Ch 22 → Helmholtz & Gibbs free energy

Helmholtz: useful for constant V, T.

$$dU = \delta q \quad \text{because } dV = 0$$

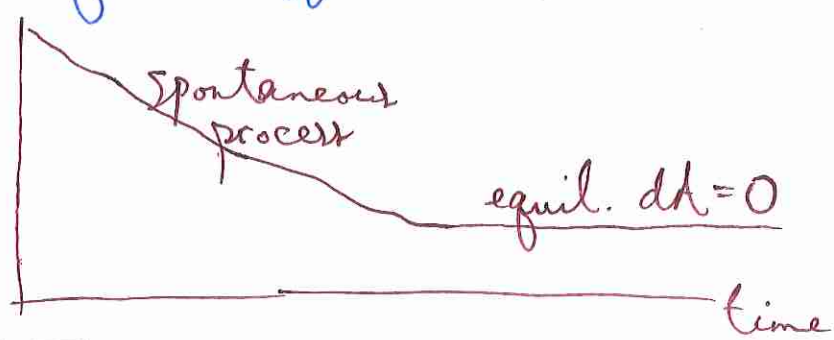
The Clausius inequality $dS \geq \delta q / T$ gives us

$$dU \leq T\,dS \implies dU - T\,dS \leq 0$$

$$\implies d(U - TS) \leq 0 \quad \text{at constant } V, T$$

$\implies dA \leq 0$ where we define the Helmholtz free energy as $A = U - TS$

At equil. $dA = 0$.



Gibbs: useful for constant P, T.

$$dU = \delta q + \delta w = \delta q - P\,dV \quad \text{since P constant, } P_{ext} = P_{sys} = P$$

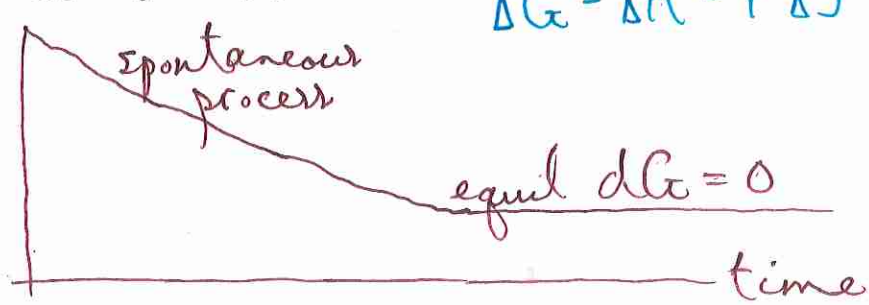
$$\leq T\,dS - P\,dV$$

$$\Rightarrow dU - T\,dS + P\,dV \leq 0 \quad \text{or} \quad d(U - TS + PV) \leq 0 \quad \text{const P, T}$$

$\Rightarrow d(H - TS) \leq 0 \Rightarrow dG \leq 0$ where we define the Gibbs free energy as $G = H - TS$

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

At equil. $dG = 0$



Relations between T, P, V, U, S, H, A, G

$$dU = \delta q_{rev} + \delta w_{rev} = T\,dS - P\,dV$$

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

Thus $\left.\frac{\partial U}{\partial S}\right)_V = T$ and $\left.\frac{\partial U}{\partial V}\right)_S = -P$

Equality of mixed partials: for $z = f(x,y)$ in calculus,

$$\left.\frac{\partial\left(\left.\frac{\partial f}{\partial x}\right)_y\right)}{\partial y}\right)_x = \left.\frac{\partial\left(\left.\frac{\partial f}{\partial y}\right)_x\right)}{\partial x}\right)_y = \frac{\partial^2 f}{\partial x \partial y}$$ order doesn't matter

Here this is $\left.\frac{\partial T}{\partial V}\right)_S = -\left.\frac{\partial P}{\partial S}\right)_V$ This is called a <u>Maxwell relation</u>

$$dH = d(U + PV) = T\,dS - P\,dV + P\,dV + V\,dP$$
$$= T\,dS + V\,dP$$

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

Thus $\left.\frac{\partial H}{\partial S}\right)_P = T$ and $\left.\frac{\partial H}{\partial P}\right)_S = V$

