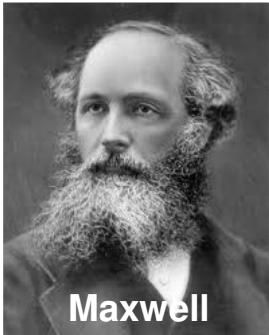
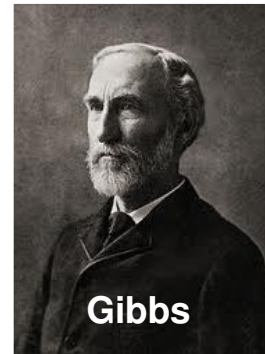


Helmholtz

Analytical thermodynamics



Maxwell



Gibbs

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Chapter 3

Analytical Thermodynamics

3.1 Overview

3.2 Thermodynamic Potentials

***Internal Energy, Enthalpy, Helmholtz, Gibbs
Free Energy***

3.3 Maxwell Relations

3.4 Applications of Analytical Thermodynamics

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3.1 Overview: The story so far

- **We have established a series of interdependent thermodynamic variables** – some obvious, (e.g. P, V, N) and some derived using the 0th (T) 1st (U) and 2nd (S) laws,
- For simplicity we have considered mainly pdV work – but remember that there are many other work possible terms ($fdl, \gamma dA...$)
- In particular **the second law** has enabled us to define a new and very useful state variable: $S = \int dQ_{rev}/T$ that tells us what can actually happen. (We have to wait for the 3rd law to get constant of integration)
- We have recognised that some processes may be described as **reversible** – these can go by infinitesimal steps either way. For these $dS_{universe} = 0$. If a process is irreversible then it has to go in the direction where small steps give $dS_{universe} > 0$.
- The most work is obtained/least work required for a reversible processes.
- **Law of conservation of energy**, transformed into state variables, and extended to include 'dN' by using the principle that defining box size, contents and energy define a system in equilibrium gives us **the master equation**: $dU = TdS - pdV + \mu dN$ – the entry point for using maths in thermodynamics '**Analytical Thermodynamics**'.

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The role of entropy in thermodynamics

- A key feature of multiparticle systems is irreversible behavior, which pretty much by definition of 'irreversible' means that the direction of a reversible change is a function of the states of the system, and entropy is the state function that quantifies this 'irreversibility'.
- Irreversible behaviour occurs when a multiparticle system can move to a more likely state (e.g. fill a box). It turns out that, when properly defined, all microstates are equally likely (every bit of the box is as likely as the others) – unless you have to worry about energy differences (fewer molecules at top of room than bottom) – so the irreversible behaviour relates to the number of microstates in the start and end macrostates.
- The relative probability of a macrostate can be encoded into a state function: entropy.
- People stumbled upon this state function when they looked carefully at the way state functions behave in reversible and irreversible processes, and found it to be defined by its change, given as the heat transferred to a system in a reversible process divided by the temperature of the system:

$$dS = \frac{dQ_{rev}}{T}$$

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Setting up the master equation

- The master equation is obtained by considering a reversible path between states to transform the 1st law (conservation of energy: $dU = \delta Q + \delta W$) to a relation between in state variables.
- The heat transfer term relates to the entropy change: $\delta Q_{rev} = TdS$
- You have to include in the work term all the different ways work can be done on the particular system of interest. So if you have a drop of liquid you would have to add in a term to do with the surface area of the drop – which will change if you deform the drop away from spherical, giving $dU = TdS - pdV + \gamma dA$ where γ is the surface tension.
- As originally conceived, the first law is set up for closed systems –no particle transfer. You can, however, change the energy stored in a party balloon not just by heat/cooling it and by changing the pressure outside it so it expands/contracts – but also by blowing more gas in – and this gives rise to an extra term, giving the master equation for a box filled with ‘stuff’ of a certain volume, no of particles and energy:

$$dU = TdS - pdV + \mu dN$$

- It is perhaps helpful to realize that the master equation is actually a re-arrangement of the expression for the change in entropy of a system in terms of changes in the variables (total energy, box size, box contents) that define its state.

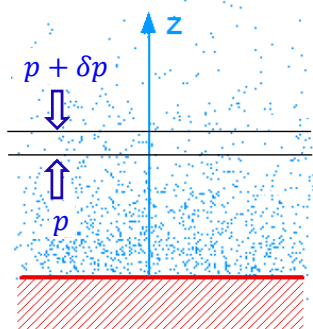
$$dS = \frac{dU}{T} + \frac{p}{T}dV - \frac{\mu}{T}dN$$

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Basic classical phenomenology: KE, PE and space

- In classical mechanics, an equilibrium state of a system is a local potential energy minimum: dissipation mechanisms are assumed/proposed to be present that remove KE from the system (usually conversion to heat).
- For multi-particle systems in flux, KE is not dissipated. The state of a system depends on both the PE and KE in the system: the KE makes it spread out to higher PE places.

Considered an ‘isothermal atmosphere’: a horizontal slice of gas, (molecules mass m) is in equilibrium – so equating the pressure drop across the slice to the weight of the slice gives:



Slice area A , thickness δz , density ρ .

$$A\delta p = -g\rho A\delta z$$

and $pV = Nk_B T \Rightarrow \rho = \frac{mN}{V} = \frac{mp}{k_B T}$

$$\delta p = -g \frac{mp}{k_B T} \delta z \Rightarrow p = p_0 e^{-\frac{mgz}{k_B T}}$$

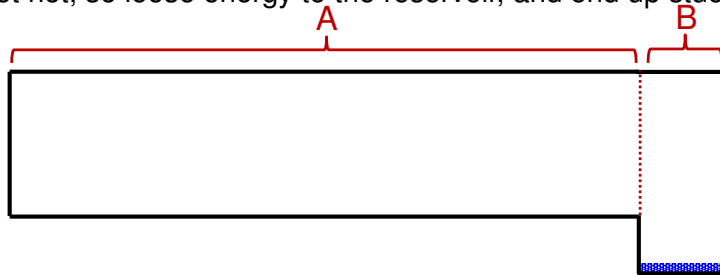
So, at very low temperature all the gas in a box would be at the bottom of a box (lowest PE) – but as temperature rises there is a trade-off between KE of the molecules and PE – and we will show this can be handled with no knowledge of the internal workings of the gas by a thermodynamic potential G which includes this KE effect as well as the PE.

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Trading off KE, PE and space

- Consider a box, where one small part is lower than the rest:

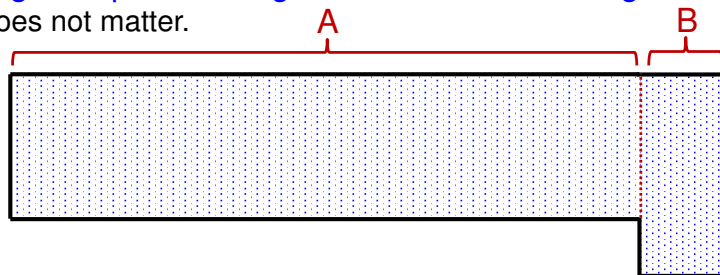
Low temperature – all gas in ‘low energy’ part of box, B’: temperature is low, so KE is low, so behaviour determined completely by PE – note we are assuming the box is connected to a thermal reservoir – so if all the particles start in A, when they diffuse to B they increase in KE, get hot, so lose energy to the reservoir, and end up stuck in B.



$$p = p_0 e^{-\frac{mgz}{kT}}$$

T low, so strong exponential decay – so all gas at low point in B side of box

High temperature – gas distributed according to volume: KE is high so gravitational PE does not matter.



$$p = p_0 e^{-\frac{mgz}{kT}}$$

T high, so exponential factor essentially one – pressure uniform throughout box.

Thermodynamic potentials can handle variation the tradeoff between KE, PE and ‘space’ to derive the distribution of molecules between A and B with no knowledge of what a gas is or how it ‘works’.

