number of microstates, it would be very useful to be able to calculate the total number of microstates without having to sum all of the microstates belonging to each possible macrostate.

To do this instead of considering how we would distribute the objects into the energy levels such that the total energy is 7, we imagine that we have 7 energy quanta to divide up amongst 7 objects. To divide a pile of 7 bricks up into 7 distinguishable groups (one group for each particle) requires 6 partitions. If we imagine instead having a pile of 6 partitions and 7 energy quanta then any arrangement of this pile is a valid configuration of the system (A valid microstate). And so assuming that quanta and partitions are simply indistinguishable objects we obtain the result that the number of microstates = $\frac{(7+6)!}{7!6!} = 1716$

In general the number of ways we can distribute N packets of energy over k objects is:

$$\frac{(N + k - 1)!}{N!(k - 1)!}$$

And thus this is the total number of microstates of the system.

9.3 Boltzmann Distribution (redux)

We wish to maximise $\Omega = \frac{N!}{\prod_{i=0}^{\infty} (n_i!)}$ subject to the constraints $\sum_{i=0}^{\infty} n_i = N$ and $\sum_{i=0}^{\infty} n_i \varepsilon_i = U$

The maximisation is achieved via the use of complicated Lagrange Undetermined Multipliers combined with Stirling's Approximation, it is too complicated to be covered here.

But we do need to know Stirling's Approximation:

$$\ln(n!) \approx n \ln(n) - n + 1$$

But the +1 is often ignored as it is negligible for large n.

The solution is: $\frac{n_i}{N} = \frac{e^{-\beta\epsilon_i}}{\sum_{i=0}^{\infty} e^{-\beta\epsilon_i}}$ where $\beta = \frac{1}{k_B T}$ thus:

$$\frac{n_i}{N} = \frac{e^{\frac{-\epsilon_i}{k_B T}}}{\sum_{i=0}^{\infty} e^{\frac{-\epsilon_i}{k_B T}}}$$

$\frac{n_i}{N}$ is the probability that a state of energy ϵ_i is occupied by a member of an ensemble which is in thermal equilibrium at temperature T.

9.3.1 Example

Ensemble of N gas atoms. Outer electron can be in ground state or in excited state which is 1 eV above ground state. At 1000K what fraction of atoms lie in the excited state relative to the ground state? We simply want the ratio $\frac{n_2}{n_1}$ so using the previous result...

$$\frac{n_2}{n_1} = \frac{e^{\frac{-\epsilon_2}{k_B T}}}{\sum_{i=0}^{\infty} e^{\frac{-\epsilon_i}{k_B T}}} \cdot \frac{\sum_{i=0}^{\infty} e^{\frac{-\epsilon_i}{k_B T}}}{e^{\frac{-\epsilon_1}{k_B T}}} = e^{\frac{-(\epsilon_2 - \epsilon_1)}{k_B T}}$$

Thus with $\Delta\epsilon = \epsilon_2 - \epsilon_1$ we obtain

$$\frac{n_2}{n_1} = e^{\frac{-\Delta\epsilon}{k_B T}}$$

Subbing in the values for $T = 1000K$, $\Delta\epsilon = 1.6 \times 10^{-19} J$, $k_B = 1.38 \times 10^{-23} JK^{-1}$ (a good rule of thumb is that at room temperature (300K) the thermal energy is $k_B T = 25 meV$ we obtain:

$$\frac{n_2}{n_1} = 6 \times 10^{-6}$$

For a temperature of 300K we obtain:

$$\frac{n_2}{n_1} = 4 \times 10^{-18}$$

and thus there is a very strong T-dependence!

9.4 Magnetic example

There is an ensemble of protons, with magnetic moment μ , in an external magnetic field, B . The magnetostatic potential energy is $+\mu B$ if the proton spin is anti-parallel to the field and $-\mu B$ if the spin is parallel to the field.

At equilibrium what is the net imbalance between spin aligned and spin anti-aligned protons (i.e. the *fractional magnetization*) at room temperature?

$$\frac{n_{\uparrow} - n_{\downarrow}}{n_{\uparrow} + n_{\downarrow}} = \frac{1 - n_{\downarrow}/n_{\uparrow}}{1 + n_{\downarrow}/n_{\uparrow}} = \frac{1 - e^{\frac{-(\epsilon_1 - \epsilon_0)}{kT}}}{1 + e^{\frac{-(\epsilon_1 - \epsilon_0)}{kT}}} = \frac{1 - e^{\frac{-2\mu B}{kT}}}{1 + e^{\frac{-2\mu B}{kT}}}$$

For protons: $\mu = 1.46 \times 10^{-26} JT^{-1}$, let $B = 1 T$, $T = 300 K$, and so $2\mu B = 2.9 \times 10^{-26}$, $kT = 3.12 \times 10^{-21} J$.

