Topic 5G. Chemical Equilibrium

5G.1 The Reversibility of Reactions

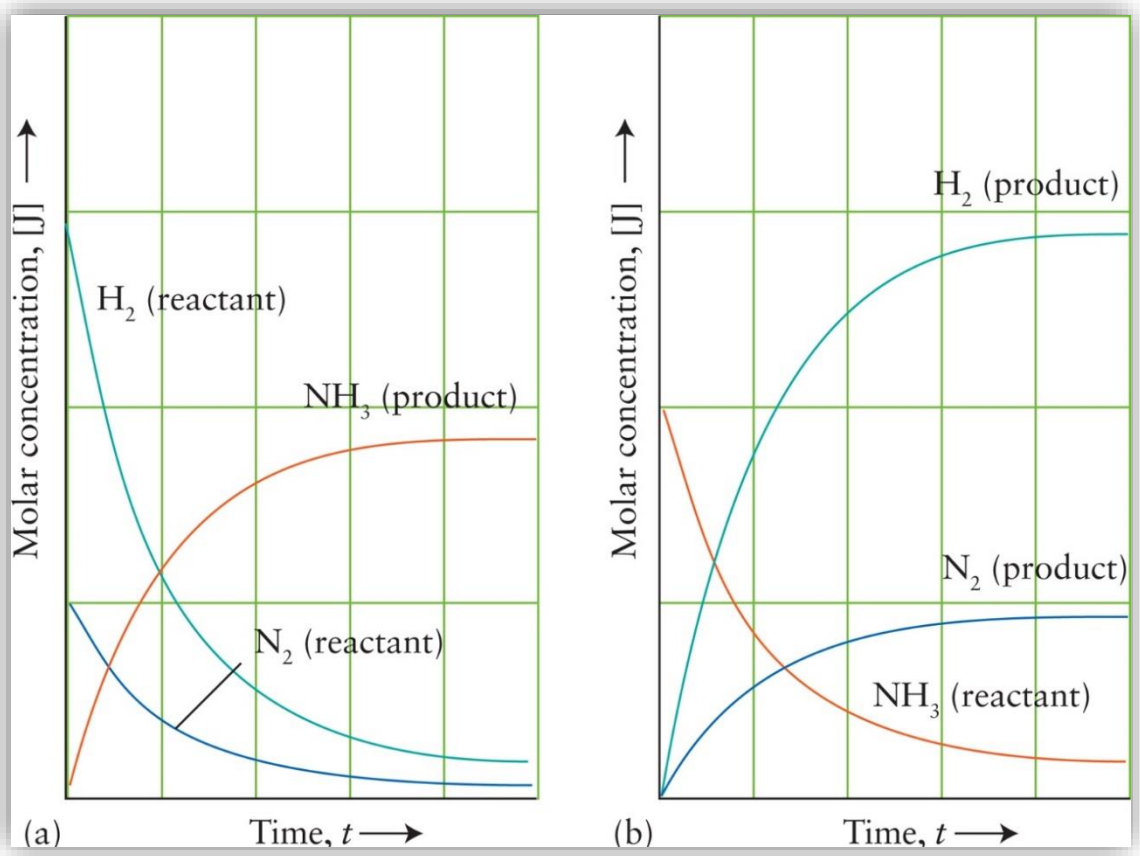
5G.2 Equilibrium and the Law of Mass Action