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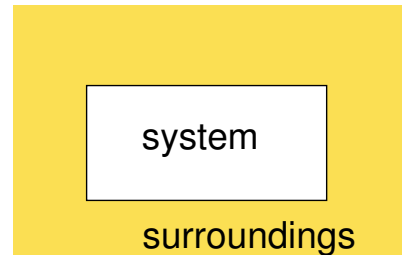
How do thermodynamic potentials work

- How a multiparticle system behaves, from a classical mechanics point of view is a function of the basic interaction forces (potential energy), the kinetic energy (relativises the importance of the potential energy) and how much ‘space’ there is in which the particles have to move in. Quantum mechanically it boils down to the nature of the eigen states of the Hamiltonian – and in particular their energy, and the spacing of the states energy: the larger the box, the closer, in general, the energies of the eigen states will be.
- We are interested in macro states established at least locally as ‘equilibrium’ macro states via microscopic fluctuations – these are the ones described by state variables – and how one can move from one such state to another. **A condition for equilibrium is that for small displacements away from it the entropy does not change and we use this to quantify the ‘trade-off’ between KE, PE and space through the entropy of the system and its surroundings.**
- The interactions between the particles is more often than not too complicated for us to accurately model the statistics of the classical or quantum mechanical states of the system directly. For real systems, however, the entropy and internal energy can be determined relatively easily from heat capacity measurements, and then we can work out how the system will behave from these with ‘analytical thermodynamics’ – thermodynamic formulae etc.
- For a system in contact with its surroundings (for example kept at constant temperature or pressure) we have to factor in how the entropy of the surroundings will change due to heat/volume/particle transfer when our system changes.
- We shall see that the thermodynamic potentials are constructed in a very ingenious way so that, under certain circumstances (eg temperature held constant by connection to a reservoir) although they are written in terms of the state function of the system, changes in them allow for the entropy changes in the reservoir induced when our system changes.

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Systems and surroundings

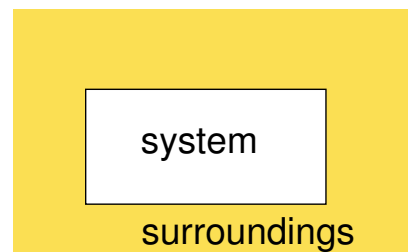
- We start by considering isolated systems, but then realise that the real interest is often how the system changes when connected to the outside world – heat transfer, particles diffusing in or out, or a volume (implies a complimentary decrease in volume of what is outside).
- Our primary interest, however, is in the system, so we make the simplifying assumption that the ‘surroundings’ are actually a ‘reservoir’, so large that their (assumed uniform) intensive variables (T , p , μ) are not changed when heat, volume or particles are transferred to or from them. This is often actually the case: the atmosphere acts pretty much as such a reservoir.
- Initially we considered isolated systems – which means their properties are defined by the conserved, extensive, variables – energy, volume and (particle) contents. We can also specify the state of a system by putting it in contact with a reservoir so that heat, volume and particles diffuse too and fro until the intensive variables (T , p , μ) of the system match those of the reservoir. (If no extensive system variable is specified, however, the system size would ‘diffuse’ without limit.)
- We can put both system and reservoir in ‘the ‘isolation box’, and within the box, global conservation laws apply, and the entropy can only increase.



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Systems and surroundings : terminology

- We need to specify the exact nature of **boundaries**, e.g. do they allow energy or particle exchange.
- If the system is “**thermally isolated**” (no heat flow) any change will be **adiabatic**. (NB an adiabatic change is not necessarily reversible, e.g. Joule expansion.)
- If heat flow is allowed, the system is in “**thermal contact**” with its surroundings. Once heat flow stops, the system is in “**thermal equilibrium**” with the surroundings.
- We can define systems according to whether they allow **flow of particles and/or energy**:
 - An **open system** is one in which particles and energy can move between the system and its surroundings.
 - A **closed system** is one in which particles do not flow between the system and its surroundings, but energy can.
 - In **isolated systems**, no energy or particles can flow between the system and its surroundings.
 - **In this course we will mostly be talking about closed systems:** the Part II course completes the picture by extending the ideas about heat flow developed in this course to include the motion of particles between the system and its surroundings.



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3.2 Thermodynamic Potentials: e.g. $U(S,V,N)$

- 'Analytical thermodynamics' sets up a scheme of equations which establishes a whole set of connections between state functions, and define the properties of systems in equilibrium, as well as reversible and irreversible processes.
- Analytical thermodynamics is based on a set of 'thermodynamic potentials', from each of which all relevant state functions (*i.e.* the ones needed to set up the master equation for that system) can be derived, and the derivatives of which under specific conditions have particular uses.
- These thermodynamic potentials are system specific: they contain all the 'relevant information' about the thermodynamical behaviour of that particular system.
- These thermodynamic potentials are derived from the (internal) energy $U(S,V,N)$, the primary thermodynamic potential, which is the integral of the master equation - which is why derivatives of $U(S,V,N)$ give you everything you want: all relevant variables are in the master equation. To integrate the master equation you need the equations of state for the constituents – e.g. $pV = nRT$ for an ideal gas.
- In this course we focus mainly on closed systems: ones containing a constant number of particles – so in general we don't worry about the ' N ' dependence of these functions – and we often write the internal energy as just $U(S,V)$
- We consider primarily ' pdV ' work (shortened to ' pV ' work) – if other terms are needed, either replace the ' pV ' ones if volume changes are not relevant (or important) , or add them if volume changes matter.

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Thermodynamic Potentials: completeness

- U is an example of a thermodynamic potential. In mechanics, forces can be derived from the gradient of potentials and similarly thermodynamic variables can be deduced from partial derivatives of thermodynamic potentials. **For $U(S,V,N)$ we already know S , V and N** , and can derive all the other relevant related variables (*i.e.* the other ones in the master equation) since:

$$dU = TdS - pdV + \mu dN$$

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

Hence: $T = \left(\frac{\partial U}{\partial S}\right)_{V,N}$ $p = -\left(\frac{\partial U}{\partial V}\right)_{S,N}$ $\mu = \left(\frac{\partial U}{\partial N}\right)_{V,S}$

- Thus we can say that $U(S,V,N)$ gives complete thermodynamic information about the system and variables. S , V and N are described as the 'natural variables' for U since they are the ones that are required to make this work.

(Of course, again, this 'completeness' relies on the master equation being set up to fit the system and that relevant forms of work have been included - if a ' γdA ' term is not in the master equation you are not going to get surface tension (γ) out of your expression for U !)

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‘Completeness’- a counter example

- Suppose we have U give in terms of T, V and N i.e. $U(T, V, N)$ and want to find S . Although the state of the system is uniquely defined, in the absence of a (material dependent) equation of state, the master equation (in some form or another) is the only one that gives the relation between thermodynamic variables:

$$dU = TdS - pdV + \mu dN$$

and rearranging gives: $dS = \frac{dU}{T} + \frac{p}{T}dV - \frac{\mu}{T}dN$

- We don't have $p(T, V, N)$ (i.e. an equation of state) and $\mu(T, V, N)$ - if you did they would supply the missing information, and you could integrate dS directly (even if you had to do it numerically). Given we don't know S , we also have no way of getting p and μ from $U(T, V, N)$ (e.g. we cannot use $p = \left(\frac{\partial U}{\partial V}\right)_{S, N}$ because we don't know what S is, and thus don't know how to hold S constant). The best we can do is to specify integration along a path where V and N are constant ($dV = dN = 0$ so no need to know p and μ)

$$S = \int_{const. N, V} \frac{dU}{T} + g(N, V)$$

- Under conditions of constant N and V , $dU = dQ$ so the integral is as expected – but S is not fully known as there is the unknown function $g(N, V)$ that is produced by the integration at constant N and V .

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Overview of Potentials for fixed N

- We will consider how we can set up a range of ‘thermodynamic potentials’, starting with $U(S, V)$, each of which still can give ‘complete information’.
- Given that (S, V) are not always the most convenient variables – we derive other functions that contain the same information but in terms of other variables which will prove more useful in certain circumstances:

eqn.s to recover other variables

Internal Energy

$$U(S, V)$$

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

Enthalpy

$$H(S, p) = U + pV$$

$$dH = TdS + Vdp \rightarrow T = \left(\frac{\partial H}{\partial S}\right)_p \quad V = \left(\frac{\partial H}{\partial p}\right)_S$$

Helmholtz Free Energy

$$F(T, V) = U - TS$$

$$dF = -SdT - pdV \rightarrow S = -\left(\frac{\partial F}{\partial T}\right)_V \quad p = -\left(\frac{\partial F}{\partial V}\right)_T$$

Gibbs Free Energy

$$G(T, p) = H - TS$$

$$dG = -SdT + Vdp \rightarrow S = -\left(\frac{\partial G}{\partial T}\right)_p \quad V = \left(\frac{\partial G}{\partial p}\right)_T$$

Internal energy, $U(S, V)$

- U is the internal energy: energy stored as potential and kinetic energy due to the relative internal positions of the particles and their microscopic motion measured w.r.t. the system centre of mass.

