17.1 Ideal Gas Equilibrium Constant Method

$$CH_4 + H_2O \rightleftarrows CO + 3\,H_2 \qquad (1)$$

ν_i	-1	- 1	1	3

ν_i is stoichiometric number

$|\nu_i|$ is stoichiometric coefficient

$$\frac{dn_1}{\nu_1} = \frac{dn_2}{\nu_2}$$

$$n_i^f = n_i^i + \nu_i \xi$$

Process

1. # phases? Method? (K_a method).
2. Find $\Delta G^o{}_T$ and K_a.
3. Material balance.
4. Solve!

For ideal gases

$$K_a = \prod (y_i P)^{\upsilon_i} = (\prod y_i^{\upsilon})P^{\sum \upsilon_i}$$

K_a = 1.422 for reaction (1) at 900 K

Feed: 1 mol CH_4, 3 mol H_2O, find equil. prod., 2 bar

CH_4

H_2O

CO

H_2

Summary at 900 K

In P(bar) X_{CH4}

17.2 Equilibrium Constraint

At reaction equilibria, Gibbs energy minimized:

$$\underline{G} = \underline{G}(T, P, n_i)$$

at constant T,P $\quad d\underline{G} = -\underline{S}dT + \underline{V}dP + \sum \mu_i dn_i$

$$d\underline{G} = \sum \mu_i dn_i = 0 = \sum \mu_i \upsilon_i d\xi$$

how get μ? $\quad dG = RTd\ln f$

$$\int_{G^\circ}^{\mu} dG_i = \mu_i - G_i^o = RT\int_{f_i^o}^{\hat{f}_i} d\ln f_i = RT\ln\frac{\hat{f}_i}{f_i^o}$$

$$\mu_i = G_i^o + RT\ln\frac{\hat{f}_i}{f_i^o} \quad \text{plug into } 0 = \sum \mu_i \upsilon_i$$

$$0 = \sum \upsilon_i\left(G_i^o + RT\ln\frac{\hat{f}_i}{f_i^o}\right)$$

$$\sum \upsilon_i G_i^o = -RT\sum \upsilon_i \ln\frac{\hat{f}_i}{f_i^o}$$

Standard State - denoted with superscript ^{o}

17.3 Equilibrium Constant (RHS)

$$-RT\sum \upsilon_i \ln \frac{\hat{f}_i}{f_i^o}$$

Note: $\upsilon \ln a = \ln a^{\upsilon}$

also $\ln a^{\upsilon_a} + \ln b^{\upsilon_b} = \ln a^{\upsilon_a} b^{\upsilon_b}$

Equlibrium Constant

For ideal gas

$\hat{f}_i^{ig} = y_i P$ ($f_i = P$ if pure) choose Standard State as pure gas at 1bar

$$f_i^o = 1bar$$

Must always express $\hat{f}_i$ in bar

17.4 Standard State Gibbs Energy of Rxn

LHS - involves properties at a standard state

$$\sum \upsilon_i G_i^o = \Delta G_T^o$$

$$CH_4 \quad + \quad H_2O \quad = \quad CO \quad + \quad 3H_2$$

$$-\Delta G^o_{f,\,CH_4} \qquad -\Delta G^o_{f,\,H_2O} \qquad \Delta G^o_{f,\,CO} \qquad 3\Delta G^o_{f,\,H_2}$$

$$C \quad + \quad 3H_2 \quad + \quad \frac{1}{2}O_2$$

find ΔG^o_f at 298.15°K $\qquad$ Appendix E, Elliott & Lira

Standard State:

T of system

Specified P^{o}, usually 1 bar

Composition

State of aggregation

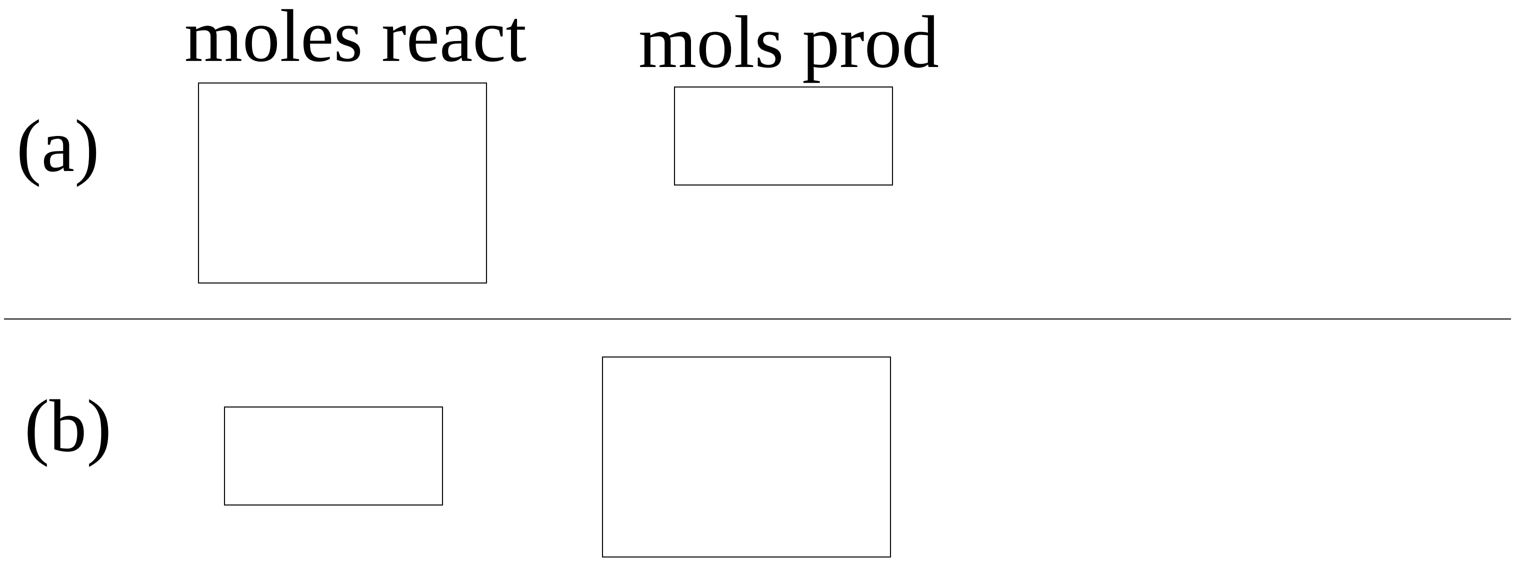
Combine RHS, LHS (slide 5)

$$\Delta G_T^o = -RT\sum \ln\left(\frac{\hat{f}_i}{f_i^o}\right)^{\upsilon_i} = -RT\sum \ln(a_i)^{\upsilon_i}$$

$$= -RT\ln K_a$$

Composition and Pressure Independence of K_a

17.5 Effect of Pressure, Inerts, Feed Ratios
Le Châtelier’s principle



Inerts -

Nonstoichiometric Feed -

17.6 Determining Spontaneity of Reactions

$$\sum_i \nu_i \mu_i = \sum_i \nu_i G_i^\circ + RT \sum_i \nu_i \ln\left[\frac{\hat{f}_i}{f_i^\circ}\right] \qquad 17.22$$

$$\Delta G_T = \Delta G_T^\circ + RT \sum_i \nu_i \ln\left[\frac{\hat{f}_i}{f_i^\circ}\right] = \Delta G_T^\circ + RT \ln \prod_i \left[\frac{\hat{f}_i}{f_i^\circ}\right]^{\nu_i} \qquad 17.23$$

$$\Delta G_T^o < 0$$

$$\Delta G_T^o > 0$$

17.4 Temperature effects on ΔG_T^o and K_a.

van't Hoff Eqn $$\frac{\partial(\Delta G_T^o / RT)}{\partial T} = -\frac{\Delta H_T^o}{RT^2} = \left(\frac{\partial \ln K_a}{dT}\right)$$

$$\boxed{\frac{\Delta G_T^o}{RT} = -\int_{T_R}^{T} \frac{\Delta H_T^o}{RT^2}\, dT + \frac{\Delta G_R^o}{RT_R}} \qquad (17.26)$$

$$\Delta H_T^o = \Delta H_R^o + \int_{T_R}^{T} \Delta C_P \, dT \qquad (3.44)$$

$$\Delta C_P = \sum \upsilon_i a_i + (\sum \upsilon_i b_i) T + (\sum \upsilon_i c_i) T^2 + (\sum \upsilon_i d_i) T^3$$

$$\Delta H_R^o = J + \Delta a T + \frac{\Delta b}{2} T^2 + \frac{\Delta c}{3} T^3 + \frac{\Delta d}{4} T^4 \quad (3.46)$$

$$\frac{\Delta G^\circ}{RT} = -\ln K_a = \frac{J}{RT} - \frac{\Delta a}{R} \ln T - \frac{\Delta b T}{2R} - \frac{\Delta c T^2}{6R} - \frac{\Delta d T^3}{12R} + I \quad (17.28)$$

