Chemical Equilibrium

$$A \underset{k_r}{\overset{k_f}{\rightleftharpoons}} B$$

If forward & rev. rx's are elementary rx's,

$$r_f = k_f [A]$$

$$r_r = k_r [B]$$

As A gets converted to B, [A] dec. & [B] inc.

Also, r_f dec.

r_r inc.

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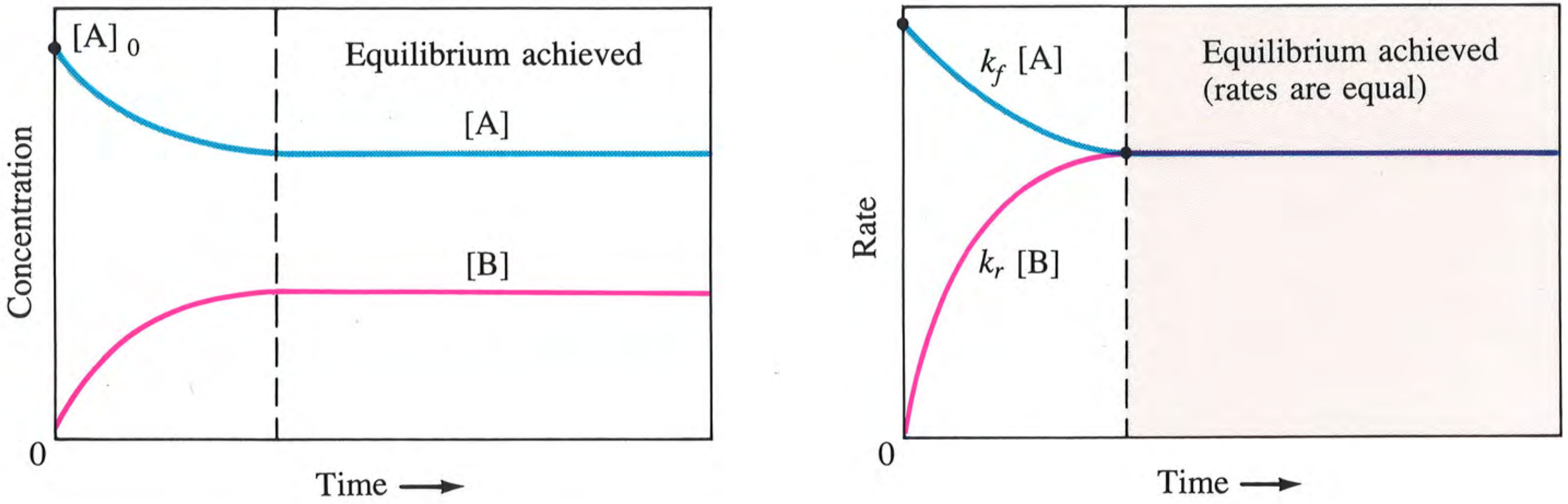
Figure 15.2 Achieving chemical equilibrium for the reaction A⇌B



(*a*)   (*b*)

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Eventually, $r_f = r_r$ & get