- Basic equation for derivative of U is the master equation:

$$dU = TdS - pdV = \delta q + \delta w \quad T = \left(\frac{\partial U}{\partial S} \right)_{V,N} \quad p = - \left(\frac{\partial U}{\partial V} \right)_{S,N}$$

- For changes at constant volume (no work done on/by the system), then $dU = \delta q$, the heat transferred to the system. e.g.:

$$C_v = \left(\frac{dQ}{dT} \right)_v = \left(\frac{\partial U}{\partial T} \right)_v$$

- For changes performed adiabatically and reversibly (S constant: isentropic) the change in a system's internal energy is given by the work done: for once it acts very much as a true 'energy' potential $dU = \delta w$.
- When a solid is stretched, adiabatically and reversibly, its internal energy goes up, even though as we shall show later, most solids also cool. i.e. you cannot calculate Young's modulus from the change in internal energy when a solid is stretched at constant temperature (except at $T=0K$).

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Enthalpy, $H(S, p)$

- S & V are not always the variables of choice. e.g. in chemical reactions are usually performed at constant p rather than at constant V and the maths is easier if p is one of the variables of the thermodynamic potential used
- In this case a more natural choice is **Enthalpy**: $H = U + pV$.

$$\begin{aligned} dH &= dU + pdV + Vdp \\ &= \underbrace{TdS - pdV}_{\text{from } dU} + pdV + Vdp \\ &= TdS + Vdp \end{aligned}$$

- S and p are the natural variables for H – when you integrate dH you get $H(S, p)$ – and the (relevant) other variables can be derived as $T = \left(\frac{\partial H}{\partial S} \right)_p$ and $V = \left(\frac{\partial H}{\partial p} \right)_S$.
- The transformation from $U(S, V)$ to $H = U - V \left(\frac{\partial U}{\partial V} \right)_S = U + pV$ is an example of a Legendre transformation: same information, but a variable, V , swapped for its 'conjugate' variable, $\left(\frac{\partial U}{\partial V} \right)_S$.

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Changes at constant p : Useful/extra/non pV work

$$dU = \delta Q + \delta w_{pV} + \delta w_e = \delta Q - pdV + \sum X_i da_i \quad \text{Non-}pV \text{ work (on system)}$$

- It is very common to run some process (a fuel cell, combustion, a chemical reaction) at atmospheric pressure. If the system volume increases, then work must be done to push back the atmosphere and make room for the expanded system.
- If a process is producing work, then you have to subtract of this ' pV ' work from the work that is available to be used – and the work that is left over to be used has various names: 'non- pV work' (probably the best) 'useful work' (but this is sometimes just another name for work) 'extractable work', 'extra work'. Here the symbols δw_{pV} and δw_e are used. Note both are for work done ON the system
- A change at constant volume does not do ' pV ' work – so there is no need to worry about the distinction.
- An aside: Carnot, in his 1824 book '**Reflections on the Motive Power of Fire and on Machines Fitted to Develop that Power**', gave the first published use of the concept of work. He defined the concept as a weight lifted through a height – *i.e.* an easily measurable quantification of how much 'work' an engine had done. Remember, energy is defined as the capacity to do work – *e.g.* lift a weight through a distance

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Enthalpy

$$dH = dU + pdV + Vdp = \delta q + \delta w_e + \delta w_{pV} + pdV + Vdp$$

- For changes at constant pressure, where only pV work is done (but it must actually be done! *i.e.* reversible changes – *e.g.* not Joule expansion):

$$dH = \delta q + \delta w_{pV} + pdV = \delta q$$

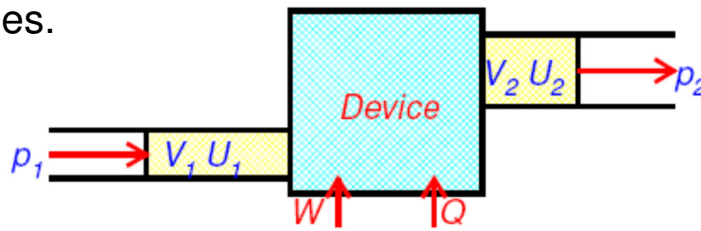
$i.e.$ dH gives the heat transfer to the system for changes at constant pressure (*if only pV work is done.*)

- Recall in chemistry the heat given out when a reaction occurs at constant pressure is referred to as the 'enthalpy change', and that the latent heat of, for example, vaporisation is often referred to as the 'enthalpy of vaporisation'.
- Heat capacities:

$$C_p = \left(\frac{dQ}{dT} \right)_p = \left(\frac{dH}{dT} \right)_p \quad c.f. \quad C_v = \left(\frac{dQ}{dT} \right)_v = \left(\frac{\partial U}{\partial T} \right)_v \quad 171$$

Enthalpy & Flow Processes

- In physics/engineering, enthalpy is important in flow processes.



- Suppose volume V_1 flows in per unit time with internal energy U_1 at pressure p_1 to some device. Flow out: V_2 , U_2 , p_2 . Also heat Q and work W are separately put into the device per unit time.
- To push the fluid into the device requires the piston to do work $p_1 V_1$ and a work $p_2 V_2$ can be recovered from the pressurised fluid that exits the device – so conservation of energy in steady flow (*i.e.* no accumulation of energy in the device) gives:

$$\underbrace{U_1 + p_1 V_1}_{H_1} + Q + W = \underbrace{U_2 + p_2 V_2}_{H_2}$$

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Enthalpy & Flow Processes

$$\underbrace{U_1 + p_1 V_1}_{H_1} + Q + W = \underbrace{U_2 + p_2 V_2}_{H_2}$$

- Rearrange $Q + W = H_2 - H_1 = \Delta H$
- Specifically, if $Q + W = 0$ (*i.e.* if no heat/work is put in externally) $H_1 = H_2$, *i.e.* enthalpy is conserved in a flow process.

- We shall see later a typical use of H in the calculation of the cooling/liquefaction of a non ideal gas when high pressure gas is expanded (below the 'inversion temperature') through a 'throttling' valve.

- As we will see with all these thermodynamic potentials, changes in H have well defined meanings under certain very carefully defined circumstances.

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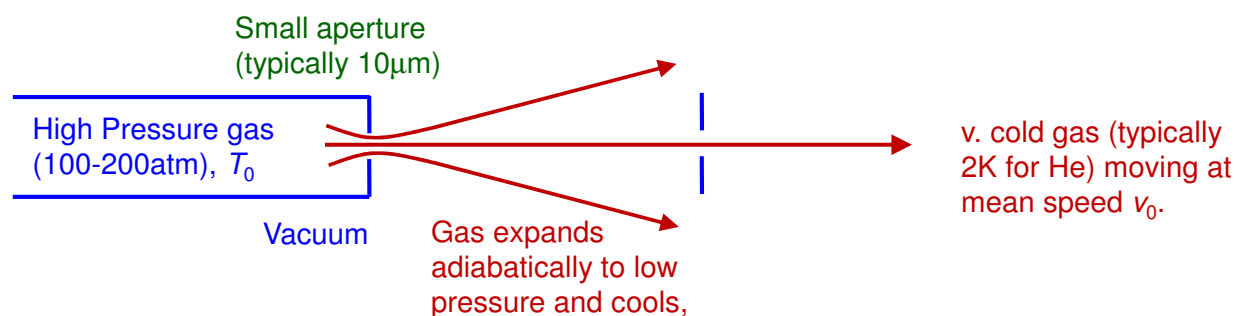
Internal energy revisited: 'U'='E'

- We have followed one standard convention in using the symbol ' U ' and referring to it as 'internal energy'. In chemistry this is particularly appropriate: one is concerned with species reacting in some reaction vessel. Throughout, actually, we have regarded it and used it simply as the energy of the system. The work we did on an object could just as well have increased the potential energy of the object by increasing its height and if we include gravitational PE in U , this automatically covers this eventuality. In some accounts of thermodynamics it is accordingly given the symbol E . One could similarly include electrostatic energy if we are dealing with charged particles (as in, for example, a consideration of semiconductor junctions), or centre of mass kinetic energy.
- Alternatively, and less attractively, one could include changes in potential or centre of mass kinetic energy (for example the potential energy change for a fluid in a pipe that goes up hill, or the change in speed as the pipe cross sectional area changes) as extra work terms, and keep U as defined purely as internal energy. This route, however, classes these extra energy terms with path dependent variables and runs the risk that one loses sight of the very useful fact that they are state variables.

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Example of use of 'U'='E'

- Realising that what we have regarded as 'internal energy', U , could just as well have been the energy ' E ' (e.g. including potential energy due to external fields and centre of mass kinetic energy) widens the use of thermodynamic potentials considerably.
- Consider, for example, the formation of atomic/molecular beams, which is a constant enthalpy expansion:



- For a monatomic gas at the start $H = \frac{5}{2}nRT_0$ but at the end the gas is very cold (pV very small) so $H \approx U$ – but almost all the ' U ' is in bulk translational KE – so, $\frac{5}{2}nRT_0 = \frac{1}{2}nm_r v_0^2$ where m_r is the molar mass and we see the beam velocity is determined by the nozzle temperature, T_0 .