5G.3 The Origin of Equilibrium Constants

5G.4 The Thermodynamic Description of Equilibrium

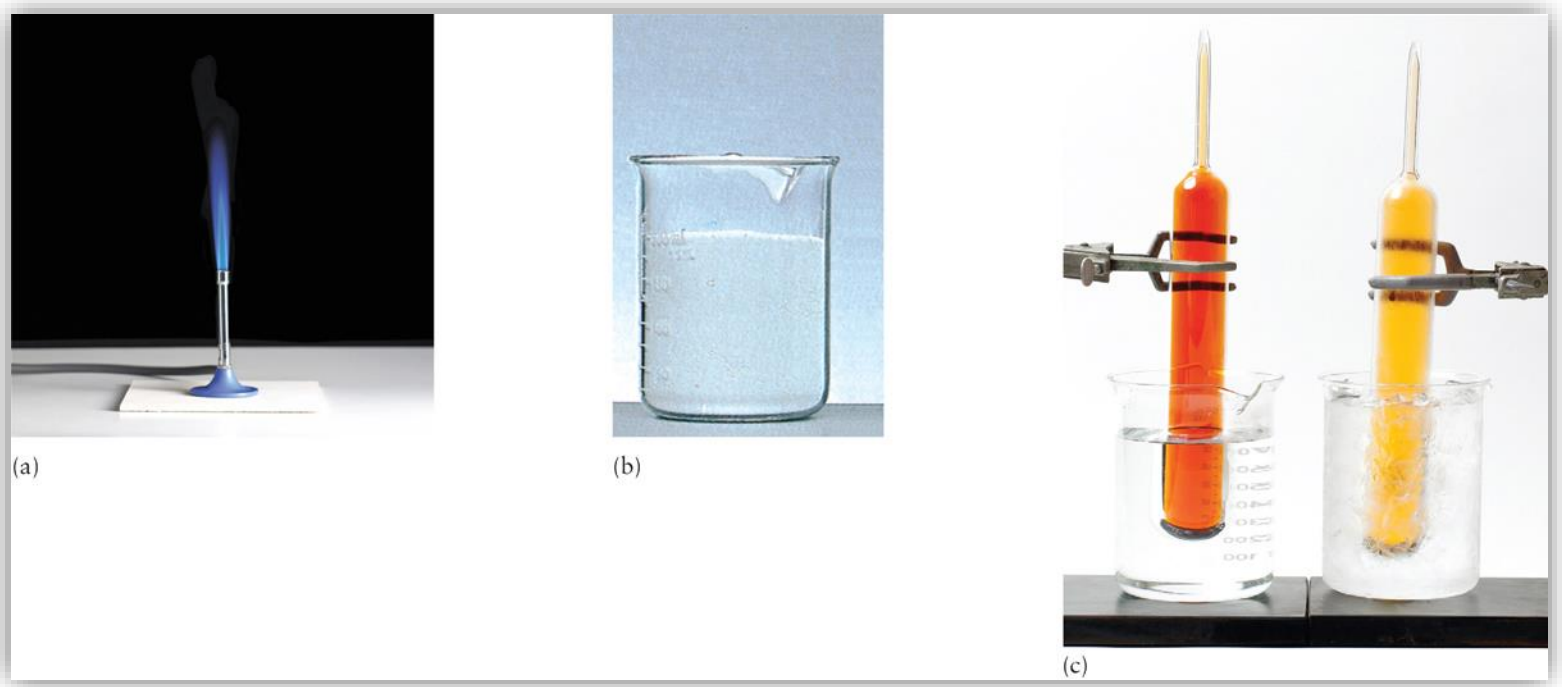
The Reversibility of Reactions

- Consider the ammonia synthesis reaction N_2 (g) + 3 H_2 (g) ↔ 2 NH_3 (g)
- The slope becomes zero to show that the concentration of each species has become constant in time: chemical equilibrium
  → Rates of the forward and reverse reactions are equal.



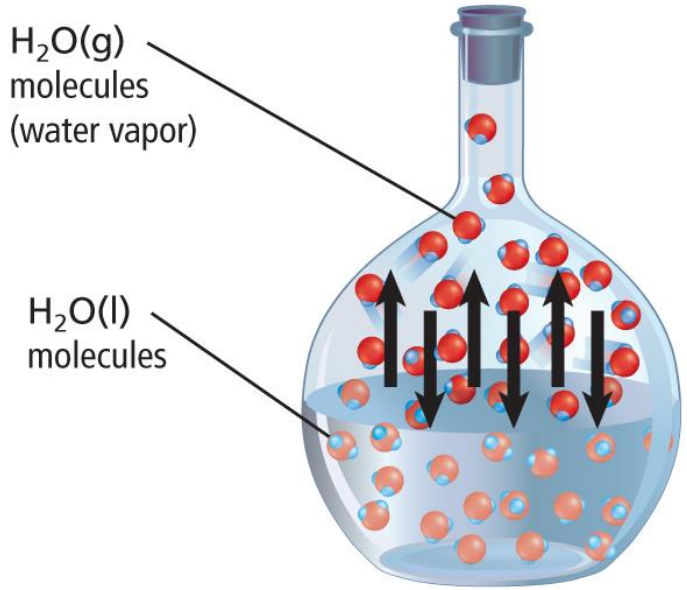
The Reversibility of Reactions

- All chemical equilibria are dynamic equilibria.
  → They respond to changes in temperature, pressure, and the addition or removal of even a small amount of reagent.
- Consider three cases