Since $2\mu B \ll kT$:

$$e^{\frac{-2\mu B}{kT}} = 1 - \frac{2\mu B}{kT}$$

$$\therefore \frac{n_{\uparrow} - n_{\downarrow}}{n_{\uparrow} + n_{\downarrow}} = \frac{\mu B}{kT}$$

So at 300K and 1T the net imbalance of spins is $1.46 \times 10^{-26} / 3.12 \times 10^{-21} = 4.7 \times 10^{-6}$. i.e. it is very *small*.

9.5 Degeneracy

Degeneracy refers to the fact that more than one state can correspond to the same energy level. For example in the case of the energy levels of an electron the state is described by the quantum numbers n (the principle quantum number) and s (the spin). In the absence of an external magnetic field the energy of the spin-up/spin-down states are equal and thus a state of $n=1$ $s=1/2$ corresponds to the same energy level as the state of $n=1$ $s=-1/2$. Thus the energy level is said to be two fold degenerate (degeneracy factor $g=2$).

This obviously affects the probability of finding certain energy levels. We already know that the probability of finding a particular microstate is:

$$\frac{n_i}{N} = \frac{e^{\frac{-\epsilon_i}{k_B T}}}{\sum_{i=0}^{\infty} e^{\frac{-\epsilon_i}{k_B T}}}$$

Thus the probability of finding any particular energy level is given by:

$$\frac{n_i}{N} = \frac{g_i e^{\frac{-\epsilon_i}{k_B T}}}{\sum_{i=0}^{\infty} g_i e^{\frac{-\epsilon_i}{k_B T}}}$$

Note that if we have different types of degeneracy we must multiply them together, e.g. if we have a three-fold spatial degeneracy and a two-fold spin degeneracy, then the total degeneracy is $2 \times 3 = 6$.

9.5.1 Example

The 1st excited energy level of He lies 19.82 eV above the ground state and is 3-fold degenerate. What is the population ratio between the ground state (which is not degenerate) and the 1st excited level, when a gas of He is maintained at 10,000K?

$$\frac{p(\epsilon_1)}{p(\epsilon_2)} = \frac{g_1}{g_0} e^{-\frac{\Delta\epsilon}{k_B T}} = 3 \times e^{-\frac{19.82 \times 1.6 \times 10^{-19}}{1.38 \times 10^{-23} \times 10^4}} = 3 \times 10^{-10}$$

10 Microscopic Interpretation of Entropy

If two identical ensembles of particles are separated from one another by a diathermal boundary (i.e. they share energy but cannot move from one side of the boundary to the other) then the most probable macrostate is that in which the total energy of the two ensembles is equally shared between them.

Over time, the ensembles will spontaneously evolve via random interactions to 'visit' all accessible microstates with equal probability (the fact that all microstates are equally probable to occur is assumed, a-priori). If initially in a macrostate of low Ω_{total} it is therefore overwhelmingly likely that at a future time they will be found in a macrostate of high Ω_{total} .

This is summarised in the 2nd Law: Systems spontaneously evolve from a state of low S to a state of higher S .

$$S = k_B \ln \Omega$$

This is the Boltzmann/Planck Hypothesis of 1905 which defines statistical entropy.

Clausius's S ('classical' thermodynamical entropy) is an extensive variable/function of state i.e. given two ensembles a and b, $S_{total} = S_a + S_b$
Statistically, $\Omega_{total} = \Omega_a \times \Omega_b$

$$\begin{aligned} S_{total} &= k_B \ln \Omega_{total} \\ &= k_B \ln \Omega_a \Omega_b \\ &= k_B \ln \Omega_a + k_B \ln \Omega_b \\ &= S_a + S_b \end{aligned}$$

Thus statistical entropy is also extensive.

Extensive variables are variables which increase with the system size.

Intensive variables do not increase with the system size.

Extensive	Intensive
Mass	Density
Energy	Temperature
Entropy	Pressure
Volume	Specific heat capacity (per mole), C_v
Heat Capacity (total), nC_v *	

*Note that sometimes Misha refers to the heat capacity total using C_v rather than nC_v in some derivations.

The equilibrium macrostate has the highest value of $\ln \Omega$ and therefore we may derive that:

$$\frac{dS_{LHS}}{d\varepsilon_{LHS}} = \frac{dS_{RHS}}{d\varepsilon_{RHS}}$$

for any two identical ensembles of particles separated by a diathermal boundary (i.e. on the LHS and RHS respectively)

Intuitively, equilibrium implies equal 'temperature' for the ensembles. Combined with dimensional arguments ($[S]/[\varepsilon] = K^{-1}$) suggests that:

$$\frac{dS}{d\varepsilon} = \frac{1}{T}$$

for any system.

Since we considered the energy levels to be fixed we implicitly assumed that V was constant (as Quantum Mechanics predicts energy spacing increases as size of well decreases), thus formally:

$$\left(\frac{dS}{d\varepsilon} \right)_V = \frac{1}{T} \quad (7)$$

11 Maxwell relations

Classically we expect $U=U(T)$ for an ideal gas but Joule observed slight cooling during isoenergetic expansion of a real gas. Suggests we need other variables to fully define U.