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Internal energy and Enthalpy: summary

- $U(S,V)$ is the internal energy

$$dU = TdS - pdV = \delta q - pdV \quad T = \left(\frac{\partial U}{\partial S} \right)_{V,N} \quad p = - \left(\frac{\partial U}{\partial V} \right)_{S,N}$$

- $H(S,p) = U(S,V) + pV$ is the enthalpy

$$dH = TdS + Vdp \quad T = \left(\frac{\partial H}{\partial S} \right)_{p,N} \quad V = \left(\frac{\partial H}{\partial p} \right)_{S,N}$$

- For changes at constant V , $dU = \delta q$ (assuming no 'non pV' work is done)
For changes at constant p , $dH = \delta q$ (if only pV work is done)

$$C_p = \left(\frac{dQ}{dT} \right)_p = \left(\frac{dH}{dT} \right)_p \quad \text{and} \quad C_v = \left(\frac{dQ}{dT} \right)_v = \left(\frac{\partial U}{\partial T} \right)_v$$

- For changes performed adiabatically (no heat transfer), or for any change notionally performed at absolute zero:

$$dU = \delta w (= \delta w_e - pdV)$$

- For a continuous flow process the heat and work done on the fluid during the process is given by:

$$Q + W = H_2 - H_1$$

and for no energy input, enthalpy is conserved.

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Helmholtz Free Energy

- Another possible Legendre transformation of $U(S,V)$ is to swap variable entropy for temperature to give the **Helmholtz Free Energy**:

$$F = U - TS$$

$$dF = \cancel{TdS} - pdV - \cancel{TdS} - SdT \\ = -pdV - SdT$$

- $F = F(T, V)$ again contains 'complete information' and the conjugate variables in the master equation may be recovered as previously from the partial derivatives:

$$p = - \left(\frac{\partial F}{\partial V} \right)_T \quad \text{and} \quad S = - \left(\frac{\partial F}{\partial T} \right)_V$$

- It turns out the F is very useful for systems in thermal equilibrium (same temperature) as a reservoir, so let's consider a system in thermal equilibrium with a reservoir.

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Helmholz Free Energy and max obtainable work

$$F = U - TS \rightarrow dF = dU - TdS - SdT = \delta q + \delta w - TdS - SdT$$

All are 'system' variables

- The heat transfer to the system, δq_{sys} , is equal to the heat transfer from the reservoir, δq_{res} , (but opposite sign), and for changes at constant temperature

$$dF = -\delta q_{\text{res}} + \delta w - TdS = -TdS_{\text{res}} + \delta w - TdS$$

$$= \delta w - TdS_{\text{tot}}$$

(For reversible heat transfer in/out of the reservoir, ie reservoir temperature remains uniform throughout, $\delta q_{\text{res}} = TdS_{\text{res}}$)

The total change of S of system + reservoir is $dS_{\text{tot}} = dS + dS_{\text{res}}$

Rearranging gives: $-\delta w = -dF - TdS_{\text{tot}} \leq -dF$

because the entropy change of an isolated system (here = 'system' + 'reservoir') must be greater than zero. NB: ' $-\delta w$ ' is work done **by** the system.

- We see therefore that for a particular change to the state of a system performed at constant temperature **the maximum amount of energy which can be converted to work is given by $-dF$**

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Helmholz Free Energy and max obtainable work

For a particular change of the state of a system at constant temperature, the maximum amount of energy which is free to be converted to work is given by $-dF$

- Consider the conversion of $\text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O}$: $-\Delta F$ for the process will tell you how much work you can get if you could figure out how to convert this irreversible process to a reversible one.
- The entropy change for the process $\text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O}$ is actually very negative (1.5 mol of gas going to 1 mol of liquid in a much smaller volume): $\Delta S = -163 \text{ JK}^{-1}$. The internal energy change if the pressure and temperature at the start and end are the standard 101325 Pa and 298 K is $\Delta U = -282.1 \text{ kJ}$, so we have $\Delta F = -282.1 \text{ kJ} + 298 \text{ K} \times 0.163 \text{ kJ K}^{-1} = -233.5 \text{ kJ}$. So if you could harness the combustion of 1 mol of H_2 in $\frac{1}{2}$ mol of O_2 in a reversible process, one could gain 233.5 kJ of work (this would include the pdV work associated with the volume changes.)
- Because the entropy change of the process is negative, not all the internal energy change can be converted to work – some must be transferred as heat to the reservoir to increase its entropy to offset the drop in entropy of the system.

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Helmholz Free Energy and Total Entropy Change

$$F = U - TS \rightarrow dF = dU - TdS - SdT \quad \text{All are 'system' variables}$$

- At constant T and V (so $\dot{d}w_{pV} = 0$), $dU - \dot{d}w_e = \dot{d}q$ is the heat transfer out of the surroundings so, for a reversible change at const. T and V **where in addition no 'non-pV' work is done**, $-\frac{dU}{T} = dS_{\text{res}}$ whereas the 'dS' term in our expression for dF is dS_{sys} . We therefore have at constant temperature ($dT=0$):

$$dF = -TdS_{\text{res}} - TdS_{\text{sys}} = -TdS_{\text{tot}}$$

$$dS_{\text{tot}} = -\frac{dF}{T} \quad \text{For constant } T, V$$

- Not doing 'non-pV' work means we are not pushing the system around – i.e. we just leave it to go where the internal flux takes it – i.e. find equilibrium by itself
- At constant T and V , therefore, $dF = 0$ (dF is just calculated for system variables) for infinitesimal steps around equilibrium. A system can decrease its entropy ($dS_{\text{system}} < 0$) provided it is giving out heat to the surroundings which will cause the entropy of the surroundings to increase. $-dF/T$ is a measure of total entropy change.
- At constant T and V , $dF < 0$ for irreversible steps – including steps towards equilibrium – so to find the equilibrium, minimise F .
- If one then allows work to be done, then if we have an irreversible change ($dS_{\text{tot}} > 0$), this entropy change can be harnessed to do work – maximal for a reversible process, achieved by taking heat $-dF$ out of the reservoir to reduce dS_{tot} to zero. This heat is converted to work – hence, as before, max work that can be done (including pV work) is $-dF$.

Gibbs Free Energy

- If one wishes to work with T & p as natural variables the natural potential is Gibbs Free Energy: $G = U - TS + pV$.

$$\begin{aligned} dG &= \underbrace{TdS - pdV}_{dU} - \underbrace{TdS - SdT}_{-d(TS)} + \underbrace{pdV + Vdp}_{d(pV)} \\ &= -SdT + Vdp \end{aligned}$$

- As usual $G = G(T, p)$ contains full information about the system and the other variables in the master equation can be recovered using partial derivatives of G :

$$\Rightarrow \quad V = \left(\frac{\partial G}{\partial p} \right)_T \quad \text{and} \quad S = - \left(\frac{\partial G}{\partial T} \right)_p$$

Gibbs Free Energy and non- pV work

$$G = U + pV - TS$$

$$dU = \delta Q + \delta w_{pv} + \delta w_e = \delta Q - pdV + \sum X_i da_i$$

Non- pV work (on system)

$$dG = \delta Q - pdV + \sum X_i da_i + pdV + VdP - TdS - SdT$$

$$dG = \delta w_e = \sum X_i da_i$$

For constant T, P , and if we are looking for maximum work, want a reversible change and so $\delta Q = \delta Q_{rev} = TdS$

- At constant T and P , therefore, **$-dG$ gives the maximum non- pV work done BY the system.** e.g. in electrochemistry the Gibbs free energy change of the electrochemical reaction can be used to derive the maximum theoretical voltage difference between the two electrodes.
- Recall equating $\delta w = -pdV$ is only meaningful if the system can be described by state variables – i.e. is in some form of internal equilibrium. More generally this assumption is of course implicit in all use of thermodynamic potentials, at least for ‘before’ and ‘after’ states.

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Gibbs Free Energy and Total Entropy Change

$$G = H - TS \rightarrow dG = dH - TdS - SdT$$

All are ‘system’ variables

- For a change at constant p and no ‘non- pV ’ work (i.e. the system left to itself and is not being pushed around), $dH = \delta q$, the heat removed from the reservoir, so $\frac{dH}{T} = dS_{res}$. The ‘ dS ’ term is dS_{sys} . We therefore have for a change at constant temperature ($dT=0$): **$dG = -TdS_{res} - TdS_{sys} = -TdS_{total}$**

$$dS_{total} = -\frac{dG}{T}$$

For a reversible change at constant T, P

- At constant T and P , for irreversible change, including steps towards equilibrium **$dS_{total} > 0$** and **$dG < 0$** so **to find equilibrium at const. T and P , minimise G .**
- At constant T and P , infinitesimal steps around equilibrium are reversible, so must have **$dG = 0$** . A system can decrease its entropy (**$dS_{sys} < 0$**) in a reversible process provided it is giving out heat to the surroundings which will cause the entropy of the surroundings to increase.
- G very useful when considering **phase equilibrium** (both phases at same T and P).
- If we have an irreversible process, then we could get it to do $-dG$ of external work, which would remove dG of heat from the reservoir, and reduce the reservoir entropy by dG/T , now giving an overall **$dS_{total} = 0$** .