Maxwell relation: $\left.\frac{\partial T}{\partial P}\right)_S = \left.\frac{\partial V}{\partial S}\right)_P$

$$dA = d(U - TS) = TdS - PdV - TdS - SdT$$
$$= -PdV - SdT$$

$$A = A(V, T) \Rightarrow dA = \left.\frac{\partial A}{\partial V}\right)_T dV + \left.\frac{\partial A}{\partial T}\right)_V dT$$

Thus $\left.\frac{\partial A}{\partial V}\right)_T = -P$ and $\left.\frac{\partial A}{\partial T}\right)_V = -S$

Maxwell relation: $\left.\frac{\partial P}{\partial T}\right)_V = \left.\frac{\partial S}{\partial V}\right)_T$

$$dG = d(H - TS) = TdS + VdP - TdS - SdT$$
$$= VdP - SdT$$

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

Thus $\left.\frac{\partial G}{\partial P}\right)_T = V$ and $\left.\frac{\partial G}{\partial T}\right)_P = -S$

Maxwell relation: $\left.\frac{\partial V}{\partial T}\right)_P = -\left.\frac{\partial S}{\partial P}\right)_T$

For spontaneous processes we have:

$dU < 0$ at constant S, V → can rearrange to get $dS > 0$ at constant U, V which is an isolated system.

$dH < 0$ at constant S, P

$dA < 0$ at constant T, V

$dG < 0$ at constant P, T

Let us address a point of possible confusion:

$dU = \delta q + \delta w$ and we are always allowed to use a reversible path to compute changes in state functions because state functions are not path dependent.

So we are always allowed to write $dU = \delta q_{rev} + \delta w_{rev}$
$= T\,dS - P\,dV$

in order to compute the change in U for some process.

If we put this into the $G = H - TS$ equation at constant T, P we get $dG = dH - T\,dS$

$$= d(U + PV) - T\,dS$$

$$= T\,dS - P\,dV + P\,dV - T\,dS = 0$$

So it looks like there is never any change in the Gibbs free energy (under constant P, T conditions) since we are allowed to choose a reversible path to calculate dG <u>even</u> if the path the actual system takes is not reversible.

What is going on? How do we ever get $dG \neq 0$?

Well, if constant T, P completely determines the state of the system, then dG is zero :

for a pure substance in a single phase, if T and P are fixed so is V and so the state of the system doesn't change so $dG = 0$!!

(e.g. ideal gas ; pure liquid water)

So if we have a single substance in a single phase there is nothing to talk about if we fix T, P since nothing happens, so of course $dG = 0$.

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Lets look at a two-phase system : then constant T, P doesn't completely determine the state of the system because if a liquid (partially) evaporates, V will change.

ex $H_2O(l) \longrightarrow H_2O(g)$ constant T, P ; 1 mol

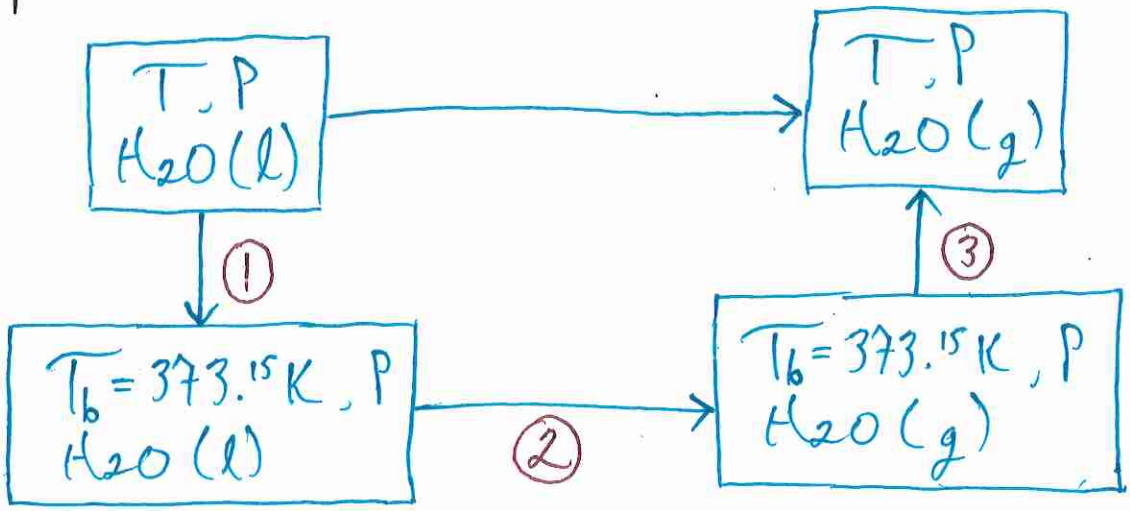
$\Delta G_{vap} = \Delta H_{vap} - T\Delta S_{vap}$

