Heterogeneous Reactions

key difference for reactants in solid phase: fugacity does not depend on pressure, cannot change as long as there is any solid present.

E.g. $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

$$K(T) = \frac{f_{CaO}\, f_{CO_2}}{f_{CaCO_3}}$$

$f_{CaO} = f_{CaCO_3} = f^{\circ} = 1$ bar as long as any $CaO, CaCO_3$ is present

$$\Rightarrow K(T) = y_{CO_2} \cdot P$$

Example 10.4

Calculate max T for stability of calcite in 390 ppm CO_2 atmosphere

$$C_p(CaCO_3) = a + bT - c/T^2 - dT^2 + e\sqrt{T}$$

$\underline{S}^{\circ}(CaCO_3) = 91.7$ J/mol K $\quad \Delta \underline{H}^{\circ}_{form} = -1207.6 \frac{kJ}{mol}$

see worksheet → Illustrate numerical integration of heat capacities, van't Hoff Equation ←

$$\Delta \underline{H}^{\circ}_{rxn}(T_2) \simeq \Delta \underline{H}^{\circ}_{rxn}(T_1) + \frac{T_2 - T_1}{2} \cdot \left[\Delta C_p^{\circ}(T_1) + \Delta C_p^{\circ}(T_2)\right]$$

$$\ln[K(T_2)] = \ln[K(T_1)] + \frac{T_2 - T_1}{2}\left(\frac{\Delta \underline{H}^{\circ}_{rxn}(T_1)}{RT_1^2} + \frac{\Delta H^{\circ}_{rxn}(T_2)}{RT_2^2}\right)$$

At $T = 298$ K $\quad \Delta H^\circ_{rxn} = 179.0$ kJ/mol

$\Delta G^\circ_{rxn} = 31.2 \frac{kJ}{mol} \Rightarrow \ln K = -53$ @ $T = 298$ K

Endothermic reaction: as $T \uparrow$ $K \uparrow$

$$y_{CO_2} P = 390 \cdot 10^{-6} \cdot 1.01 \text{ bar} = 4.0 \cdot 10^{-4} \text{ bar} = K(T)$$

$\Rightarrow$ $\boxed{T = 804 \text{ K}}$ for $T < 804$ K $CaCO_3$ stable

$T > 804$ K $CaCO_3$ decomposes

Multiple Reactions

Independent reactions $1, 2, \ldots r$

$$K_j(T) = \exp\left(-\frac{\Delta G^\circ_{rxn,j}}{RT}\right) \quad j = 1, 2, \cdots, r$$

$$f_1^{\nu_{11}} f_2^{\nu_{12}} \cdots f_n^{\nu_{1n}} = K_1(T)$$

$$f_1^{\nu_{21}} f_2^{\nu_{22}} \cdots f_n^{\nu_{2n}} = K_2(T)$$

$$\vdots$$

$$f_1^{\nu_{r1}} f_2^{\nu_{r2}} \cdots f_n^{\nu_{rn}} = K_r(T)$$

Example - Coal Gasification (10.5)

$C + H_2O \rightleftharpoons CO + H_2$ $\quad$ $C + CO_2 \rightleftharpoons 2CO$

$C + 2H_2O \rightleftharpoons CO_2 + 2H_2$ $\quad$ $CO + H_2O \rightleftharpoons CO_2 + H$

$C + 2H_2 \rightleftharpoons CH_4$

} How many independent reactions?

CBE 246 Heterogeneous Rxn, Multiple Rxn ③

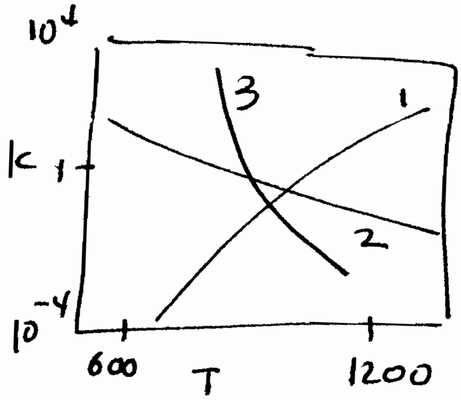
$$M = \begin{bmatrix} & C & H_2O & CO & H_2 & CO_2 & CH_4 \\ & -1 & -1 & 1 & 1 & 0 & 0 \\ & -1 & -2 & 0 & 2 & 1 & 0 \\ & -1 & 0 & 0 & -2 & 0 & 1 \\ & -1 & 0 & 2 & 0 & -1 & 0 \\ & 0 & -1 & -1 & 1 & 1 & 0 \end{bmatrix} \rightarrow \begin{bmatrix} -1 & -1 & 1 & 1 & 0 & 0 \\ 0 & -1 & -1 & 1 & 1 & 0 \\ 0 & 1 & -1 & -3 & 0 & 1 \\ 0 & 1 & 1 & -1 & -1 & 0 \\ 0 & -1 & -1 & 1 & 1 & 0 \end{bmatrix} \rightarrow \begin{bmatrix} -1 & -1 & 1 & 1 & 0 & 0 \\ 0 & -1 & -1 & 1 & 1 & 0 \\ 0 & 0 & -2 & -2 & 1 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

rank(M) = 3, 3 independent reactions:
(Rows of final matrix – not unique, other choices possible)

$C + H_2O \rightleftharpoons CO + H_2$ rxn 1 endothermic

$CO + H_2O \rightleftharpoons CO_2 + H_2$ rxn 2 ~weakly exoth.

$2CO + 2H_2 \rightleftharpoons CO_2 + CH_4$ rxn 3 exothermic



Species	Amount
H_2O	$1 - \xi_1 - \xi_2$
CO	$\xi_1 - \xi_2 - 2\xi_3$
H_2	$\xi_1 + \xi_2 - 2\xi_3$
CO_2	$\xi_2 + \xi_3$
CH_4	ξ_3
total	$1 + \xi_1 - 2\xi_3$

$$K_1 = \frac{y_{H_2} y_{CO} P}{y_{H_2O}} \qquad K_2 = \frac{y_{H_2} y_{CO_2}}{y_{CO} y_{H_2O}} \qquad K_3 = \frac{y_{CO_2} y_{CH_4}}{y_{CO}^2 \, y_{H_2}^2}$$

Hard to find ξ_1, ξ_2, ξ_3 initial guesses / need solution with constraints:

$0 \le y_i \le 1$ for all species