Chap 14

14.1	Reaction Coordinate
14.2 - 14.3	Equilibrium Compositions
14.4-5, 14.7	Effect of T,P on Equilibrium
14.6	Energy Balances for Reacting Systems
14.8	Multiple Reactions

14.1 Reaction Coordinate

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

ν_i	-1	- 1	1	3

Note: Elliott and Lira

ν_i is stoichiometric number - USE THIS

Felder and Rousseau

ν_i is stoichiometric coefficient

β_i is stoichiometric number

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

Reaction Coordinate $d\xi = dn_i / \nu_i$

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

At reaction equilibria, Gibbs energy minimized:

Standard State - denoted with superscript ^{o}

T of system

Specified P^o, usually 1 bar or 1 atm

Composition

State of aggregation

14.2 Equilibrium Constraint

Standard State Gibbs Energy of Rxn at T.

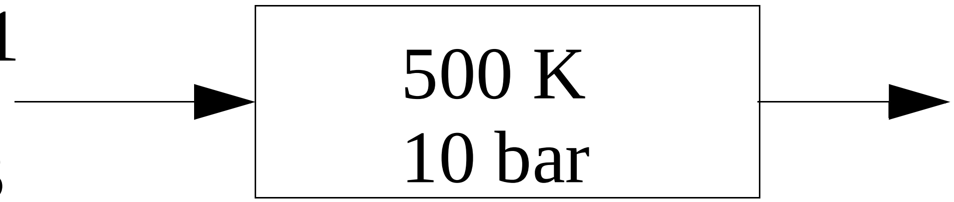
14.3 Equilibrium Constant for Gas Phase Reaction

Modification of Example 14.3

$CO + 2H_2 \text{ --> } CH_3OH$

$\dot{n}_{CO_2} = 1$

$\dot{n}_{H_2} = 3$



Relation of Kinetic Constants to K_a for elementary reaction.

14.4 Temperature effects on ΔG_T^o and K_a.

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

$$\boxed{\frac{\Delta G_T^o}{RT} = -\int_{T_R}^{T} \frac{\Delta H_T^o}{RT^2}\, dT + \frac{\Delta G_R^o}{RT_R}} \qquad (14.25)$$

$$\Delta H_T^o = \Delta H_R^o + \int_{T_R}^{T} \Delta C_P \, dT \qquad (14.26)$$

Standard Heat of Reaction

$$\Delta H_R^o \equiv \sum v_i H_{R,\,i}^o \; = \; \sum v_i \Delta H_{fR,\,i}^o \; = \; \sum_{products} |\nu_i| \Delta H_{fR,\,i}^o - \sum_{reactants} |\nu_i| \Delta H_{fR,\,i}^o \qquad (14.27)$$

Eqn 14.26 becomes

$$\Delta H_T^o = \Delta H_R^o + \Delta a(T - T_R) + \frac{\Delta b}{2}(T^2 - T_R^2) + \frac{\Delta c}{3}(T^3 - T_R^3) + \frac{\Delta d}{4}(T^4 - T_R^4)$$

$$= J + \Delta a T + \frac{\Delta b}{2} T^2 + \frac{\Delta c}{3} T^3 + \frac{\Delta d}{4} T^4$$

$$\frac{\Delta G^o}{RT} = \frac{J}{RT} - \frac{\Delta a}{R} \ln T - \frac{\Delta b T}{2R} - \frac{\Delta c T^2}{6R} - \frac{\Delta d T^3}{12R} + I$$