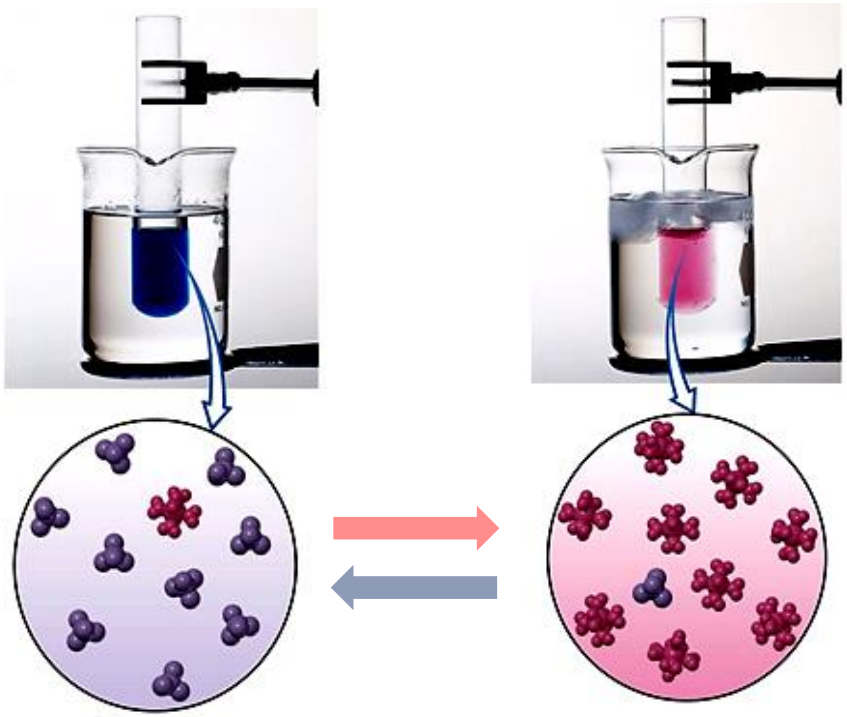


The Reversibility of Reactions

- Dynamic equilibria



$$H_2O\ (l) \rightleftharpoons H_2O\ (v)$$



$$Co(H_2O)_6{}^{2+}\ (aq) + 4\ Cl^-\ (aq) \rightleftharpoons CoCl_4{}^{2-}\ (aq) + 6\ H_2O\ (g)$$

Equilibrium and the Law of Mass Action

- Guldberg and Waage (1884) proposed the law of mass action.

$$2\,SO_2\,(g) + O_2\,(g) \leftrightarrow 2SO_3\,(g)$$

TABLE 5G.1 Equilibrium Data and the Equilibrium Constant for the Reaction $2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g)$ at 1000. K

P_{SO_2}/bar	P_{O_2}/bar	P_{SO_3}/bar	K^*
0.660	0.390	0.0840	0.0415
0.0380	0.220	0.00360	0.0409
0.110	0.110	0.00750	0.0423
0.950	0.880	0.180	0.0408
1.44	1.98	0.410	0.0409

*Average: 0.0413.

$$K = \frac{(P_{SO_3}/P^\circ)^2}{(P_{SO_2}/P^\circ)^2(P_{O_2}/P^\circ)} \qquad K = \frac{(P_{SO_3})^2}{(P_{SO_2})^2 P_{O_2}}$$

Equilibrium and the Law of Mass Action

- Equilibrium constant, *K*

  → characteristic of the composition of the reaction mixture at equilibrium

- For a reaction

$$a\,\mathrm{A}\,(g) + b\,\mathrm{B}\,(g) \leftrightarrow c\,\mathrm{C}\,(g) + d\,\mathrm{D}\,(g)$$

$$K = \frac{(P_\mathrm{C})^c (P_\mathrm{D})^d}{(P_\mathrm{A})^a (P_\mathrm{B})^b}$$

Equilibrium and the Law of Mass Action

- For a general case, activity is introduced.

substance	Activity	Simplified form (no unit)
Ideal gas	$a_{\mathrm{A}} = P_{\mathrm{A}}/P^{\mathrm{o}}$	$a_{\mathrm{A}} = P_{\mathrm{A}}$
Solute in a dilute solution	$a_{\mathrm{A}} = [\mathrm{A}]/c^{\mathrm{o}}$	$a_{\mathrm{A}} = [\mathrm{A}]$
Pure solid and liquid	$a_{\mathrm{A}} = 1$	$a_{\mathrm{A}} = 1$