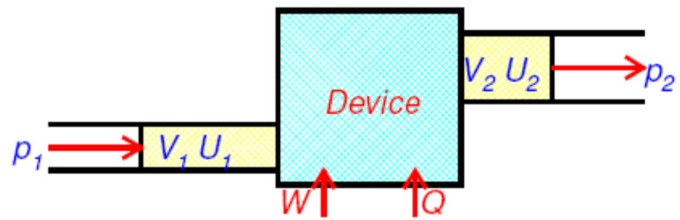
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Gibbs free energy & Flow Processes

- We saw previously that for a flow process conservation of energy gave:

$$U_1 + p_1 V_1 + Q + W = U_2 + p_2 V_2$$

$$H_2 - H_1 = Q + W$$



- Changes in G are given by:

$$dG = dH - TdS - SdT$$

- If the process is done at constant temperature (*i.e.* connected at all stages to a heat reservoir at temperature T), T is a constant and we can integrate to give a finite change in G :

$$\Delta G = \Delta H - T\Delta S$$

- If no work is done externally on the material as it flows then $\Delta H = Q$ the heat transfer from the reservoir so: $-T\Delta S_{\text{res}} = \Delta H$ and:

$$\Delta G = -T\Delta S_{\text{res}} - T\Delta S = -T\Delta S_{\text{Total}}$$

- So, if the material is transported from '1' to '2' reversibly, at constant temperature and without external (*i.e.* non pV) work being done on it – *i.e.* '1' and '2' are in equilibrium, then $G_1 = G_2$

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Gibbs free energy and chemical potential, μ

- Recall the master equation:

$$dU = TdS - pdV + \mu dN$$

this leads to:

$$dG = Vdp - SdT + \mu dN$$

- p and T are intensive variables, so one can keep them constant and add more 'stuff' to the system, and we have:

$$dG = \mu dN \quad \begin{array}{l} \text{Integrating, } T \\ \text{and } p \text{ const.} \end{array} \Rightarrow G = \mu N \Rightarrow \mu = \frac{G}{N}$$

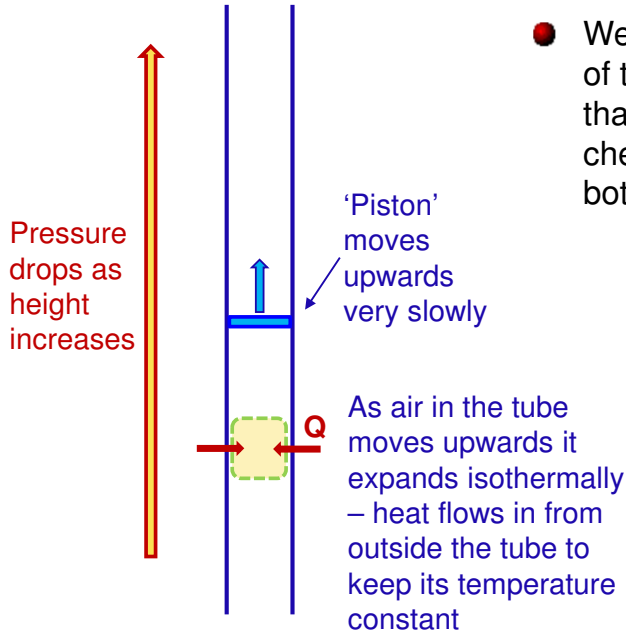
The chemical potential, μ is the Gibbs free energy per particle

- So, if we have a species in two states, provided they are kept at constant temperature, then if particles can move between them reversibly (*i.e.* an equilibrium has been established), if a certain amount of material is moved from one state to another, its Gibbs free energy does not change and the chemical potential of that species in the two states must be the same.

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Isothermal atmosphere as a 'flow process'??

- Imagine a tall room (concert hall), with a pipe running from floor to ceiling. One could envisage a 'piston' in the pipe that moves, friction free, very slowly upwards causing the gas in the pipe likewise to move very slowly up the pipe. The pressure distribution in the pipe remains as outside the pipe. The gas in the pipe expands isothermally as it rises, with heat flowing in to keep its temperature constant.



- We thus see that the gas at the top and bottom of the room can be connected by a flow process that is functioning entirely reversibly, so the chemical potential of the gas at the top and bottom of the room must be the same.

- The entropy of the gas in the pipe increases as it rises and expands isothermally, but it draws in heat from the rest of the room as it does so, causing the entropy of the room drops by a corresponding amount.
- Even without the piston the gas in the pipe diffuses in an 'equilibrium state', so μ must be everywhere the same.

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Example of use of μ : isothermal atmosphere

- In an isothermal atmosphere we have a density gradient that causes atoms to diffuse upwards, counteracted by a gravitational potential gradient that makes them tend to diffuse downwards. We can use the fact that the chemical potential must be the same at all heights – the particles are in dynamic equilibrium and no work is being done (work is done when some external constraint is moved).

$$\mu = \frac{G}{n} = \frac{1}{n}(U + pV - TS)$$

- For an ideal gas at a height h and temperature T , and molar mass m_r :

$$U = 'E' = nC_{v,m}T + nm_rgh$$

$$S = nC_{v,m} \ln T + nR \ln(V/n) + nS'_0$$

$$pV = nRT$$

$$\mu = \frac{G}{n} = C_{v,m}T + m_rgh + RT - TC_{v,m} \ln T - TR \ln(V/n) + TS'_0$$

Equating chemical potential at two different heights gives (same T , so pure T terms cancel):

$$m_rgh_1 - TR \ln(V_1/n) = m_rgh_2 - TR \ln(V_2/n)$$

$$\frac{V_1}{V_2} = \frac{p_2}{p_1} = e^{-\frac{m_rg(h_2-h_1)}{RT}}$$

$$p = p_0 e^{-\frac{m_rgh}{RT}}$$

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Example of use of μ : contact potential

- Many conductors have stationary positive charges (e.g. metal ion cores) and mobile electrons, which are in a state of thermal flux.
- Electrons in different materials can be expected to have different chemical potentials – the electron densities will be different and the nature of the ion cores which hold the electrons (roughly) in the conductor will be different.
- When two conductors are placed in electrical contact there will, therefore, be a net diffusion of electrons from the one with the higher electron chemical potential, μ_1 , to the one with the lower value chemical potential μ_2 , since, if dn electrons move, the overall change in G (T and P constant) is:

$$dG = dn(\mu_2 - \mu_1) \leq 0$$

- This flow of electrons sets up a charge imbalance between the two conductors and a hence a contact potential, meaning electrons have to go 'up a potential' hill (to lower electrostatic potential) to arrive at the lower μ conductor – and eventually the voltage difference between the conductors is enough to balance out the difference in μ . If we keep the values of μ as referring to the electron states w/o charge separation and add the electrons electrostatic potential energy to μ we have:

$$\mu_2 - e\phi_2 = \mu_1 - e\phi_1 \Rightarrow \mu_2 - \mu_1 = e(\phi_2 - \phi_1)$$

Where $-e$ is the charge on the electron ($\phi_2 - \phi_1$) is the difference in electrostatic potential between the two conductors

- As temperature varies, μ for both conductors will change – so the contact potential does as well -> production of thermoelectric e.m.fs.

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Gibbs v. Helmholtz Free Energy

- We see therefore that the maximum amount of energy which is free for a system at constant temperature to convert to work is given by $-dF$
- 'ΔF = the max work obtainable' only requires the temperature to be constant – so in that sense it is more generally applicable than ΔG, for which temperature and pressure need to be constant – BUT the work derived from ΔF includes the 'pV' work that one cannot use, and ΔF is written in terms of ΔU which is harder than ΔH to measure directly (ΔH is just the heat transfer at constant T and P).
- Many process of interest actually take place at constant T and P , so in practice ΔG for a change is much more widely used, especially as the work prediction it gives does not include the unusable 'pV' work.
- At constant T and V , $dF < 0$ for irreversible steps, and F is minimised to find equilibrium.
- At constant T and P , $dG < 0$ for irreversible steps, and G is minimised to find equilibrium.