If we recall the Fundamental Thermodynamic Relationship:

$$dU = TdS - pdV$$

and that for any general function

$$df(x, y) = \left(\frac{\partial f(x, y)}{\partial x} \right)_y dx + \left(\frac{\partial f(x, y)}{\partial y} \right)_x dy$$

This suggests that $U = U(S, V)$ and:

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

Notice that the first relation is the same as that found earlier(7).

S and V are the **Natural Variables** of U . By considering the fact that:

$$\frac{\partial^2 U}{\partial V \partial S} = \frac{\partial^2 U}{\partial S \partial V}$$

We obtain the **First Maxwell Relation**:

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

11.1 The Joule-Thompson Process

In the Joule-Thompson(Joule-Kelvin) process there is obstructed flow of gas from a uniform high pressure to a uniform low pressure through a semi-permeable 'porous plug'. A small mass of gas Δm traverses the obstruction: initial pressure p_1 , volume V_1 , internal energy U_1 , final pressure p_2 , volume V_2 , internal energy U_2 . The process is adiabatic thus $q=0$.

The total work done is simply $-p_1(0 - V_1) - p_2(V_2 - 0)$. Since the process is adiabatic, 1st law implies: $U_2 - U_1 = p_1 V_1 - p_2 V_2$ hence $U_1 + p_1 V_1 = U_2 + p_2 V_2$ so we may define a $U+pV$ as a new constant, H thus $H = U + pV$.

Therefore $H_1 = H_2$ where H_1 is the enthalpy of the small mass of gas Δm before traversing the obstruction, ditto H_2 .

Therefore enthalpy is conserved in the J-T process, i.e. J-T expansion is **isenthalpic**.

Differentiating:

$$dH = dU + p dV + V dp$$

but since $dU = T ds + V dp$ we may obtain:

$$dH = T dS + V dp$$

Hence $H = H(S, p)$, i.e. H has natural variables S and P . Using the same methods of partial derivatives as with $U(S, V)$ we obtain:

$$\left(\frac{\partial H}{\partial S}\right)_p = T \quad \left(\frac{\partial H}{\partial p}\right)_S = V$$

And similarly by equating the cross-derivatives we obtain the **Second Maxwell Relation**:

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$$

For n moles of an ideal gas $U = \frac{3}{2}nRT$ and $pV = nRT$.

$$\therefore H = \frac{5}{2}nRT$$

Therefore for an ideal gas $H=H(T)$ and thus the J-T process does NOT cool an ideal gas (as H constant implies T constant).

Since $dH = TdS + Vdp$ for a reversible isobaric process ($dp = 0$) we obtain: $dH = TdS = \delta Q$. Therefore H represents the heat flow during a reversible isobaric process so $dH = C_p dT$ in an analogous manner to how $dU = C_v dT$ as U represents the heat flow during an isochoric process.

This means that H is useful in studying processes that occur at constant pressure such as chemical reactions in open containers.

$$\alpha_{JT} = \left(\frac{\partial T}{\partial p} \right)_H = - \frac{(\partial H / \partial p)_T}{(\partial H / \partial T)_p}$$

Since $H = U + pV$:

$$\frac{- \left(\frac{\partial U}{\partial p} \right)_T - \left(\frac{\partial (pV)}{\partial p} \right)_T}{C_p}$$

However as $(\partial U / \partial p)_T$ in this relation can not be obtained from measurements or from the equation of state. Therefore, a more convenient form for α_{JT} follows from the relation:

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

so:

$$\alpha_{JT} = \frac{1}{C_p} \left[T \left(\frac{\partial V}{\partial T} \right)_p - V \right]$$

It is easy to see that for an ideal gas α_{JT} vanishes. The equation of state for one mole of a real gas can be written (via virial expansion) as:

$$pV = RT \left[1 + \frac{B_2}{V} + \frac{B_3}{V^2} + \dots \right]$$

so for a gas of low density (keeping terms up to B_2 only) we obtain

$$pV = RT + B_2(T)p$$

therefore

$$\alpha_{JT} = \frac{T \frac{dB_2(T)}{dT} - B_2(T)}{C_p}$$

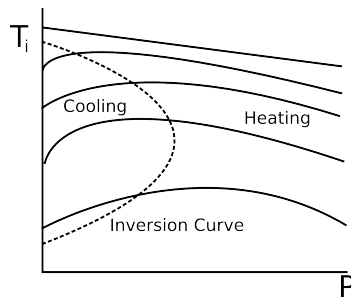


Figure 1: Curves of constant enthalpy. The dashed curve is the inversion curve on it $(\partial T / \partial p)_H = 0$. Inside it the gas is warmed on JT expansion whilst outside it the gas is cooled on JT expansion.

Inversion temperatures of some gases:

gas	He	H_2	N_2	Ar	O_2
$T_i(K)$	23.6	195	621	723	893

JT process can cool (and ultimately liquefy) O_2 and N_2 directly. Must pre-cool H_2 and He e.g. by heat exchange with liquified N_2 .

JT expansion is a step in the "Linde Liquefaction Cycle". Very widely used to manufacture cryogenics, rocket fuel etc.

12 Thermodynamic Potentials