At $P = 1$ atm ; $T_b = 373.^{15}$ K (boiling point of water)

$\Delta H_{vap} = 40.^{65}$ kJ/mol , $\Delta S_{vap} = 108.^{9}$ $JK^{-1}mol^{-1}$

$\Rightarrow \Delta G_{vap} = 0$. Still zero! Why? Because this process is reversible. Actually, we defined $\Delta S_{vap} = \Delta H_{vap}/T_{vap}$ so it had to come out as $\Delta G_{vap} = 0$.

What about if we want to calculate ΔG for this process at $T \neq 373.15$ K? (still constant T, P)



We can use a pathway as shown

no phase transitions

$$\Delta S = \int_{T_1}^{T_2} \frac{C_p(T)}{T}\, dT \qquad \text{Eq. 21.9}$$

$$\Delta H = \int_{T_1}^{T_2} C_p(T)\, dT \qquad \text{Eq. 19.44}$$

C_p of $H_2O(l) = 75.3\ \mathrm{J\,K^{-1}\,mol^{-1}}$

C_p of $H_2O(g) = 33.6\ \mathrm{J\,K^{-1}\,mol^{-1}}$

These depend on temperature but not strongly, so we will neglect temp. dependence.

We know $\Delta G_2 = 0$ so we just need ΔG_1 and ΔG_3.

Quickest way: use $\left.\dfrac{\partial G}{\partial T}\right)_P = -S$

So $\Delta G = \Delta G_1 + \Delta G_3 \approx -S^l(T_b - T) - S^g(T - T_b)$

$$= \Delta S_{vap}(T_b - T)$$

Here we assumed S^l is its value at T_b; same for S^g.

$\Delta S_{vap} = 108.95\ J\,K^{-1}mol^{-1}$ so $T = 374.15\,K$: $\Delta G = -108.95\ J/mol$

$T = 372.15\,K$: $\Delta G = 108.95\ J/mol$

Longer, more correct way:

$$\Delta G_1 = \Delta H_1^l - T_b S^l(T_b) + T S^l(T)$$

$$= (T_b - T)C_p^l - T_b S^l(T_b) + T S^l(T) + T_b S^l(T) - T_b S^l(T)$$

$$= (T_b - T)C_p^l - T_b \underbrace{\left(S^l(T_b) - S^l(T)\right)}_{\ln T_b/T \cdot C_p^l} - (T_b - T)S^l(T)$$

ΔG_3 similar

Thus $\Delta G = (T_b - T)(C_p^l - C_p^g) - T_b \ln T_b/T\ C_p^l - T \ln T/T_b\ C_p^g$

$$- (T_b - T)\underbrace{\left(S^l(T) - S^g(T_b)\right)}_{S^l(T) - S^l(T_b) + S^l(T_b) - S^g(T_b)}$$

$$= \ln T/T_b\ C_p^l - \Delta S_{vap}$$

$$\Rightarrow \Delta G = (T_b - T)(C_p^l - C_p^g) + T \ln T/T_b (C_p^l - C_p^g) + (T_b - T)\Delta S_{vap}$$

Try $T = 374.15K$: $\Delta G = (-1)(41.7) + 374.15 \ln \frac{374.15}{373.15} \cdot 41.7 + (-1)(108.95) \approx -108.95$

reason: $(x+1)\ln\left(\frac{x+1}{x}\right) = (x+1)\ln\left(1 + \frac{1}{x}\right) \approx (x+1)\left(\frac{1}{x}\right) \approx 1$ using $\ln(1+x) \approx x$ for small x.

Physical interpretation of the Helmholtz and Gibbs free energies.

Helmholtz:

$$\Delta U = q + w \qquad 1^{st} \text{ Law}$$

We will express the work as the sum of two terms: expansion work ($-p\Delta V$) and "useful" work (w_{useful})

At constant volume, there is no expansion work.

