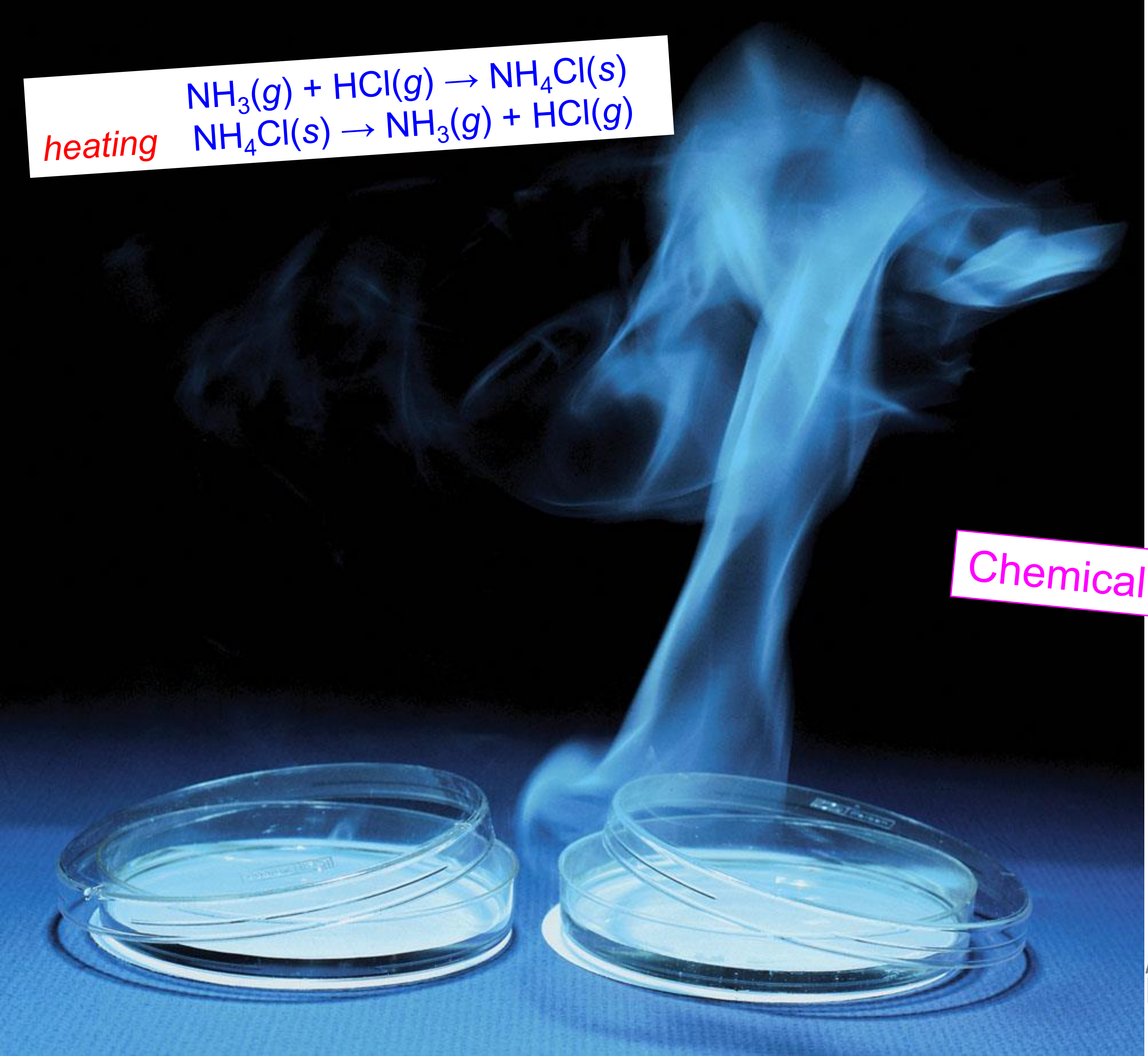
14

CHAPTER

CHEMICAL EQUILIBRIUM



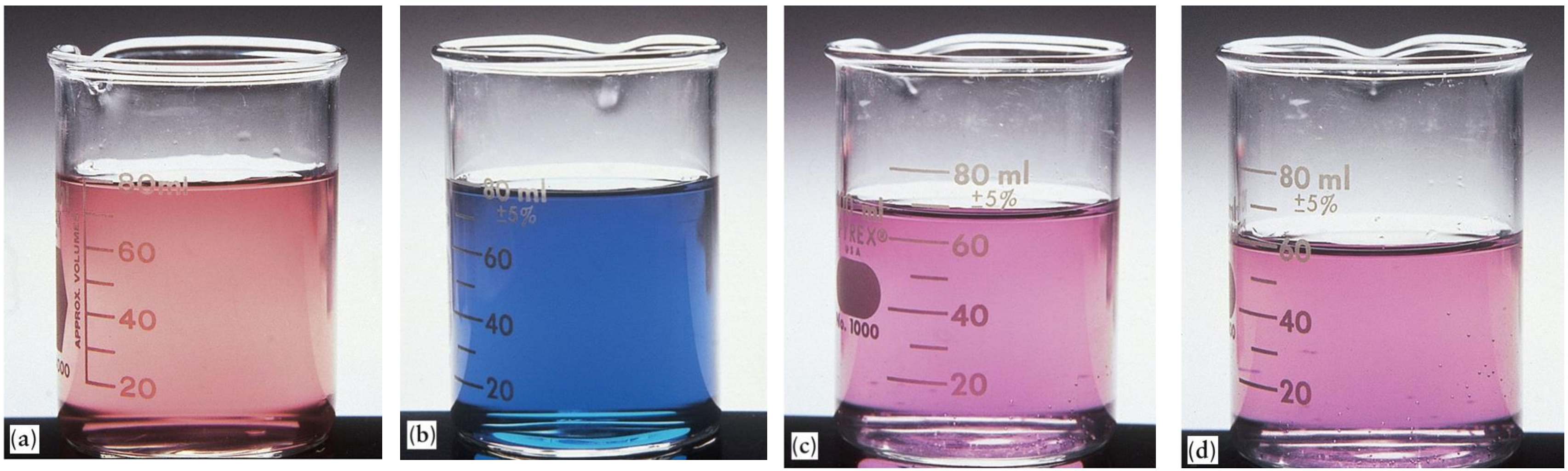
$NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$

heating $NH_4Cl(s) \rightarrow NH_3(g) + HCl(g)$

Chemical Equilibrium

14.1 THE NATURE OF CHEMICAL EQUILIBRIUM

$$\underset{A}{[Co(H_2O)_6]^{2+}} + \underset{B}{4\ Cl^-} \rightleftharpoons \underset{C}{[CoCl_4]^{2-}} + \underset{D}{6\ H_2O}$$



$[Co(H_2O)_6]^{2+}$	$[CoCl_4]^{2-}$	Add HCl to (a): Some Co(II) → $[CoCl_4]^{2-}$	Add water to (b): Some Co(II) → $[Co(H_2O)_6]^{2+}$

