P. Chem I 2/13/23

$dS > \frac{\delta q}{T}$ Clausius inequality $A \equiv U - TS$

Last class defined A = Helmholtz free energy
at constant T, V: A decrease for a spontaneous process.
Also, for a spontaneous process, ΔA represents the maximum useful work obtainable

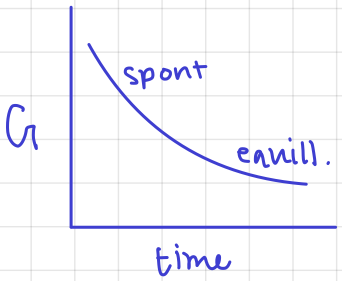
For a non-spontaneous process
ΔA represents the minimum work we need to supply to make this proccess happen.

Const T, P: $dH = \delta q + \underset{\cancel{-P\Delta V}}{\delta w} + \cancel{PdV} + \cancel{VdP}^{0} = d(U+PV)$

$\Rightarrow dH = TdS$ $\Rightarrow \underbrace{d(H - TS)}\leq 0$

$G \equiv H - TS$

Gibb's free energy



$dH = \delta q + \cancel{\delta w} + \delta w_{useful} + \cancel{PdV} - \cancel{VdP}$

rev: $\delta w_{useful\ max} = dH - TdS - dG$
or $w_{useful} = \Delta G$

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

$PV = nRT$ ← you only need to know 2 variables to know all 3

$\boxed{U}$ $dU = \delta q + \delta w = \delta q_{rev} + \delta w_{rev} = TdS - PdV$ ← same concept

regard $U = U(S, V)$ S and V are natural variables of U

like HW I $dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$ $\Rightarrow T = \left(\frac{\partial U}{\partial S}\right)_V$ and $P = \left(\frac{\partial U}{\partial V}\right)_S$

$\frac{\partial}{\partial V}$ $\frac{\partial}{\partial S}$

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

Maxwell Relation

These are equal $\frac{\partial^2 U}{\partial S \partial V}$ or $\frac{\partial^2 U}{\partial V \partial S}$

Now for $\boxed{H}$

$$dH = dU + PdV + VdP = \overbrace{TdS - \cancel{PdV}}^{U} + \cancel{PdV} + VdP$$

$$dH = TdS + VdP$$ S,P natural variables

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

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$\boxed{A}$ $$dA = d(U - T) = TdS - PdV - TdS - SdT$$

$$dA = -PdV - SdT$$ V,T natural variables

$$dA = \left(\frac{\partial A}{\partial V}\right)_T dV + \left(\frac{\partial A}{\partial T}\right)_V dT \qquad \left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$$ Maxwell

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$\boxed{G}$ $$dG = d(H - TS) = TdS + VdP - TdS - SdT = VdP - SdT$$

P,T natural variables

Maxwell

$$dG = \left(\frac{\partial G}{\partial P}\right)_T dP + \left(\frac{\partial G}{\partial T}\right)_P dT \Rightarrow V = \left(\frac{\partial G}{\partial P}\right)_T \quad S = \left(\frac{\partial G}{\partial T}\right)_P \qquad \left(\frac{\partial V}{\partial T}\right)_P = \left(\frac{\partial S}{\partial P}\right)_T$$

Spontaneity

$PV = nRT$

$dU \le 0$ at const. S,V
$dH \le 0$ at const. S,P
$dA \le 0$ at const V,T
$dG \le 0$ at const P,T