Class 2a

More Equilibrium Concepts

A. Review

1. Kinetic view of equilibrium: forward rate = backward rate

$$K_{eq} = \frac{k_1}{k_{-1}} = \left[\prod_{i=1}^{n} C_i^{\alpha_i}\right]_{at\ equil}$$

2. Thermodynamic view of equilibrium

a. $\Delta G^\circ_{rxn} = -RT \ln K_{eq}$

b. ΔG° and K_{eq} independent of pressure

c. $G = H - TS$; $dG = -SdT + VdP$

d. $K_{eq} = \prod_{i=1}^{n} a_i^{\alpha_i}$

a_i = activity coefficient = $\frac{f_i}{f_i^0}$ [$=P_i$ for ideal gases]

e. Table available for ΔG°_f; $\Delta G^o_{react} = \sum_{i=1}^{n} \alpha_i \left(\Delta G^o\right)_{fi}$

f. $K_{eq} = K_{y_i} K_{P_{tot}} = K_{P_i} = \frac{K_{C_i}}{K_T}$

both K_y and K_{Ptot} are dependent on total pressure if $\Delta n = 0$, but they compensate for eachother so K_{eq} is <u>independent</u> of pressure!

g. Given K_{eq} and P_{tot}, we can find y_i's @ equilbrium if we have y_{feed} (one reaction only)

B. More Concepts on equilibrium

- Hand-written notes…

C. Code Inputs

- Z^L_{1-7} low T range coefficients 300-1000 K
- Z^H_{1-7} high T range coefficients 1000-5000 K

$$\frac{h^o}{RT} = \left(\sum_{i=1}^{5} \frac{z_i T^{i-1}}{i}\right) + \frac{z_6}{T}$$

$$\frac{S^o}{R} = z_1 \ln T + \left(\sum_{i=2}^{5} \frac{z_i T^{i-1}}{i-1}\right) + z_7$$

- for ideal gas, $C_p - C_v = R$
- $dH = C_p\, dT$
  (i.e., no pressure dependence for ideal gas)
- $dS = C_p\, d\ln T - R\, d\ln P$
  (also, $dH = TdS + VdP$)
- $dU = C_v\, dT$

Approach

- Given expression for $H_i^\circ(T)$ and $S_i^\circ(T)$

Get S_i $\qquad S_i - S_i^0 = \int_{P_0}^{P} -R\, d\ln P$

Get S and H $\qquad S = \sum_i n_i S_i$, $\quad H = \sum_i n_i H_i$

get $G = H - TS$

minimize G

Change T

Change n_i

Sample Input Thermo Data

- (from NASA-Lewis)

Name | Source & Date | Elemental Composition | Phase | T_{low} | T_{high}

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H2                       J 3/61H   200   000   000   0G   300.000  5000.000         1
 0.30989658E 01 0.51321595E-03 0.51397641E-07-0.34609047E-10 0.36695462E-14    2
-0.87694041E 03-0.19569318E 01 0.30564452E 01 0.26833104E-02-0.58288567E-05    3
 0.55426526E-08-0.18209110E-11-0.98878140E 03-0.22961187E 01                   4
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Z_i's, low T range | Z_i's, high T range | Card Number