- For a generalized version of equation

$$a\,\mathrm{A} + b\,\mathrm{B} \leftrightarrow \mathrm{c}\,\mathrm{C} + d\,\mathrm{D}$$

$$K = \frac{(a_{\mathrm{C}})^{c}(a_{\mathrm{D}})^{d}}{(a_{\mathrm{A}})^{a}(a_{\mathrm{B}})^{b}}$$

Equilibrium and the Law of Mass Action

- *K* is a constant for a given temperature (*T*)
- However, the equilibrium concentrations will not always be the same.
- Example: A + B → C: $K = [C]/([A][B]) = 10$

Equilibrium concentrations can be any of the following

[C] = 10, [A] = 1, [B] = 1 ; K = 10/ (1 x 1) = 10

[C] = 20, [A] = 2, [B] = 1 ; K = 20 / (2 X 1) = 10

Equilibrium and the Law of Mass Action

- Homogeneous equil.: reactants and products all in the same phase
- Heterogeneous equil.: reactants and products with different phase
  - The position of a heterogeneous equilibrium does not depend on the amounts of pure solids or liquids present, as long as there exist some amount of the solid and liquid in the equilibrium mixture.
  - Pure solid and pure liquid concentration do not appear in the equilibrium equation.
- Why do we omit pure liquids and solids in equilibrium expression?
  - Densities of pure liquids and solids are constant for a given temperature.
  - Therefore, "concentration" of pure liq. and solids are constant.

Equilibrium and the Law of Mass Action

- Examples of heterogeneous equilibria
  - $H_2O\ (l) \leftrightarrow H^+\ (aq) + OH^-\ (aq)$

    $K = [H^+][OH^-] = 10^{-14}$
    For neutral water , $[H^+] = [OH^-] = x$
    $K = [H^+][OH^-] = x^2 = 10^{-14}$
    Therefore, $[H^+]=[OH^-]= 10^{-7}$ M

  - $Ca(OH)_2\ (s) \leftrightarrow Ca^{2+}\ (aq) + 2OH^-\ (aq)$

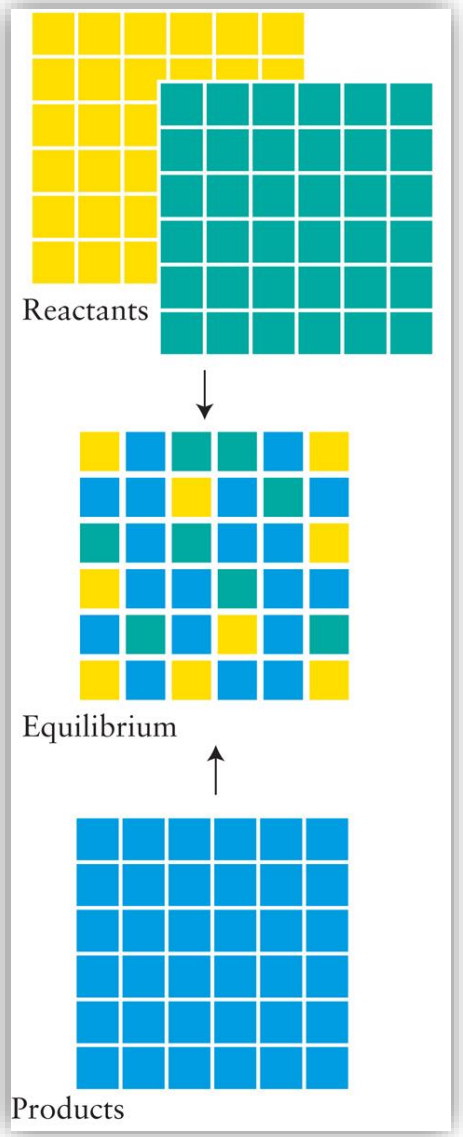
$$K = \frac{a_{Ca^{2+}}(a_{OH^-})^2}{\underbrace{a_{Ca(OH)_2}}_{\text{1 for a pure solid}}} = [Ca^{2+}][OH^-]^2$$