17.8 Shortcut van't Hoff

$$\boxed{\ln\left(\frac{K_a}{K_{aR}}\right) = \frac{\Delta G_R^\circ}{RT_R} - \frac{\Delta G_T^\circ}{RT} = \frac{-\Delta H_R^\circ}{R}\left(\frac{1}{T} - \frac{1}{T_R}\right)} \quad (17.29)$$

Example 17.4

$C_2H_4 + H_2O \rightleftarrows C_2H_5OH$

Kcalc.xls, Kcalc.m

1) Be careful with stoich

2) Don't use incomplete Cp data

3) $\Delta(H_T < 0)$ K_a with T ξ Exothermic

$\Delta(H_T > 0)$ K_a with T ξ Endothermic

4) if all $C_P = 0$ - shortcut method .

Plugging into Eqn 3.44 (slide 12) becomes

use $\Delta H^o_{298} = -45.63\text{kJ/mol}$ at $T = 298.15$ to find J into Eqn. 17.26

$\Delta G^o_{298} = -7.55\text{kJ/mol}$ at 298.15 find I

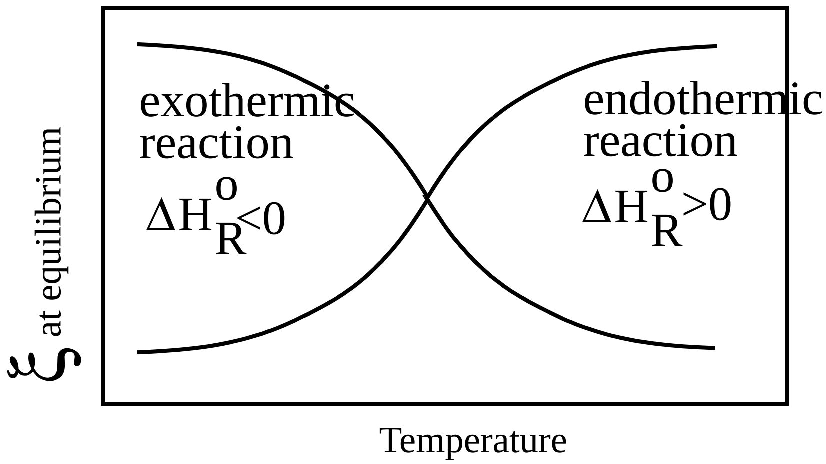
Example 17.5 (repeat Ex17.4 by shortcut method)

$C_2H_4 + H_2O = C_2H_5OH$

$$\ln K_a = -\frac{\Delta H^o_{298}}{R}\left(\frac{1}{T} - \frac{1}{298.15}\right) - \frac{\Delta G^o_{298}}{R(298.15)}$$