Example 14.5

$C_2H_4 + H_2O = C_2H_5OH$

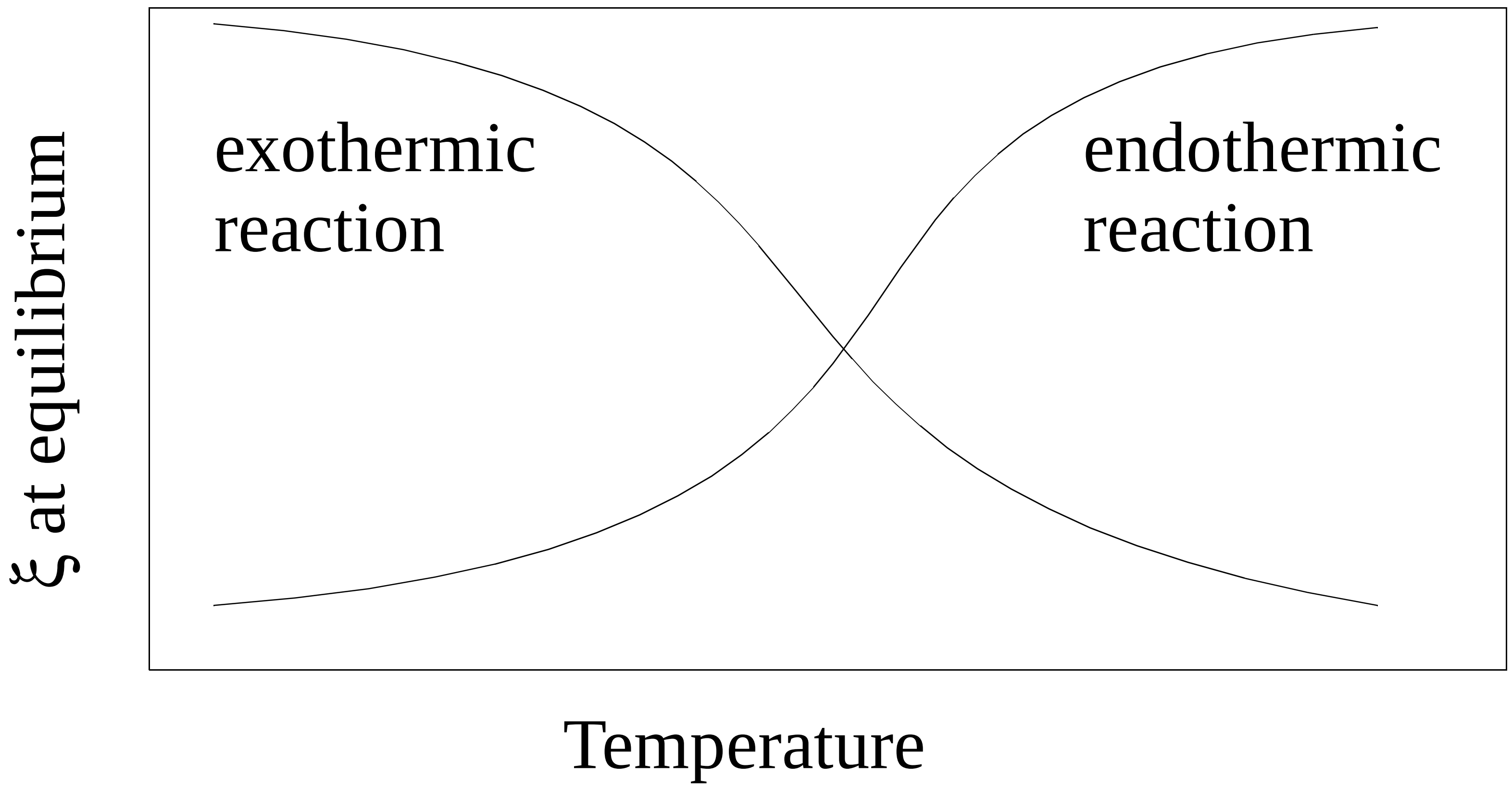
Kcalc.xls

Shortcut van't Hoff

$$\ln\left(\frac{K_a}{K_{aR}}\right)=\frac{\Delta G_T^o}{RT}-\frac{\Delta G_R^o}{RT_R}=\frac{-\Delta H_R^o}{R}\left(\frac{1}{T}-\frac{1}{T_R}\right) \quad (14.31)$$

Example 14.6 (repeat Ex14.5 by shortcut method)

$C_2H_4 + H_2O = C_2H_5OH$



Qualitative behavior of equilibrium conversion for exothermic and endothermic reactions.

15.6 Energy Balances for Reacting Systems

Method 1

$$0 = \sum_{components} \dot{n}_i^{in} \int_{T_R}^{T^{in}} C_{P,\,i} dT - \sum_{components} \dot{n}_i^{out} \int_{T_R}^{T^{out}} C_{P,\,i} dT + \underline{\dot{Q}} + \underline{\dot{W}}_S - \dot{\xi} \Delta H_R^o$$

Method 2

$$0 = H^{in}\dot{n}^{in} - H^{out}\dot{n}^{out} + \underline{\dot{Q}} + \underline{\dot{W}}_S$$

where

$$H^{in}\dot{n}^{in} = \sum_{components} \dot{n}_i^{in}\left(\Delta H^o_{fR,\,i} + \int_{T_R}^{T^{in}} C_P dT\right)$$

and

$$H^{out}\dot{n}^{out} = \sum_{components} \dot{n}_i^{out}\left(\Delta H^o_{fR,\,i} + \int_{T_R}^{T^{out}} C_P dT\right)$$