Equilibrium and the Law of Mass Action

TABLE 5G.2 Equilibrium Constants for Various Reactions

Reaction	T/K*	K	K_c†
$H_2(g) + Cl_2(g) \rightleftharpoons 2\,HCl(g)$	300	4.0×10^{31}	4.0×10^{31}
	500	4.0×10^{18}	4.0×10^{18}
	1000	5.1×10^{8}	5.1×10^{8}
$H_2(g) + Br_2(g) \rightleftharpoons 2\,HBr(g)$	300	1.9×10^{17}	1.9×10^{17}
	500	1.3×10^{10}	1.3×10^{10}
	1000	3.8×10^{4}	3.8×10^{4}
$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$	298	794	794
	500	160	160
	700	54	54
$2\,BrCl(g) \rightleftharpoons Br_2(g) + Cl_2(g)$	300	377	377
	500	32	32
	1000	5	5
$2\,HD(g) \rightleftharpoons H_2(g) + D_2(g)$	100	0.52	0.52
	500	0.28	0.28
	1000	0.26	0.26
$F_2(g) \rightleftharpoons 2\,F(g)$	500	3.0×10^{-11}	7.3×10^{-13}
	1000	1.0×10^{-2}	1.2×10^{-4}
	1200	0.27	2.7×10^{-3}
$Cl_2(g) \rightleftharpoons 2\,Cl(g)$	1000	1.0×10^{-5}	1.2×10^{-7}
	1200	1.7×10^{-3}	1.7×10^{-5}
$Br_2(g) \rightleftharpoons 2\,Br(g)$	1000	3.4×10^{-5}	4.1×10^{-7}
	1200	1.7×10^{-3}	1.7×10^{-5}
$I_2(g) \rightleftharpoons 2\,I(g)$	800	2.1×10^{-3}	3.1×10^{-5}
	1000	0.26	3.1×10^{-3}
	1200	6.8	6.8×10^{-2}
$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$	298	6.8×10^{5}	4.2×10^{8}
	400	41	4.5×10^{4}
	500	3.6×10^{-2}	62
$2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g)$	298	4.0×10^{24}	9.9×10^{25}
	500	2.5×10^{10}	1.0×10^{12}
	700	3.0×10^{4}	1.7×10^{6}
$N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$	298	0.15	6.1×10^{23}
	400	47.9	1.44
	500	1.7×10^{3}	41

*Three significant figures.
†K_c is the equilibrium constant in terms of molar concentrations of gases (Topic 5H).



Thermodynamic Description of Equilibrium

- For an ideal gas: a A + b B $\leftrightarrow$ c C + d D

$$\Delta G = \sum nG_{\mathrm{m}}(\text{products}) - \sum nG_{\mathrm{m}}(\text{reactants})$$

$$\Delta G_{\mathrm{r}} = \sum n_{\mathrm{r}}G_{\mathrm{m}}(\text{products}) - \sum n_{\mathrm{r}}G_{\mathrm{m}}(\text{reactants})$$

$$G_{\mathrm{m}}(\mathrm{J}) = G_{\mathrm{m}}{}^{\circ}(\mathrm{J}) + RT\ln\frac{P_{\mathrm{J}}}{P^{\circ}}$$

$$G_{\mathrm{m}}(\mathrm{J}) = G_{\mathrm{m}}{}^{\circ}(\mathrm{J}) + RT\ln a_{\mathrm{J}}$$

Thermodynamic Description of Equilibrium

$$\Delta G_r = \overbrace{\{cG_m(C) + dG_m(D)\}}^{\text{products}} - \overbrace{\{aG_m(A) + bG_m(B)\}}^{\text{reactants}}$$

$$= \{c[G_m°(C) + RT\ln a_C] + d[G_m°(D) + RT\ln a_D]\}$$

$$- \{a[G_m°(A) + RT\ln a_A] + b[G_m°(B) + RT\ln a_B]\}$$

$$= \overbrace{\{cG_m°(C) + dG_m°(D)\} - \{aG_m°(A) + bG_m°(B)\}}^{\Delta G_r°}$$

$$+ RT\{(c\ln a_C + d\ln a_D) - (a\ln a_A + b\ln a_B)\}$$

$$\Delta G_r° = \{cG_m°(C) + dG_m°(D)\} - \{aG_m°(A) + bG_m°(B)\}$$

$$\Delta G_r = \Delta G_r° + RT\{(c\ln a_C + d\ln a_D) - (a\ln a_A + b\ln a_B)\}$$

