Chap 5

Chemical Thermodynamics

Chap 5 uses relations between systems to determine properties of mixtures, reactions phase transitions, energies that can be released...

Important to make a clear distinction between extensive and intensive properties

If you double the system, some properties remain same and some double (nothing else interesting)

Quantities that don't double = <u>intensive</u> quantity
P, T, μ, density

Quantities that double = <u>extensive</u> quantity
V, N, S, U, mass

extensive quantity x intensive quantity = extensive
examples, V x P ; density x V ; Nk_BT
extensive quantity / intensive quantity = extensive
examples S/T ; $(\partial U/\partial T)$
extensive quantity / extensive quantity = intensive
examples mass/V ; U/N ; $(\partial S/\partial N)_{V,U}$; $(\partial S/\partial V)_{U,N}$

extensive x extensive = nonsense

extensive + extensive = OK ($TdS - PdV$)
intensive + intensive = OK

intensive + extensive = nonsense

Chap 5.1 Free energy ⟷ available work

From Chap 1 Enthalpy = $H \equiv \underbrace{U}_{\text{ext.}} + \underbrace{P}_{\text{intens.}}\underbrace{V}_{\text{ext.}}$ is extensive quant

H = energy needed to create system and put in environment at constant pressure

Other cases of interest depending how system formed in environment.

Helmholtz Free Energy: $F \equiv \underbrace{U}_{\text{ext}} - \underbrace{T}_{\text{int.}}\cdot\underbrace{S}_{\text{ext.}}$ is extensive quant

This is total energy needed to create the system, minus the heat you get (for free) from an environment at const temp T.

Gibbs Free Energy: $G = \underbrace{U}_{\text{ext}} - \underbrace{T}_{\text{int}}\underbrace{S}_{\text{ext}} + \underbrace{P}_{\text{int}}\underbrace{V}_{\text{ext}} = \underbrace{H}_{\text{ext}} - \underbrace{T}_{\text{int}}\underbrace{S}_{\text{ext}} = \underbrace{F}_{\text{ext}} + \underbrace{P}_{\text{int}}\underbrace{V}_{\text{ext}}$ is extens.

This is total energy needed to create the system, minus the heat you get from environment at const temp T, plus work you have to do on environment at const pressure P.

U, H, F, G are called thermodynamic potentials and are related to the energy needed to manipulate system from one state to another taking into account simultaneous effect on environment.

See pgs 404-5 for ΔG

Prob 5.2 $N_2 + 3H_2 \rightarrow 2NH_3$ $\Delta G = \Delta H - T\Delta S$

	ΔH	S	ΔG
N_2	0	191.61 J/K	0
H_2	0	130.68 J/K	0
NH_3	−46.11 kJ	192.45 J/K	−16.45 kJ

$2(-16.45\text{ kJ}) \overset{?}{=} 2(-46.11\text{ kJ}) - 298\text{K}\left(2\times 192.45\frac{\text{J}}{\text{K}} - 191.61\frac{\text{J}}{\text{K}} - 3\times 130.68\frac{\text{J}}{\text{K}}\right)$

$-32.9\text{ kJ} = -33.0\text{ kJ}$

We almost never create/destroy system. Changes in U, F, G H are important.

If you change system at constant T

$\Delta F = \Delta U - T\Delta S - \cancel{\Delta T S}^{\,0} = Q + W - T\Delta S$

For quasistatic $Q = T\Delta S \Rightarrow \Delta F = W$

For general transformation $Q < T\Delta S \Rightarrow \Delta F \leq W$ in general

where W is <u>all</u> work done on system

If environment at constant P and T

$\Delta G = \Delta U - T\Delta S - \cancel{\Delta T S}^{\,0} + P\Delta V + \cancel{\Delta P V}^{\,0} = Q + W - T\Delta S + P\Delta V$

Again $Q \leq T\Delta S$

New info $W = W_{environment} + W_{other\ you?} = -P\Delta V + W_{you}$

$\Rightarrow \Delta G \leq W_{you,other}$

For quasistatic $\Delta G = W_{you/other}$

Book example $H_2O(\ell) \rightarrow H_2(g) + \frac{1}{2} O_2(g)$

How much energy do <u>you</u> have to put in

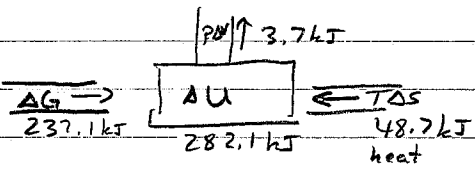
	ΔH	S	ΔG	
H_2O	$-285.83\,kJ$	$69.91\frac{J}{K}$	$-237.13\,kJ$	$\Delta G = \Delta H - T\Delta S$
H_2	0	$130.68\frac{J}{K}$	0	$237.13\,kJ = 285.83\,kJ - 298K\left(130.68\frac{J}{K} + \frac{1}{2}\,205.14\frac{J}{K}\right.$
O_2	0	$205.14\frac{J}{K}$	0	$\left. - 69.91\frac{J}{K}\right)$