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Gibbs v. Helmholtz Free Energy: Chemistry v. Physics

- G has natural variables T and p and for constant (T, p) , $-dG/T = dS$. A lot of chemistry (including phase changes) is done at constant pressure, and temperature, hence extensive use of G by chemists.
- In physics we often focus more on F (natural variables T and V) - but why? The answer lies in statistical mechanics. **Firstly in statistical thermodynamics F is easier to evaluate than G** , but more fundamentally, as is clear from quantum mechanics, **if you change the size of the box you change the nature (including energy) of the fundamental states**, which significantly complicates the maths.
- **i.e. Chemists want something that is useful in the real world, physicists want something for which the basic maths is simpler, so they tend to do thought experiments at constant T and V .** Physicists typically want to know how it works on a finer scale, but are not so worried about trying to actually use it. The chemists have more complex fish to fry, and want to USE thermodynamics rather than model the fine details.
- **The powerful thing about both G and F is that they allow the entropy change of the surroundings to be written in terms of the properties of the system**, i.e. the total entropy change of the universe –system plus surroundings - is written in system variables .

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Gibbs-Helmholtz Equation

- In statistical thermodynamics, F is often the easiest potential to evaluate. But the other potentials can readily be obtained from it since $F = F(T, V)$ contains full info:

$$U = F + TS = F - T \left(\frac{\partial F}{\partial T} \right)_V = -T^2 \left(\frac{\partial}{\partial T} \frac{F}{T} \right)_V$$

(The Gibbs-Helmholtz equation.)

- Similarly we can derive

$$G = F + pV = F - V \left(\frac{\partial F}{\partial V} \right)_T = -V^2 \left(\frac{\partial}{\partial V} \frac{F}{V} \right)_T$$

$$H = F + pV + TS = F - V \left(\frac{\partial F}{\partial V} \right)_T - T \left(\frac{\partial F}{\partial T} \right)_V$$

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$\mathcal{U}, \mathcal{H}, \mathcal{G}, \mathcal{F}$ summary

Internal Energy

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

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

Enthalpy

$$H(S, p) = U + pV \quad dH = TdS + Vdp \quad \rightarrow \quad T = \left(\frac{\partial H}{\partial S}\right)_p \quad V = \left(\frac{\partial H}{\partial p}\right)_S$$

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

Gibbs Free Energy

$$G(T, p) = H - TS \quad dG = -SdT + Vdp \quad \rightarrow \quad S = -\left(\frac{\partial G}{\partial T}\right)_p \quad V = \left(\frac{\partial G}{\partial p}\right)_T$$

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

Helmholtz Free Energy

$$F(T, V) = U - TS \quad dF = -SdT - pdV \quad \rightarrow \quad S = -\left(\frac{\partial F}{\partial T}\right)_V \quad p = -\left(\frac{\partial F}{\partial V}\right)_T$$

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

- Infinitesimal changes have specific meanings if specific variables held constant

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$\mathcal{U}, \mathcal{H}, \mathcal{G}, \mathcal{F}$ derivatives: summary

- We have shown how that under certain circumstances derivatives of \mathcal{U} , \mathcal{H} , \mathcal{F} and \mathcal{G} have very useful meanings:

Heat transfer

$d\mathcal{U}$ gives the heat transfer δq to a system at constant V .

$d\mathcal{H}$ gives the heat transfer δq to a system at constant p , hence its use in the energetics of chemical reactions.

(these first 2 conditions only apply if ' pV ' work is the sole type of work)

Work

- $d\mathcal{U}$ at constant S (reversible adiabatic change) or zero T gives the work done, $-\delta w$, by a system.

- $d\mathcal{F}$ at constant T gives the maximum work that can be done.

- $d\mathcal{G}$ at constant T and p gives the maximum non- pV work that can be done.

Direction of change/equilibrium condition

- $-d\mathcal{F}/T = d\mathcal{S}_{\text{sys}} + d\mathcal{S}_{\text{res}} = d\mathcal{S}_{\text{total}}$ at constant V and T and no ' $\text{non-}pV$ ' work, so for infinitesimal 'un-driven' steps (eg thermal fluctuations) around equilibrium $d\mathcal{F}=0$, and for any change $d\mathcal{F} \leq 0$ at constant V and T , and \mathcal{F} is minimised at equilibrium for constant V and T .

- $-d\mathcal{G}/T = d\mathcal{S}_{\text{sys}} + d\mathcal{S}_{\text{res}} = d\mathcal{S}_{\text{total}}$ at constant p and T and no ' $\text{non-}pV$ ' work (hence importance in chemistry), so for infinitesimal un-driven steps around equilibrium, $d\mathcal{G}=0$, and for any change $d\mathcal{G} \leq 0$, and \mathcal{G} is minimised at eq. for const. p and T .

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3.3 Maxwell Relations

- There are convenient ways of exploiting the redundancies between thermodynamic variables.

- Consider $dU = TdS - pdV$

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

$$\left(\frac{\partial^2 U}{\partial S \partial V} \right)_{V,S} = \left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial p}{\partial S} \right)_V$$

- Likewise, starting from H : $dH = TdS + Vdp$

$$\left(\frac{\partial^2 H}{\partial S \partial p} \right)_{p,S} = \left(\frac{\partial T}{\partial p} \right)_S = \left(\frac{\partial V}{\partial S} \right)_p$$

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Maxwell Relations

- We can derive two further Maxwell relations, starting from F :

$$dF = -SdT - pdV$$

$$- \left(\frac{\partial^2 F}{\partial V \partial T} \right)_{T,V} = \left(\frac{\partial p}{\partial T} \right)_V = \left(\frac{\partial S}{\partial V} \right)_T$$

- and starting from G : $dG = -SdT - Vdp$

$$\left(\frac{\partial^2 G}{\partial p \partial T} \right)_{T,p} = \left(\frac{\partial V}{\partial T} \right)_p = - \left(\frac{\partial S}{\partial p} \right)_T$$

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Maxwell Relations - Summary

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

- Remember you can invert these when needed, e.g.

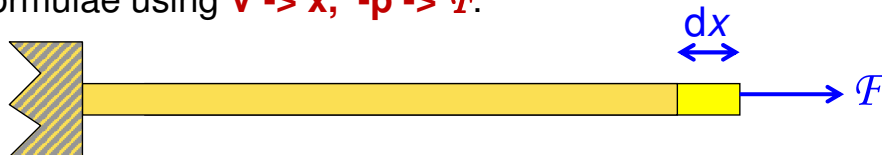
$$\left(\frac{\partial T}{\partial V}\right)_p = -\left(\frac{\partial p}{\partial S}\right)_T$$

- Mnemonics exist for remembering these Maxwell relations.
Better to remember how to derive them when you need them.

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Maxwell Relations for non 'pV' systems

- The Maxwell relations we derived apply to a $p - V$ system. But we can extend the relations to other cases.
- Example:* stretched wire of extension x under tension \mathcal{F} : translate existing formulae using $V \rightarrow x$, $-p \rightarrow \mathcal{F}$.



$$dU = TdS + \mathcal{F}dx, \quad H = U - \mathcal{F}x \quad \text{and} \quad dH = TdS - x d\mathcal{F}$$

$$\left(\frac{\partial^2 H}{\partial S \partial \mathcal{F}}\right)_{\mathcal{F}, S} = \left(\frac{\partial T}{\partial \mathcal{F}}\right)_S = -\left(\frac{\partial x}{\partial S}\right)_{\mathcal{F}}$$

- Or similarly $F = U - TS \quad dF = -SdT + \mathcal{F}dx$

$$\left(\frac{\partial^2 F}{\partial T \partial x}\right)_{x, T} = -\left(\frac{\partial S}{\partial x}\right)_T = \left(\frac{\partial \mathcal{F}}{\partial T}\right)_x$$

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Maxwell Relations for non 'pV' systems

- Maxwell relations can be derived even if system has more than **2** independent variables.
- Best to work these out *ad hoc* from first principles as required. We won't be using any. See Blundell or Adkins if you are interested.
- Now, move on to look at some **applications** of this analytical approach to thermodynamics.

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3.4.1 Applications: Relation between C_v and C_p

- Previously we had:
$$C_p = C_v + \left[\left(\frac{\partial U}{\partial V} \right)_T + p \right] \left(\frac{\partial V}{\partial T} \right)_p$$
- But suppose we knew nothing about U , but did have an equation of state (e.g. $p = p(T, V, N)$) – lets see what we could do
- Recall $C_V = \left(\frac{dQ}{dT} \right)_V = T \left(\frac{\partial S}{\partial T} \right)_V$ and $C_p = T \left(\frac{\partial S}{\partial T} \right)_p$
- S is a function of state. Write it as $S(T, V)$:

Starting with an equation that has something that looks like one of them is a good idea.