Lavender color of (c) & (d): $[CoCl_4]^{2-}$ + $[Co(H_2O)_6]^{2+}$

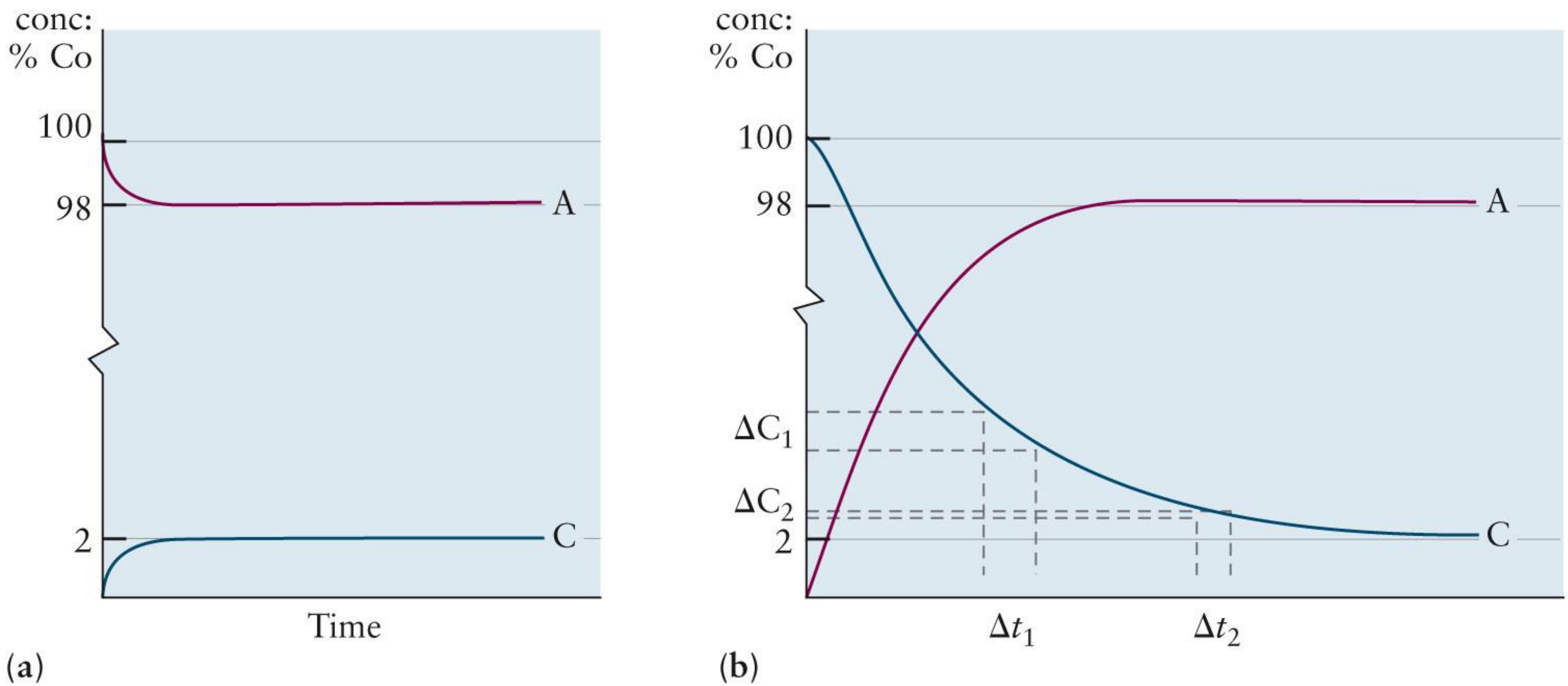


Fig. 14.2. Time dependence of reactants and products in the spontaneous reaction: $[Co(H_2O)_6]^{2+}$ + 4 Cl^- ⇆ $[CoCl_4]^{2-}$ + 6 H_2O.
(a) Partial conversion of $[Co(H_2O)_6]^{2+}$ into $[CoCl_4]^{2-}$.
(b) Partial conversion of $[CoCl_4]^{2-}$ into $[Co(H_2O)_6]^{2+}$.

◆ Characteristics of the Equilibrium State

$$H_2O(l) \rightleftharpoons H_2O(g)$$

Forward reaction: Evaporation of liquid water to water vapor

Backward reaction: Condensation of water vapor to liquid water

At equilibrium, the forward and backward rates become equal.