dynamic chemical equilibrium

Also, at equilibrium

$[A]$ & $[B]$ are constant

Since $r_f = r_r$,

$$k_f [A] = k_r [B]$$

$$\frac{[B]}{[A]} = \frac{k_f}{k_r} = K_c$$

$K_c \equiv$ Equilibrium Constant

II) Equilibrium Constant

Equilibrium can be reached from either direction

For general rx,

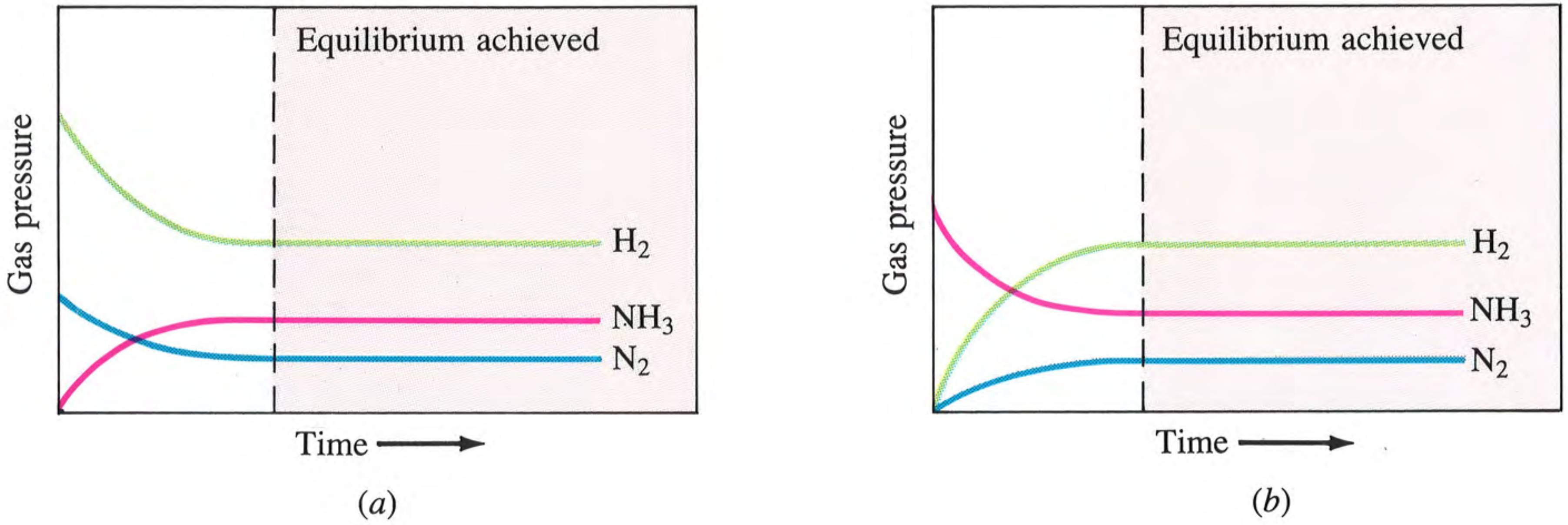
$$aA + bB \rightleftharpoons dD + eE$$

A) Law of Mass Action

At equil. the relative conc. of reactants & products can be expressed in terms of a constant quantity called the equilibrium constant.

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

Transparency 109 Figure 15.5 Variation in pressures achieving equilibrium for $N_2 + 3H_2 \rightleftharpoons 2NH_3$



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Remember,

Rate law can only be determined from exp.

Law of mass action, K_c, can be written from balanced chemical equation.

1) coef. in bal. eqn. are used as exponents of conc.'s.

2) Products in numerator
Reactants in denominator

Note:

Condition of equilibrium is,

$$r_f = r_r$$

& K_c = constant

1) **Ex**

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \quad (1)$$

$K_c =$

Exp. determine K_c
- look at a number of equil. systems

At 500°C

$[H_2]$	$[N_2]$	$[NH_3]$	K_c
0.500	1.00	8.66×10^{-2}	
1.35	1.15	4.12×10^{-1}	

2) Ex : Variation of K_c w. form of bal. eqn.

a) What is K_c for rx. below in terms of K_{c_1} for previous rx.

$$2\,NH_3 \rightleftharpoons N_2 + 3\,H_2 \qquad (2)$$

b) Give K_c for rx. below in terms of K_{c_1}

$$\frac{1}{2}\,N_2 + \frac{3}{2}\,H_2 \rightleftharpoons NH_3 \qquad (3)$$

General Rule

If 2 rx's (eqn's) can be added to give a 3rd rx. (eqn.) then K_3 is product of K_1 & K_2

$$\boxed{\begin{array}{l} Rx_1 + Rx_2 = Rx_3 \\ K_1 \times K_2 = K_3 \end{array}}$$

B) Magnitude of K

Tells us about position of equil.
- extent to which a rx. proceeds toward completion

1) Ex

$$H_2 + Cl_2 \rightleftharpoons 2\,HCl, \; 25°C$$

$$K_c = \frac{[HCl]^2}{[H_2][Cl_2]} = 4.4 \times 10^{32}$$

rx. essentially complete
(equil. lies to right)

2) Ex

$$2\,H_2O \rightleftharpoons 2\,H_2 + O_2, \; 25°C$$

$$K_c = \frac{[H_2]^2[O_2]}{[H_2O]^2} = 1.1 \times 10^{-81}$$

equil. lies to left - NO rx.

3) a) K is very large ($>10^2$):

- mostly products

rx. goes to "completion"

b) K is very small (<0.01):

- mostly reactants

forward rx. does not occur to any great extent

c) K close to 1 (0.01 – 100)

appreciable amt's of both reactants & products

III) Evaluating K

A) Determine K_c given equil. conc. if

1.20 mole PCl_5 is put in 1.0L container at 200°C. At equil. 1.00 mole remains. Calc. K_c.

	PCl_5	$\rightleftharpoons$	PCl_3	$+$	Cl_2
initial	$1.20\,M$		0		0
change	$-x$		$+x$		$+x$
equil.	$1.20-x$		x		x

$$1.20 - x = 1.00$$

$$x = [PCl_3] = [Cl_2] = 0.20\,M$$

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{[0.20][0.20]}{[1.00]}$$

$$= 0.040\ (M)$$

B) Gas Phase Rx's (K_p)

Express equil. constant in terms of conc., K_c, or pressure, K_p.

$$K_p = \frac{P_D^d \cdot P_E^e}{P_A^a \cdot P_B^b}$$

numerically diff. from K_c

Derive relationship of K_p to K_c

Assume ideal gas,
$PV = nRT$

Relate partial pressure to conc.