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

← $= C_v/T$

- Divide by dT at fixed p :

Especially if you can then use it to derive the other one.

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

← $= C_p/T$

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Heat Capacities (contd.)

$$\left(\frac{\partial S}{\partial T}\right)_p = \left(\frac{\partial S}{\partial T}\right)_v + \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p$$

- Multiplying by T :

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

Things are looking up – but we need to swap S for one of P, V, and T – hence:

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

- Use Maxwell Relation to eliminate S : $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v$

$$C_p - C_v = T \left(\frac{\partial p}{\partial T}\right)_v \left(\frac{\partial V}{\partial T}\right)_p$$

- Can now calculate the r.h.s. from the equation of state for the gas. e.g. if $p(V - b) = RT$:

$$C_p - C_v = T \cdot \frac{R}{V - b} \cdot \frac{R}{p} = R$$

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Heat Capacities (contd.)

- Can relate $C_p - C_v$ to other measurable quantities:
- Introduce *isobaric expansivity*:

$$\beta_p = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_p$$

i.e. the fractional increase in volume per unit change in temperature, at constant pressure.

- and *isothermal compressibility* (= 1/Bulk Modulus):

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_T$$

i.e. fractional change in volume per unit change in pressure, at constant temperature.

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Heat Capacities (contd.)

- Reciprocity theorem: $\left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_p \left(\frac{\partial V}{\partial p}\right)_T = -1$

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

$\beta_p = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_p$
 $\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_T$

substituting in

$$C_p - C_V = T \left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_p \Rightarrow \boxed{C_p - C_V = \frac{TV\beta_p^2}{\kappa_T}}$$

- This is a general relationship between three different quantities: **heat capacities**, **thermal expansion** and an **elastic modulus**.

This result is true for any substance: ideal gas, real gas, solid...

3.4.2 Isothermal/Adiabatic Compressibility

- When compressing a substance, could consider doing this either **isothermally** (const. T) or **adiabatically** (const. S).

Adiabatic compressibility $\kappa_S = -\frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_S$

Isothermal compressibility $\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_T$

- We can use thermodynamics to find how they are related. And this will be a general result; not just applicable for gases...
- Why are we doing all this?? Some quantities are easier to measure than others, and often you can work out what you need from what has already been measured...

Isothermal/Adiabatic Compressibility

$$\frac{\kappa_T}{\kappa_S} = \frac{\left(\frac{\partial V}{\partial p}\right)_T}{\left(\frac{\partial V}{\partial p}\right)_S} = \frac{\left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_V}{\left(\frac{\partial V}{\partial S}\right)_p \left(\frac{\partial S}{\partial p}\right)_V} \quad (\text{using reciprocity})$$

$$= \frac{\left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial S}{\partial V}\right)_p}{\left(\frac{\partial S}{\partial p}\right)_V \left(\frac{\partial p}{\partial T}\right)_V} \quad (\text{using reciprocal theorem})$$

$$= \frac{\left(\frac{\partial S}{\partial T}\right)_p}{\left(\frac{\partial S}{\partial T}\right)_V} \quad (\text{using chain rule})$$

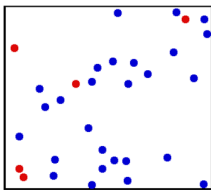
$$\frac{\kappa_T}{\kappa_S} = \frac{C_p}{C_V} = \gamma$$

- i.e. the ratio of compressibilities equals the ratio of heat capacities.

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3.4.3 Ideal Gas in Classical Thermodynamics

- From statistical thermodynamics point of view, characteristics of ideal gas are:



- ✱ Identical particles in random motion
- ✱ Molecules small - take up negligible volume
- ✱ No long-range forces
- ✱ Elastic collisions

- From a classical thermodynamics point of view, an ideal gas:

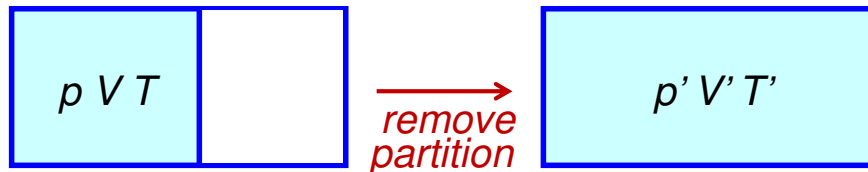
- ✱ Obeys Boyle's law
"If temperature is constant, then $pV = \text{constant}$."
- ✱ Obeys Charles' law
"Fractional change in volume between two fixed temperatures same for all gases."
- ✱ Obeys Joule's law
"No change of temperature in a free expansion."

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Joule's Law

“No change of temperature in a free expansion.”

- For free expansion (known as ‘Joule expansion’) there is no heat transfer or work done – so U is constant.



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

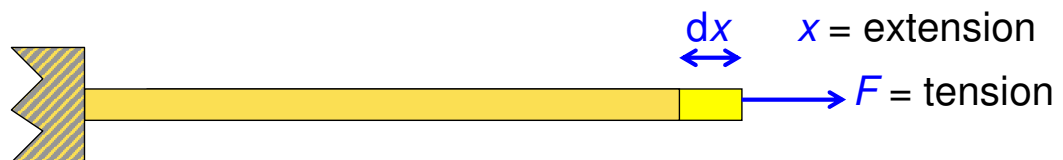
- Now $\left(\frac{\partial U}{\partial T}\right)_V = C_V$, which is certainly finite. Hence

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

- The internal energy of an ideal gas depends on temperature only.**
(We previously deduced this from simple stat. thermo. calculations, and derived Joule's law.)

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3.4.4 Elastic Wire or Rod



$$dU = TdS + \mathcal{F}dx$$

- A = cross-sectional area of wire, L = unstretched length of wire.

- Introduce (isothermal) **Young's modulus** Y_T = stress/strain:

$$\text{stress} = \delta F/A, \text{ strain} = \delta x/L: \quad Y_T = \frac{L}{A} \left(\frac{\partial \mathcal{F}}{\partial x}\right)_T$$

- Also introduce coefficient of linear expansion at constant tension:

$$\alpha_{\mathcal{F}} = \frac{1}{L} \left(\frac{\partial x}{\partial T}\right)_{\mathcal{F}}$$

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Elastic Wire



- Stretch between fixed supports (i.e. **fixed x**). If we heat the wire, the tension will change.

$$\begin{aligned} \left(\frac{\partial \mathcal{F}}{\partial T}\right)_x &= - \left(\frac{\partial \mathcal{F}}{\partial x}\right)_T \left(\frac{\partial x}{\partial T}\right)_{\mathcal{F}} \quad (\text{using reciprocity}) \\ &= - \frac{AY_T}{L} L \alpha_{\mathcal{F}} = -A \alpha_{\mathcal{F}} Y_T \end{aligned}$$

- n.b. depends on **area** but not on **length** of wire.
- This is usually < 0 . All materials have $Y > 0$. Most have $\alpha > 0$ (though not rubber - see 2nd example sheet).

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Elastic Wire

- If wire is extended **adiabatically**, its temperature will change:

$$\begin{aligned} \left(\frac{\partial T}{\partial x}\right)_S &= - \underbrace{\left(\frac{\partial T}{\partial S}\right)_x \left(\frac{\partial S}{\partial x}\right)_T}_{\text{reciprocity}} \quad \left. \begin{array}{l} \text{Maxwell} \\ \left(\frac{\partial S}{\partial x}\right)_T = \left(\frac{\partial F}{\partial T}\right)_x \end{array} \right\} \\ &= \left(\frac{\partial T}{\partial S}\right)_x \left(\frac{\partial \mathcal{F}}{\partial T}\right)_x = \frac{-T A \alpha_{\mathcal{F}} Y_T}{C_x} \end{aligned}$$

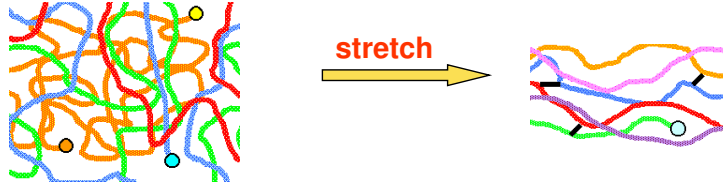
where the heat capacity at constant x is $C_x = T \left(\frac{\partial S}{\partial T}\right)_x$

- This is usually < 0 , though again not for rubber. *Note: all materials have heat capacity $C > 0$.*

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Aside on Rubber Elasticity

- Rubber consists of long chain molecules (polymers) that are entangled **AND** cross-linked. Extend it by straightening out links, not by stretching bonds – U remains relatively unchanged with length, (as for the an ideal gas: U independent of V), except entropy *reduces* as length increases.