Adiabatic Reactors

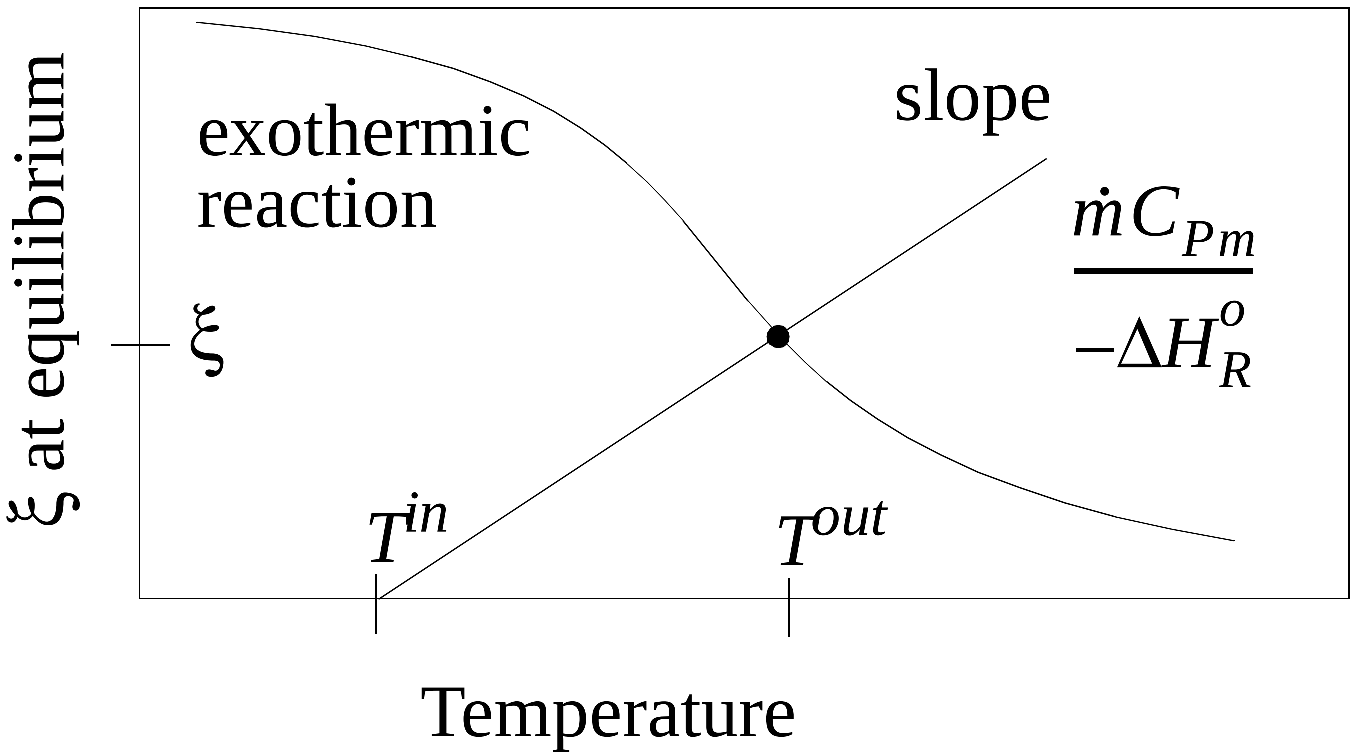
$$0 = \sum_{components} \dot{n}_i^{in} \int_{T_R}^{T^{in}} C_{P,\,i} dT - \sum_{components} \dot{n}_i^{out} \int_{T_R}^{T^{out}} C_{P,\,i} dT$$
$$- \dot{\xi} \Delta H_R^o$$

Example 14.7
$1/2\ N_2 + 3/2\ H_2 \rightarrow NH_3$
Feed 25°C, 100 bar, stoichiometric feed. Find outlet T, ξ for reaction (provided we get it started).

Graphical Energy Balance

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

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


ξ at equilibrium
ξ
exothermic
reaction
slope
$\frac{\dot{m} C_{Pm}}{-\Delta H_R^o}$
T^{in}
T^{out}
Temperature

14.7 Pressure Effects (Doesn't change K_a)

14.8 Multiple Reactions

Example 14.8 solved by Excel

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.

Determination of equilibria for multiple reactions.