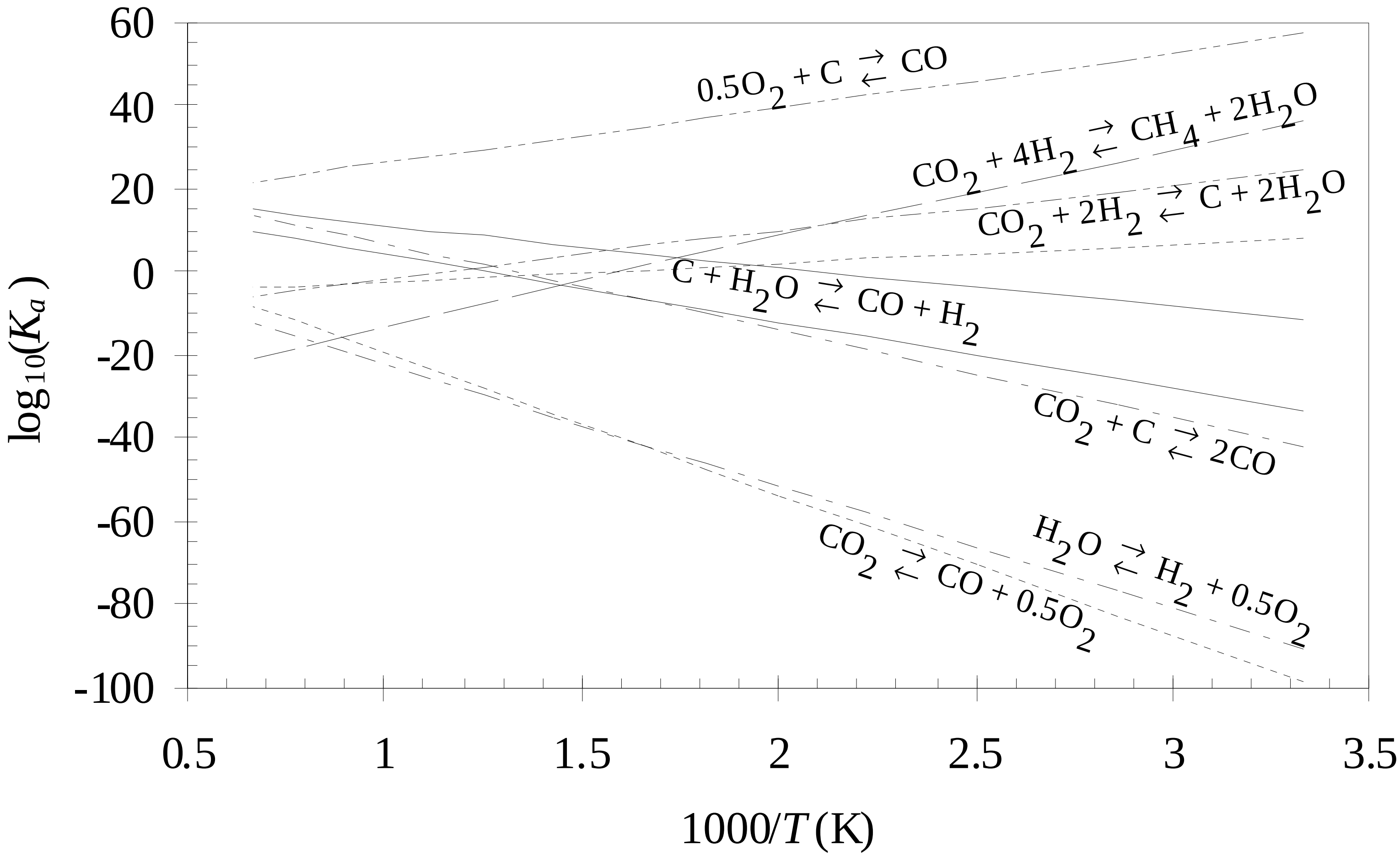
K_a shortcut $\quad K_a$ full

at 593.15



Qualitative behavior of equilibrium conversion for exothermic and endothermic reactions

17.9 Visualizing Multiple Equilibrium Constants



17.10 Multiple Reactions
Example 17.6 solved by Excel
Gas-Phase

$$A + B \; = \; C + D \qquad\qquad K_{a1} \; = \; 2.667$$

$$A + C \; = \; 2\mathrm{E} \qquad\qquad K_{a2} \; = \; 3.200$$

Feed 2 *mol A*, 1 *mol B*, *P* =10bar

$$K_{a1} = 2.667 =$$

$$K_{a2} = 3.2 =$$

$$OBJ1 = 2.667(2 - \xi_1 - \xi_2)(1 - \xi_1) - (\xi_1 - \xi_2)\xi_1 = 0$$

$$OBJ2 = 3.2(2 - \xi_1 - \xi_2)(\xi_1 - \xi_2) - 4\xi_2^2 = 0$$

Solver

Solve $OBJ1 = 0$ subject to constraint that $OBJ2 = 0$, by varying ξ_1, ξ_2 .