$$\Delta G_r = \Delta G_r° + RT\ln\frac{(a_C)^c(a_D)^d}{(a_A)^a(a_B)^b}$$

Thermodynamic Description of Equilibrium

- The above equation can be written as

$$\Delta G_r = \Delta G_r^\circ + RT \ln Q$$

- Reaction quotient

$$Q = \frac{(a_C)^c (a_D)^d}{(a_A)^a (a_B)^b}$$

Thermodynamic Description of Equilibrium

- At equilibrium, $Q = K$ and $\Delta G_r = 0$

$$0 = \Delta G_r^\circ + RT \ln K$$

$$\boxed{\Delta G_r^\circ = -RT \ln K}$$

- Predicting the direction of reactiuon
  - If ΔG_r° is negative, then K > 1; products are favored at equilibrium.
  - If ΔG_r° is positive, then K < 1; reactants are favored at equilibrium.

Thermodynamic Description of Equilibrium

- The above equation can be written as

$$\ln K = -\frac{\Delta G_r^\circ}{RT} = -\frac{\Delta H_r^\circ}{RT} + \frac{\Delta S_r^\circ}{R}$$

$$K = e^{-\Delta H_r^\circ/RT + \Delta S_r^\circ/R} = e^{-\Delta H_r^\circ/RT}\, e^{\Delta S_r^\circ/R}$$

Topic 5H. Alternative Forms of the Equilibrium Constant

5H.1 Multiples of Chemical Equation

5H.2 Composite Equations

5H.3 Molar Concentrations of Gases

Multiples of Chemical Equation

$$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g) \qquad K_1 = \frac{(P_{HI})^2}{P_{H_2}P_{I_2}} = 160$$

$$2\,H_2(g) + 2\,I_2(g) \rightleftharpoons 4\,HI(g) \qquad K_2 = \frac{(P_{HI})^4}{(P_{H_2})^2(P_{I_2})^2} = K_1^2 = 160^2 = 2.96 \times 10^4$$

$$2\,HI(g) \rightleftharpoons H_2(g) + I_2(g) \qquad K_3 = \frac{P_{H_2}P_{I_2}}{(P_{HI})^2} = \frac{1}{K_1} = \frac{1}{160} = 0.0063$$

Multiples of Chemical Equation

TABLE 5H.1 Relations Between Equilibrium Constants*

Chemical equation	Equilibrium constant
$a\,A + b\,B \rightleftharpoons c\,C + d\,D$	K_1
$c\,C + d\,D \rightleftharpoons a\,A + b\,B$	$K_2 = 1/K_1 = K_1^{-1}$
$N(a\,A + b\,B \rightleftharpoons cC + dD)$	$K_3 = K_1^N$

*For a reaction that can be expressed as the sum of other reactions, the equilibrium constant is the product of the equilibrium constants of the component reactions. Thus, for A $\rightleftharpoons$ B (K_1) and B $\rightleftharpoons$ C (K_2), then for A $\rightleftharpoons$ C, $K = K_1K_2$.

Composite Equations

$$2\,P(g) + 3\,Cl_2(g) \rightleftharpoons 2\,PCl_3(g) \qquad K_1 = \frac{(P_{PCl_3})^2}{(P_P)^2(P_{Cl_2})^3}$$

$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g) \qquad K_2 = \frac{P_{PCl_5}}{P_{PCl_3}P_{Cl_2}}$$

$$2\,P(g) + 5\,Cl_2(g) \rightleftharpoons 2\,PCl_5(g) \qquad K_3 = \frac{(P_{PCl_5})^2}{(P_P)^2(P_{Cl_2})^5}$$

$$K_3 = \frac{(P_{PCl_5})^2}{(P_P)^2(P_{Cl_2})^5} = \overbrace{\frac{(P_{PCl_3})^2}{(P_P)^2(P_{Cl_2})^3}}^{K_1} \times \overbrace{\frac{(P_{PCl_5})^2}{(P_{PCl_3})^2(P_{Cl_2})^2}}^{K_2^2} = K_1K_2^2$$

Molar Concentrations of Gases

- For a reaction a A + b B ↔ c C + d D

$$K = \frac{(a_C)^c (a_D)^d}{(a_A)^a (a_B)^b}$$

- For gases, the following constant is also used.

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g) \qquad K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

- K and K_c

$$K = \left(\frac{c^\circ RT}{P^\circ}\right)^{\Delta n_r} K_c$$