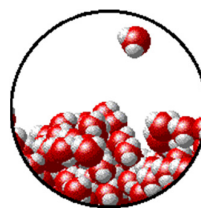
- Stretch by increasing F at constant T must decrease entropy S .
- Using Maxwell relations, we obtain

$$\left(\frac{\partial x}{\partial T}\right)_{\mathcal{F}} = \left(\frac{\partial S}{\partial \mathcal{F}}\right)_T < 0$$

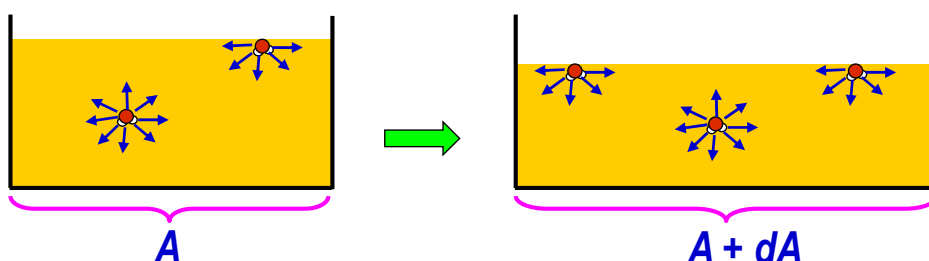
- Interpretation:* increasing T increases random thermal motions and shortens the length – c.f. a gas expanding at high temperatures. 210

3.4.5 Surface Tension & Surface Energy

- In liquids, atoms on surfaces have fewer neighbours. They are less tightly bound.



- Therefore, need energy to create extra surface area dA (at constant T). Surface energy = $u(T)dA$



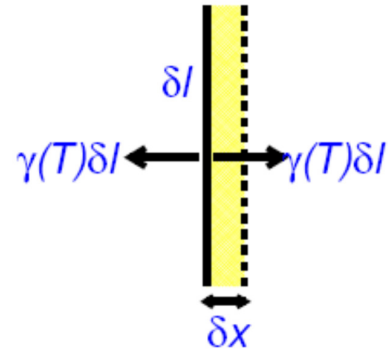
Surface Tension & Surface Energy

- Surface energy is often described in terms of surface tension γ . In effect, there is a force acting across any line element δl in the surface equal to $\gamma(T)\delta l$
- Move δl by orthogonal distance δx . This increases area by $\delta A = \delta l \delta x$.

Work done to increase the area is

$$dW = \gamma \delta l \delta x = \gamma \delta A$$

and $dU = TdS + \gamma dA$



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Surface Tension & Surface Energy

- Surface Tension $\gamma(T)$ and Surface Energy $u(T)$ are not identical because there is an entropy change when you create more surface. For $\Delta S_{\text{universe}}$ to be zero, heat must be exchanged with the surroundings (as in isothermal expansion of a gas) or the liquid must change temperature (as in adiabatic gas expansion) to compensate for the change in entropy due to the creation of more surface. We can relate them as follows:

$$\begin{aligned}
 dU &= TdS + \gamma dA && \left(\text{using: } dS = \left(\frac{\partial S}{\partial T} \right)_A dT + \left(\frac{\partial S}{\partial A} \right)_T dA \right) \\
 &= T \left(\frac{\partial S}{\partial T} \right)_A dT + \left(\gamma + T \left(\frac{\partial S}{\partial A} \right)_T \right) dA \\
 &= T \left(\frac{\partial S}{\partial T} \right)_A dT + \left(\gamma - T \left(\frac{\partial \gamma}{\partial T} \right)_A \right) dA && \text{(Maxwell)}
 \end{aligned}$$

- Hence energy gain per unit area created at constant temperature is:

$$u(T) = \left(\frac{\partial U}{\partial A} \right)_T = \gamma - T \left(\frac{\partial \gamma}{\partial T} \right)_A = \gamma - T \frac{d\gamma}{dT}$$

(Since γ is generally independent of A .)²¹³

Surface Tension & Surface Energy

- We just derived $u(T) = \left(\frac{\partial U}{\partial A}\right)_T = \gamma - T \frac{d\gamma}{dT}$
- Usually, $d\gamma/dT < 0$, so $u(T) > \gamma$, owing to exchange (usually absorption) of heat with surroundings.
- $\chi(T)$ can be thought of as the Helmholtz free energy per unit area at constant T since

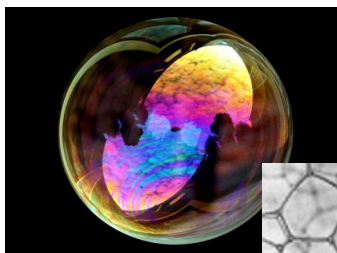
$$dF = dU - d(TS) = -SdT + \gamma dA$$

(Remember that at constant T $-dF$ gives the max work a system can do – hence its link to surface tension)

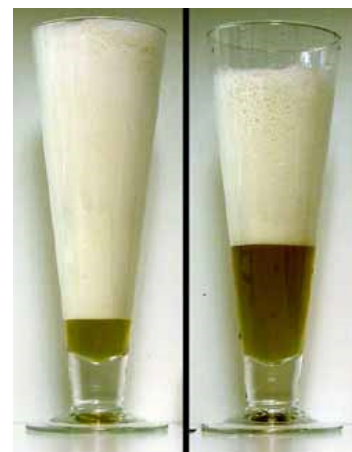
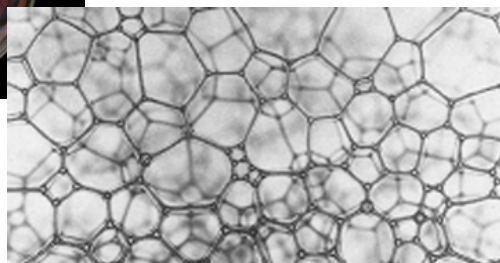
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Surface Tension & Laplace pressure

- The curved surface of a small droplet/bubble produces an increase in internal pressure, the ‘Laplace pressure’:
- $$\Delta p = p_{\text{inside}} - p_{\text{outside}} = \frac{2\gamma}{R}$$
- Since $G = U - TS + pV$, the smaller the droplet/bubble the higher the free energy of its contents – making small bubbles/droplets unstable with respect to big ones – so with time a foam will coarsen, and Ostwald ripening occurs as smaller droplets evaporate with the vapour condensing on bigger ones.



Coarsening of Foam



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Chapter 3 - Summary

● Thermodynamic potentials

Internal Energy	U	$dU = TdS - pdV$
Enthalpy	$H = U + pV$	$dH = TdS + Vdp$
Helmholtz Free Energy	$F = U - TS$	$dF = -SdT - pdV$
Gibbs Free Energy	$G = U - TS + pV$	$dG = -SdT - Vdp$

Each contains full information about the system.

● Maxwell relations, e.g. for a p - V system

$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$	$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$	216
$\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$	$\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T$	

Chapter 3 Summary: derivatives of U , H , G , F

- We have shown how that under certain circumstances derivatives of **U** , **H** , **F** and **G** have very useful meanings:

Heat transfer

dU gives the heat transfer δq to a system at constant V .

dH gives the heat transfer δq to a system at constant p , hence its use in the energetics of chemical reactions.

(these first 2 conditions only apply if ' pV ' work is the sole type of work)

Work

- **dU** at constant S (reversible adiabatic change) gives the work done, $-\delta w$, by a system.

- **dF** at constant T gives the maximum work that can be done.

- **dG** at constant T and p gives the maximum non- pV work that can be done.

Direction of change/equilibrium condition

$-dF/T = dS_{\text{sys}} + dS_{\text{res}} = dS_{\text{total}}$ at constant V and T , so for infinitesimal steps around equilibrium $dF=0$, and for any change $dF \leq 0$ at constant V and T , and F is minimised at equilibrium for constant V and T .

$-dG/T = dS_{\text{sys}} + dS_{\text{res}} = dS_{\text{total}}$ at constant p and T and no ' $\text{non-}pV$ ' work (hence importance in chemistry), so for infinitesimal un-driven steps around equilibrium, $dG=0$, and for any change $dG \leq 0$, and G is minimised at eq. for const. p and T .

Chapter 3 - Summary

● Applications

✱ Heat Capacities

$$C_p - C_V = T \left(\frac{\partial p}{\partial T} \right)_V \left(\frac{\partial V}{\partial T} \right)_p = \frac{TV\beta_p^2}{\kappa_T}$$

✱ Compressibilities

$$\frac{\kappa_T}{\kappa_S} = \frac{C_p}{C_V} = \gamma$$

✱ Ideal Gas equation from Boyle's and Joule's Laws.

✱ Elastic wire

✱ Surface tension