17.11 Chemical Coupling

17.12 Energy Balances with equilbrium constraint
Graphical Energy Balance - Heat of reaction method

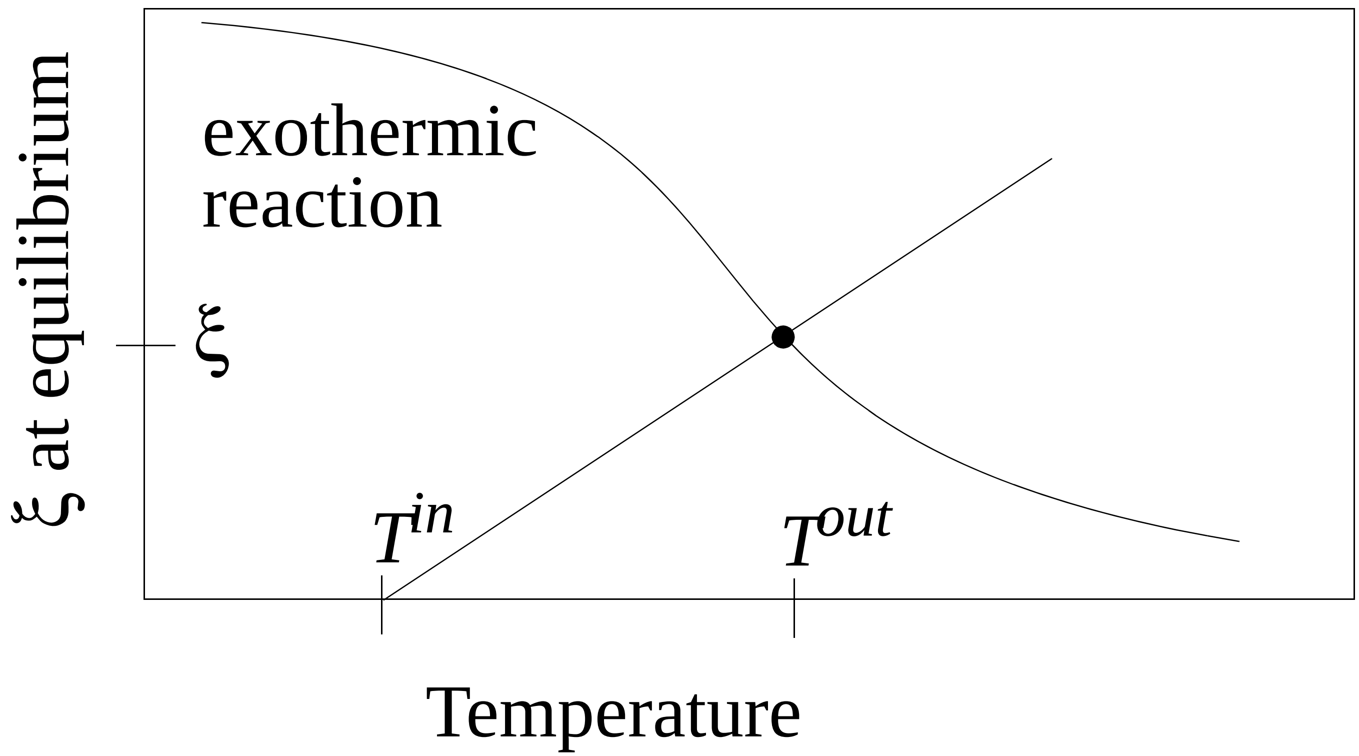
$$0 = \sum_{components} \dot{n}_i^{in} \int_{T_R}^{T^{in}} C_{P,\,i} dT - \sum_{components} \dot{n}_i^{out} \int_{T_R}^{T^{out}} C_{P,\,i} dT$$

$$- \dot{\xi} \Delta H_R^o$$

$$\dot{m}^{in} = \dot{m}^{out} \qquad \dot{m}C_{P_m}^{in} \approx \dot{m}C_{P_m}^{out}$$

$$0 = \dot{m}C_{P_m}(T^{in} - T^{out}) - \dot{\xi}\Delta H_R$$

$$T^{out} \approx T^{in} - \frac{\dot{\xi}\Delta H_R^o}{\dot{m}C_{Pm}}$$



ξ at equilibrium
exothermic
reaction
ξ
T^{in}
T^{out}
Temperature

for given ξ, T^{in} find

a)

b)

for $\underline{\dot{Q}} = 0$ can find

c)

Example 17.9

$1/2\ N_2 + 3/2\ H_2 \rightarrow NH_3$

Feed 400 K, 100 bar, stoichiometric feed.