$= 237.15\,kJ$ ✓

$P \cdot \Delta V = \frac{3}{2}\,1\,mol\,8.31\frac{J}{mol\,K}\,298K = 3.7\,kJ$

$\Delta U = H - P\Delta V = 282.1\,kJ$

$T\Delta S = 48.7\,kJ$ (get for free-ish)



You add $237.1\,kJ$ and get a change $\Delta S = 282.1\,kJ$

Prob 5.6 $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O(\ell)$

	ΔH	S	ΔG
$C_6H_{12}O_6$	$-1273\ kJ$	$212\ \frac{J}{K}$	$-910\ kJ$
O_2	0	$205\ \frac{J}{K}$	0
CO_2	$-393.5\ kJ$	$213.7\ \frac{J}{K}$	$-394.4\ kJ$
H_2O	$-285.8\ kJ$	$69.9\ \frac{J}{K}$	$-237.1\ kJ$

a) $\Delta H = 6(-393.5\ kJ - 285.8\ kJ) + 1273\ kJ$
$= -2802.8\ kJ$

$\Delta G = 6(-394.4\ kJ - 237.1\ kJ) + 910\ kJ$
$= -2879\ kJ$

b) $\max(W_{other}) = -\Delta G = 2879\ kJ$

c) $Q = T\Delta S = 298K\{6\left[69.9\frac{J}{K} + 213.7\frac{J}{K} - 205\frac{J}{K}\right] - 212\frac{J}{K}\} = 77.4\ kJ$

d) could also have done this by $\Delta H - \Delta G$

e) Q decreases W_{other} decreases.
Q might even become negative $\Rightarrow$ system giving off heat
ΔG and ΔH doesn't change though even when non-ideal.

Thermodynamic identities

From Chap 3 $dU = TdS - PdV + \mu dN \Rightarrow \left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{1}{T}$ etc.

Can construct new identities using G, F, H

For example $dH = dU + PdV + VdP = TdS - \cancel{PdV} + \mu dN + \cancel{PdV} + VdP$
$= TdS + VdP + \mu dN$

More useful $dF = dU - TdS + SdT = -SdT - PdV + \mu dN$

$\Rightarrow \quad S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} \qquad P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} \qquad \mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}$

From G: $dG = dF + PdV + VdP = -SdT + VdP + \mu dN$

$\Rightarrow \quad S = -\left(\frac{\partial G}{\partial T}\right)_{P,N} \qquad V = \left(\frac{\partial G}{\partial P}\right)_{T,N} \qquad \mu = \left(\frac{\partial G}{\partial N}\right)_{T,P}$

Note: the relations using Gibbs free energy all involve derivative with respect to intensive variables.

Can use these relations to extend data in table pg 404-5

Prob 5.10 1 mole $H_2O(\ell)$ at $P = 1$ atm

$\Delta G(30^\circ C) = \Delta G_f(25^\circ C) - S\Delta T = -237.13\,kJ - 69.9\,\frac{J}{K}\,5K$

$= -349.5\,J$

The change in pressure to compensate

$V \cdot \Delta P = -349.5\,J$ $\quad$ $1\,mol = 18\,g = 0.018\,m^3 \times 10^{-3}$

$\Delta P = -349.5\,J / 0.018\,m^3 = 1.94 \times 10^7\,Pa \approx 194\,atm.$

prob 5.12 Use relation $\left(\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial S}\right)_{N,V}\right)_{S,N} = \left(\frac{\partial}{\partial S}\left(\frac{\partial U}{\partial V}\right)_{S,N}\right)_{V,N}$

$\left(\frac{\partial U}{\partial S}\right)_{N,V} = T \qquad \left(\frac{\partial U}{\partial V}\right)_{S,N} = -P \Rightarrow \left(\frac{\partial T}{\partial V}\right)_{S,N} = -\left(\frac{\partial P}{\partial S}\right)_{V,N}$

$\frac{\partial H}{\partial S} = T \qquad \frac{\partial H}{\partial P} = V \Rightarrow \left(\frac{\partial T}{\partial P}\right)_{S,N} = \left(\frac{\partial V}{\partial S}\right)_{V,N}$

$\left(\frac{\partial F}{\partial T}\right) = -S \qquad \left(\frac{\partial F}{\partial V}\right) = -P \Rightarrow \left(\frac{\partial S}{\partial V}\right)_{T,N} = \left(\frac{\partial P}{\partial T}\right)_{V,N}$

$\left(\frac{\partial G}{\partial T}\right) = -S \qquad \left(\frac{\partial G}{\partial P}\right) = V \Rightarrow -\left(\frac{\partial S}{\partial P}\right)_{T,N} = \left(\frac{\partial V}{\partial T}\right)_{P,N}$