$$P = \frac{n}{V} RT = M\, RT$$

$$P_A = [A]\, RT$$

Substitute into K_p,

$$K_p = \frac{[D]^d (RT)^d\, [E]^e (RT)^e}{[A]^a (RT)^a\, [B]^b (RT)^b}$$

$$\boxed{K_p = K_c\, (RT)^{\Delta n}}$$

$$\Delta n = (d+e) - (a+b)$$

$$\Delta n = \sum_{prod} n_{prod} - \sum_{react} n_{react}$$

$K_p = K_c$ when $\Delta n = 0$

$$K_p = \frac{[D]^d (RT)^d [E]^e (RT)^e}{[A]^a (RT)^a [B]^b (RT)^b}$$

$$= \frac{[D]^d [E]^e}{[A]^a [B]^b} \cdot \frac{(RT)^d (RT)^e}{(RT)^a (RT)^b}$$

$$= K_c \cdot \frac{(RT)^{d+e}}{(RT)^{a+b}}$$

$$= K_c \cdot (RT)^{(d+e)-(a+b)}$$

$$= K_c \cdot (RT)^{\Delta n}$$

1) Ex. 1 : Evaluate K_p given K_c

Determine K_p for decomp. of PCl_5 at 200°C. $K_c = 0.040$

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

2) Ex. 2 : How are K_p & K_c related?

$$X + 2Y \rightleftharpoons 3Z$$

IV) Heterogeneous Equilibria

Substances in equilibrium are in different phases.

$$2\,NaHCO_3(s) \underset{\Delta}{\rightleftharpoons} Na_2CO_3(s) + CO_2(g) + H_2O(g)$$

$$K_c = \frac{[Na_2CO_3][CO_2][H_2O]}{[NaHCO_3]^2}$$

However, conc. of Na_2CO_3 & $NaHCO_3$ are constant

For Na_2CO_3, $D = 2.51\,g/cm^3$

$$\frac{2.51\,g}{cm^3} \times \frac{1\,mol}{106\,g} \times \frac{10^3\,cm^3}{1\,L} = 23.7\,M$$

Conc. of solid does not change to any appreciable extent.

Incorporate these into K_c

$$K_c \cdot \frac{[NaHCO_3]^2}{[Na_2CO_3]} = [CO_2][H_2O]$$

$$K_c' = [CO_2][H_2O]$$

Same thing applies to liquids

$$[H_2O(l)] = 55.\bar{5}\ M$$

Effectively, ignore conc. of pure liquids or solids even though must be physically present in equil. mixture

Ex: Saturated AgCl soln.

$$AgCl(s) + H_2O(l) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

$$K_{sp} = [Ag^+][Cl^-]$$

Solubility Product Constant

A) Ex: What is the expression for K_c for the reaction below?

$$CaCO_3(s) + 2HCl(aq) \rightleftharpoons CaCl_2(aq) + H_2O(l) + CO_2(g)$$

B) **Ex**: What is the expression for K_p & K_c for the rx. below?

$$2KClO_3(s) \rightleftharpoons 2KCl(s) + 3O_2(g)$$

V) Applications of Equilibrium Constants

A) Reaction Quotient

If start rx. w. some initial conc., system moves toward equil. in direction req'd. to satisfy the constancy of K expression.

$$\boxed{Q_c = \frac{[D]_i^d \, [E]_i^e}{[A]_i^a \, [B]_i^b}}$$

$[D]_i \equiv$ initial conc

Compare to equil. constant, K_c

1) $\underline{Q_c = K_c}$

rx. at equilibrium

2) $\underline{Q_c > K_c}$

numerator too large

- rx. goes to left -

[Products] dec.

[Reactants] inc.

until equil. reached

3) $\underline{Q_c < K_c}$

denominator too large

- rx. goes to right -

[Products] inc.

[Reactants] dec.

Ex:

Is the following rx. at equil? If not in which direction will rx. proceed?

$K_c = 100 \ (M^{-1})$ Vol. = 10L

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

1 mol 2 mol 8 mol

$Q_c =$

B) Determine Equil. Conc.

Calc. equil. conc. given initial conc. & K_c

1) Write chem. eqn.

2) Determine equil. conc. using table of initial conc. and change in conc.

ICE

3) Write K_c expression

4) substitute & solve for equil. conc.

Ex:

Gas phase dissociation of NOCl has $K_c = 4.7 \times 10^{-7}$ at a particular temp. Calc. equil. conc's of all species if 0.10 mole NOCl is placed in a 1.0 L container.

	$2NOCl$ $\rightleftharpoons$	$2NO$ +	Cl_2
initial	0.10 M	0	0
change	$-2x$	$+2x$	$+x$
equil.	$0.10 - 2x$	$2x$	x

$$K_c = \frac{[NO]^2[Cl_2]}{[NOCl]^2} =$$

Small K_c - equil. lies to left

- very little NOCl dissociates

$2x \ll 0.10$

$\therefore$ assume, $0.10 - 2x \cong 0.10$