Find outlet T, ξ for reaction.

$$\Delta G^o_{298} = \text{-16,401 J/mol} \quad \Delta H^o_{298} = \text{-45,940 J/mol}$$

	n_i^{in}	n_i^{out}	y_i
H_2	$3/2$		
N_2	$1/2$		
NH_3	0		

$$K_a = 742.91\ \exp\left(5526.6\left(\frac{1}{T} - \frac{1}{298.15}\right)\right)$$

$$K_a P\left(\frac{3^3}{2^4}\right)^{\frac{1}{2}} = \frac{\xi(2-\xi)}{(1-\xi)^2} = M\text{, depends on } T, P$$

rearrange

$$\xi = 1 - \sqrt{1 - \left(\frac{M}{1+M}\right)}$$

$K_a = f(\xi)$, find ξ , find y_i

ξ depends on ratio of reactants fed and inerts

Strategy:

1. guess T^{out}
2. calc K_a , M , ξ
3. $n_i^{out} = n_i^{in} + \upsilon_i\xi$, use n_i^{out} , ξ E-bal.

   E-bal close?

17.13 Liquid Components

$$\frac{\hat{f}_i}{f_i^\circ} = \frac{x_i \gamma_i \varphi_i^{sat} P_i^{sat} \exp\left(\frac{V^L(P - P^{sat})}{RT}\right)}{\varphi_i^{sat} P_i^{sat} \exp\left(\frac{V^L(1 - P^{sat})}{RT}\right)}$$

$$= x_i \gamma_i \exp\left(\frac{V^L(P - 1)}{RT}\right) \approx x_i \gamma_i$$

Example, dimerization of LA

17.14 Solid Components in Reactions

$$CO_{(g)} + H_{2(g)} = C_{(s)} + H_2O_{(g)}$$

Solid activity is 1 when pure. Need Gibbs energy of formation for solid.

17.15 Rate Perspectives

$$2A_{(g)} + B_{(g)} \rightleftarrows C_{(g)} + D_{(g)}$$

$$-r_{A,f} = k_f\,[A]^2[B] \qquad r_{A,r} = k_r\,[C][D]$$

$$r_{A,f} + r_{A,r} = -k_f\,[A]^2[B] + k_r\,[C][D] = 0$$

$$\frac{[C][D]}{[A]^2[B]} = \frac{k_f}{k_r} = \frac{(y_C P)(y_D P)}{(y_A P)^2(y_B P)} = K_a(RT)^{\Sigma\nu_i}$$

17.16 Entropy Generation

17.17 Gibbs Minimization

$$\underline{G} = \sum n_i \overline{G}_i$$

and $$\frac{\overline{G}_i}{RT} = \frac{G_i}{RT} + \left(\frac{\overline{G}_i - G_i}{RT}\right) = \frac{G_i}{RT} + \ln y_i \quad \text{(ig)} \quad 17.31$$

Pressure correction $$\frac{G_i}{RT} = \frac{\Delta G^o_{f,i}}{RT} + \ln\frac{P}{P^o} \quad \text{(ig)} \quad 17.32$$

$$\underline{G}/RT = \Sigma\, n_i \Delta G_{f,i}{}^o/RT + \Sigma\, n_i \ln y_i P$$

$$\frac{\Delta G_T{}^\circ}{RT} = \frac{\Delta G_{298}{}^\circ}{RT_{298}} + \frac{\Delta H_{298R}{}^\circ}{R}\left(\frac{1}{T} - \frac{1}{T_{298}}\right)$$

Summary

Relation of ξ to K_a. Relation of K_a to ΔG_T^o.

Calculation of ΔG_T^o from ΔG_{298}^o and ΔH_{298}^o.

Calculation of ΔG_{298}^o from $\Delta G_{f,298}^o$ for species.

Calculation of ΔH_{298}^o from $\Delta H_{f,298}^o$ for species.

Energy Balances for Reacting Systems
  Adiabatic reactions

Determination of equilibria for multiple reactions.

Liquids and Solids
Gibbs Minimization