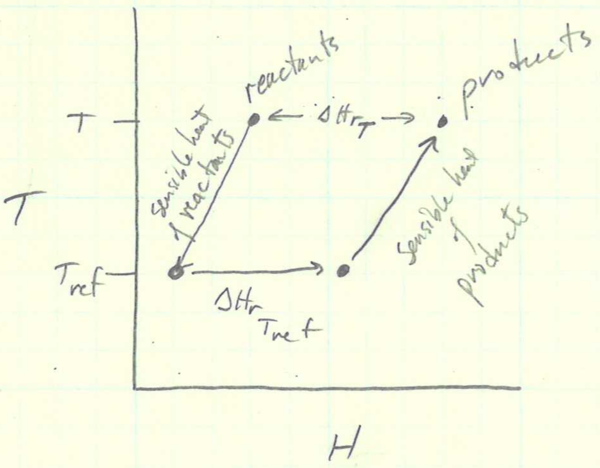
How do we get k_{eq} at different temperatures?

$$\frac{\partial \ln k_{eq}}{\partial T} = \frac{\Delta H_{react}}{RT^2}$$

Note that

$$\Delta H_{react} = f(T) \text{ as well}$$

$$(\Delta H_{react})_T = \left(\int_T^{T_{ref}} \Sigma n_i c_{p_i}\, dT\right)_{reactants} + (\Delta H_{react})_{T_{ref}} + \left(\int_{T_{ref}}^{T} \Sigma n_j c_{p_j}\, dT\right)_{pro}$$



idea:

$$\frac{\partial \ln k_{ea}}{\partial T} = \frac{\Delta H_{rxn}}{RT^2} = \frac{f(T)}{RT^2}$$

$$\int_{T_{ref}}^{T} d \ln K_{eq} = \int_{T_{ref}}^{T} \frac{f(T)}{RT_2}\, dT$$

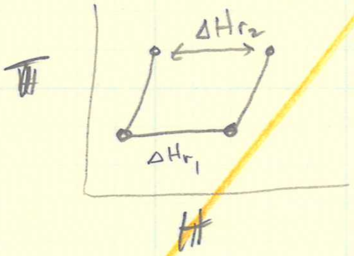
f(T) is usually some combination of polynomials.

B. More Concepts on Equilibrium

1. How do we get k_{eq} at different temperatures?

$$\frac{\partial \ln k_{eq}}{\partial T} = \frac{\Delta H_{react}}{RT^2}$$

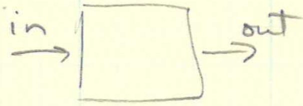
$$(\Delta H_{react})_{T_2} = \left(\int_{T_2}^{T_1} \Sigma n_i c_{p_i}\, dT\right)_{reactants} + (\Delta H_{react})_{T_1} + \left(\int_{T_1}^{T_2} \Sigma n_j c_{p_j}\, dT\right)_{prod}$$



i.e., $\Delta H_r = f(T, c_{p_i}\text{'s})$

see previous sheet

2. How do we do equilibrium when we have lots of species?



$$G_{out} = (\Sigma n_i G_i)_{out}$$

$\Rightarrow$ chemical equilibrium occurs when G_{out} is at a minimum!

$$dG_{out} = 0 = \Sigma(G_i\, dn_i)_{out} + \Sigma(n_i\, dG_i)_{out}$$

$\Downarrow$

a. find n_i's to minimize G_{out} (constant T, H varies)

b. find n_i's <u>and</u> T to minimize G_{out} (constant H)

3. So what do you need to calculate chemical equilibrium?

(Input)

(a) feed composition

(b) pressure

(c) energy level { 1. Temperature
{ 2. Enthalpy { a. adiabatic
{ c. heat loss calculated

so if $y_{i_{feed}}$, P_{tot} & T are specified,

$$\left(dG_{out}\right)_{constant\ P, T, y_{i_{feed}}} = 0$$

→ guess $n_{i_{out}}$

⇓

get Cp's

⇓

get H & S level

⇓

calculate G ┘

4. Constraints (i.e., boundary conditions on solution)

a. element, mass balance on each element k

$$\Sigma\left(\alpha_{ik} n_i\right)_{feed} = \Sigma\left(\alpha_{ik} n_i\right)_{out}$$

b. energy balance (or constant T)

5. Problems with using equilibrium codes

a. solid & liquid species $C(s)$, $H_2O(l)$, $Al_2O_3(s)$
(single species ok, multiple condensed species of same element are very difficult)

b. ideal gas

c. need data for all relevant species

6. All major codes (EDWARDS, NASA-Lewis, StanJan) use minimization of Gibb's free energy

$$\frac{h}{RT} = z_1 + \frac{z_2 T}{2} + \frac{z_3 T^2}{3} + \frac{z_4 T^3}{4} + \frac{z_5 T^4}{5} + \frac{z_6}{T}$$

$$dH = c_p dT + \left[\underline{V} - T \left(\frac{\partial \underline{V}}{\partial T} \right)_P \right] dP$$ Balzhiser p. 167,

$$P\underline{V} = RT$$

$$\underline{V} = \frac{RT}{P} \qquad \left(\frac{\partial \underline{V}}{\partial T} \right)_P = \frac{R}{P}$$

$$T \left(\frac{\partial \underline{V}}{\partial T} \right)_P = \frac{RT}{P} = \underline{V}$$

so for ideal gas, no change in enthalpy with pressure!