

THERMODYNAMIC POTENTIALS

It is useful to recast what we've learnt in a way that tells us what processes are likely to occur naturally.

Central Equation

1st Law: $dQ = dU - dW$

For reversible processes $\begin{matrix} ? \\ T dS \end{matrix} \quad \begin{matrix} ? \\ - PdV \end{matrix}$

$$\Rightarrow \boxed{T dS = dU + PdV}$$

Since everything here is a function of state this equation must be generically true, not just for reversible processes!

Entropy of An Ideal Gas

For one mole $P = RT/V$ & $dU = C_V dT$

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

We integrate &

$$S = S_0 + C_V \ln T + R \ln V$$

need a \uparrow
microscopic understanding
to fix constant.

raise V or T
& there's more states
open to the gas

One naturally thinks a process will proceed if the final state has lower U than the initial state ... and then $Q = \Delta U$

ie "1st law"

However, work & the 2nd law need to be considered also:

HELMHOLTZ FREE ENERGY

Even at constant volume (no work) a system can interact with the surroundings by thermalizing at the start & end

$$Q = \Delta U$$

$$\& \Delta S_{\text{UNIVERSE}} = \Delta S_{\text{SYST.}} + \Delta S_{\text{SURR}} \geq 0$$

? $-\frac{Q}{T_0} = -\frac{\Delta U}{T_0}$

$$-\Delta F = T_0 \Delta S_{\text{SYST}} - \Delta U \geq 0$$

Here $\boxed{F = U - TS}$ & $\Delta F \leq 0$

So reactions still happen if U decreases, giving out heat...

But if $S \uparrow$ then ΔU can even be negative & the process proceed eg ammonium nitrate + water react endothermically since entropy rises...

ENTHALPY

If we now work at constant pressure P_0 , eg by taking a bung out of the test tube, then work can occur

$$\begin{aligned}\text{Heat out } -Q &= -(\Delta U + P_0 dV) \\ &= -\Delta(U + PV) \\ &\equiv -\Delta H\end{aligned}$$

$$\boxed{H = U + PV}$$

If $\Delta H \leq 0$ a reaction will occur.

Note: enthalpy is a function of state ... and

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p$$



↑ enthalpy of formation set to zero for plain elements

enthalpy of formation of	CO	-110.5 kJ/mole
"	CO ₂	-393.5 kJ/mole

So in this reaction

$$\begin{aligned}+\Delta H &= +(\Delta H(\text{CO}_2) - \Delta H(\text{CO})) \\ &= -283 \text{ kJ/mole.}\end{aligned}$$

so 283 kJ/mole of energy is released as heat.

GIBBS FREE ENERGY

If we work at constant pressure and allow thermalization with the surroundings we must again impose

$$\Delta S_{\text{UNIVERSE}} \geq 0$$

The argument is the same that took us from

$$U \rightarrow F = U - TS$$

Except $U \rightarrow H$ $H = U + PV$

So $G = H - TS$ & for a reaction to occur $\Delta G \leq 0$

$G = U - TS + PV$

$$dG = d(U - TS + PV)$$

internal energy released change in entropy work done

This is the available energy to do work - hence "free energy"

NATURAL VARIABLES

We can find some useful relations by again remembering (at least for an ideal gas)

$$\begin{array}{ccc}
 U, P, V, n, T, S & \xrightarrow{\text{FIXED } N} & \text{eg } S, V \\
 & & \text{or } T, P \\
 & & PV = n_m RT \\
 & & U = \frac{3N}{2} kT \\
 & & S = S_0 + C_v \ln T + R \ln V
 \end{array}$$

EG is $U(S, V)$

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

but this is just the central equation

$$dU = T dS - P dV$$

so we learn $T = \left(\frac{\partial U}{\partial S}\right)_V$ & $P = -\left(\frac{\partial U}{\partial V}\right)_S$

EG we can get a similar relation involving F

$$dF = d(U - TS) = T dS - P dV - d(TS) = T dS - P dV - T dS - S dT$$

$$dF = -S dT - P dV$$

Is we consider $F(T, V)$

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

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

$$\underline{EG} \quad \&H = U + PV$$

$$\begin{aligned} dH &= dU + PdV + VdP \\ &= TdS - PdV + PdV + VdP \\ &= TdS + VdP \end{aligned}$$

So $H(S, P)$

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

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

EG & finally $G = H - TS$

$$\begin{aligned} dG &= TdS + VdP - TdS - SdT \\ &= VdP - SdT \end{aligned}$$

So $G(P, T) \Rightarrow dG = \left(\frac{\partial G}{\partial P}\right)_T dP + \left(\frac{\partial G}{\partial T}\right)_P dT$

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

We will use $dG = VdP - SdT$ in examples to come. Note $G = U + VP - TS$

$$dG = \underbrace{dU + PdV - TdS}_0 + VdP - SdT$$

by central equation

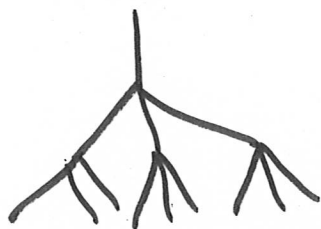
Confirming our result!

EXAMPLE - FORMS OF CARBON

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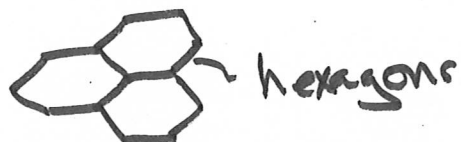
We've always had in mind ideal gases as we derived our thermodynamic relations but they have wider application...

DIAMOND



$$\rho = 3.51 \times 10^3 \text{ kg m}^{-3}$$

GRAPHITE



$$\rho = 2.25 \times 10^3 \text{ kg m}^{-3}$$

At 298K

$$\Delta H_g = 0$$

$$\Delta H_g = -1.897 \text{ kJ mole}^{-1}$$

& graphite has a lower entropy $\Delta S = -3.36 \text{ JK}^{-1} \text{ mole}^{-1}$

$$\begin{aligned} G_{\text{dia}} - G_{\text{graph}} &= H_{\text{dia}} - H_{\text{gra}} - T(S_{\text{dia}} - S_{\text{gra}}) \\ &= 1897 - 298 \times (-3.36) \\ &= 2898 \text{ J mole}^{-1} \end{aligned}$$

Diamond is not preferred because it has higher free energy at room temperature. If you have a diamond it doesn't convert to graphite because of the huge activation energy of the re-arrangement.

If we add pressure at constant T

$$dG = -SdT + VdP$$

$$= (V_{\text{dia}} - V_{\text{gm}}) \Delta P$$

$\frac{0.012 \text{ kg m}^3}{3570 \text{ kg m}^{-3}} \quad \frac{0.012 \text{ kg m}^3}{2250 \text{ kg m}^{-3}}$

$$= -1.91 \times 10^{-6} \text{ m}^3 \text{ mole}^{-1} dP$$

this cancels the room temp dG when

$$dP = 1.5 \times 10^9 \text{ Nm}^{-2}$$
$$= 15000 \text{ atmospheres.}$$