Also, for a ~~revs~~ reversible process $\Delta S = q_{rev}/T = q/T$

Thus $w_{useful} = \Delta U - T\Delta S = \Delta(U - TS) = \Delta A$

↳ constant T

Here we see that only the part of the internal energy U minus TS can be used to produce work. Therefore, the TS quantity is called the "bound energy" and $(U - TS)$ the "free energy" or "available energy".

For example w_{useful} could be used to charge a battery.

Gibbs: at constant P, T: (reversible)

$$w_{useful} = \Delta U - T\Delta S + P\Delta V = \Delta H - T\Delta S = \Delta(H - TS) = \Delta G$$

$\Delta G < 0$: spontaneous ; w_{useful} = maximum work that can be obtained.

$\Delta G > 0$: non-spontaneous ; w_{useful} = minimum work required to drive this non-spontaneous process.

Also: mechanical work of muscle movement; electrical work of electric potential across cell membrane

Equations (22.22) and (22.34) :

$$A = U - TS \Rightarrow \underbrace{\left.\frac{\partial A}{\partial V}\right)_T}_{-P} = \left.\frac{\partial U}{\partial V}\right)_T - T \underbrace{\left.\frac{\partial S}{\partial V}\right)_T}_{\left.\frac{\partial P}{\partial T}\right)_V}$$

$$\Rightarrow \left.\frac{\partial U}{\partial V}\right)_T = -P + T \left.\frac{\partial P}{\partial T}\right)_V \quad \text{Eq. 22.22.}$$

This kind of equation is called a thermodynamic equation of state because it relates a thermo. expression to P-V-T data.

ideal gas: $\left.\frac{\partial P}{\partial T}\right)_V = \frac{\partial}{\partial T}\left(\frac{nRT}{V}\right)_V = \frac{nR}{V}$

$$\Rightarrow \left.\frac{\partial U}{\partial V}\right)_T = -P + \frac{nRT}{V} = -P + P = 0$$

$$G = H - TS \Rightarrow \underbrace{\left.\frac{\partial G}{\partial P}\right)_T}_{V} = \left.\frac{\partial H}{\partial P}\right)_T - T \underbrace{\left.\frac{\partial S}{\partial P}\right)_T}_{-\left.\frac{\partial V}{\partial T}\right)_P}$$

$$\Rightarrow \left.\frac{\partial H}{\partial P}\right)_T = V - T \left.\frac{\partial V}{\partial T}\right)_P \quad \text{Eq. 22.34}$$

Also a thermodynamic equation of state

ideal gas: $\left.\frac{\partial H}{\partial P}\right)_T = V - T \frac{\partial}{\partial T}\left(\frac{nRT}{P}\right)_P = V - T\frac{nR}{P} = 0$

§22.7 Gibbs-Helmholtz Equation

$$\left.\frac{\partial G}{\partial P}\right)_T = V \implies \Delta G = \int_{P_1}^{P_2} V\,dP \quad \text{at constant } T$$

ideal gas: $\Delta \bar{G} = RT \int_{P_1}^{P_2} \frac{dP}{P} = RT \ln P_2/P_1$

Put $P_1 = 1$ bar to obtain $\bar{G}(T,P) = G^\circ(T) + RT \ln\left(\frac{P}{1\,\text{bar}}\right)$

where $G^\circ(T)$ is the standard molar Gibbs energy.

$$G = H - TS \implies \frac{G}{T} = \frac{H}{T} - S \Rightarrow \frac{\partial}{\partial T}\left(\frac{G}{T}\right)_P = -\frac{H}{T^2} + \underbrace{\frac{1}{T}\left.\frac{\partial H}{\partial T}\right)_P}_{C_P} - \underbrace{\left.\frac{\partial S}{\partial T}\right)_P}_{C_P/T}$$

$$\left.\begin{aligned} &\Rightarrow \frac{\partial}{\partial T}\left(\frac{G}{T}\right)_P = -\frac{H}{T^2} \\ &\text{or } \frac{\partial}{\partial T}\left(\frac{\Delta G}{T}\right)_P = -\frac{\Delta H}{T^2} \end{aligned}\right\} \text{Gibbs-Helmholtz Eq.}$$

Could show some computational free energy data; for example docking or from my pubs.

so that students can see where ΔG gets used