➢ Fundamental Characteristics of equilibrium states

1. No macroscopic evidence of change
2. Reached by spontaneous processes
3. Dynamic balance of forward and reverse processes
4. Same regardless of direction of approach

14.2 THE EMPIRICAL LAW OF MASS ACTION

◆ Expressions of Equilibrium Constant: Law of Mass Action

➢ Reactions in solution (C.M. Guldberg & P. Waage, 1864)

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

$$K_\mathrm{C} = \frac{[\mathrm{C}]_\mathrm{eq}^{c}[\mathrm{D}]_\mathrm{eq}^{d}}{[\mathrm{A}]_\mathrm{eq}^{a}[\mathrm{B}]_\mathrm{eq}^{b}} \quad \sim \text{ dimensions of (conc)}^{c+d-a-b}$$

➢ Reactions in the gas phase

$$K_\mathrm{P} = \frac{(P_\mathrm{C})_\mathrm{eq}^{c}(P_\mathrm{D})_\mathrm{eq}^{d}}{(P_\mathrm{A})_\mathrm{eq}^{a}(P_\mathrm{B})_\mathrm{eq}^{b}} \quad \sim \text{ dimensions of (press)}^{c+d-a-b}$$

Dalton's Law of Partial Pressures

The total pressure of a mixture of gases is the sum of the partial pressures of its component.

$$P = P_A + P_B + \cdots = \sum_i P_i$$

▶ **Mole fraction** of the component A, x_A

$$x_A = \frac{n_A}{n_A + n_B + \cdots}, \qquad x_A + x_B + \cdots = 1$$

$$P_A = \frac{n_A RT}{V}, \quad P = \frac{nRT}{V} = (n_A + n_B + \cdots)\frac{RT}{V} \longrightarrow P_A = \frac{n_A P}{n_A + n_B + \cdots} = x_A P$$

$$\therefore \quad P_A = x_A P$$

➢ Law of Mass Action for Gas-Phase Reactions

❖ Thermodynamic Equilibrium Constant, *K* ~ dimensionless

$$\frac{(P_C/P_{ref})^c(P_D/P_{ref})^d}{(P_A/P_{ref})^a(P_B/P_{ref})^b} = K \qquad \frac{P_C^c P_D^d}{P_A^a P_B^b} = K(P_{ref})^{(c+d-a-b)} = K_P$$

For $P_{ref} = 1$ atm, $K = K_P$ numerically.

- **Mass action law for a general reaction involving ideal gases**

$$\frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b} = K$$

➢ Law of Mass Action for Reactions in Solution

$$\frac{([C]/c_{ref})^c([D]/c_{ref})^d}{([A]/c_{ref})^a([B]/c_{ref})^b} = K \xrightarrow{c_{ref}=1\text{ M}} \frac{[C]^c[D]^d}{[A]^a[B]^b} = K$$

➢ Law of Mass Action for Reactions

1. Gases appear in *K* as partial pressures, measured in atm.
2. Dissolved species enter as concentrations, in moles per liter.
3. Pure solids, pure liquids, solvent in chemical reaction do not appear in *K*.
4. Partial pressures and concentrations of products appear in the numerator, and those of reactants in the denominator; each is raised to a power equal to its coefficient in the balanced chemical equation for the reaction.

14.3 THERMODYNAMIC DESCRIPTION OF THE EQUILIBRIUM STATE

◆ Dependence of Gibbs Free Energy of a Gas on Pressure

At constant T, $P_1 \rightarrow P_2$ (ideal gas)

$\Delta G = \Delta(H - TS) = \Delta H - T\,\Delta S = -T\Delta S$

($\Delta H = 0$ at constant T for an ideal gas)

$$\Delta S = nR\ln\left(\frac{V_2}{V_1}\right) = nR\ln\left(\frac{P_1}{P_2}\right) = -nR\ln\left(\frac{P_2}{P_1}\right)$$

$$\Delta G = nRT\ln\left(\frac{P_2}{P_1}\right)$$

➢ ΔG of taking the gas from the *reference state* ($P_{\mathbf{ref}}$ = 1 atm) to any P:

$$\Delta G = nRT\ln\left(\frac{P}{P_{\mathbf{ref}}}\right) = nRT\ln P$$

◆ Equilibrium Expression for Reactions in the Gas Phase

Ex. $3\ NO(g) \rightleftharpoons N_2O(g) + NO_2(g)$

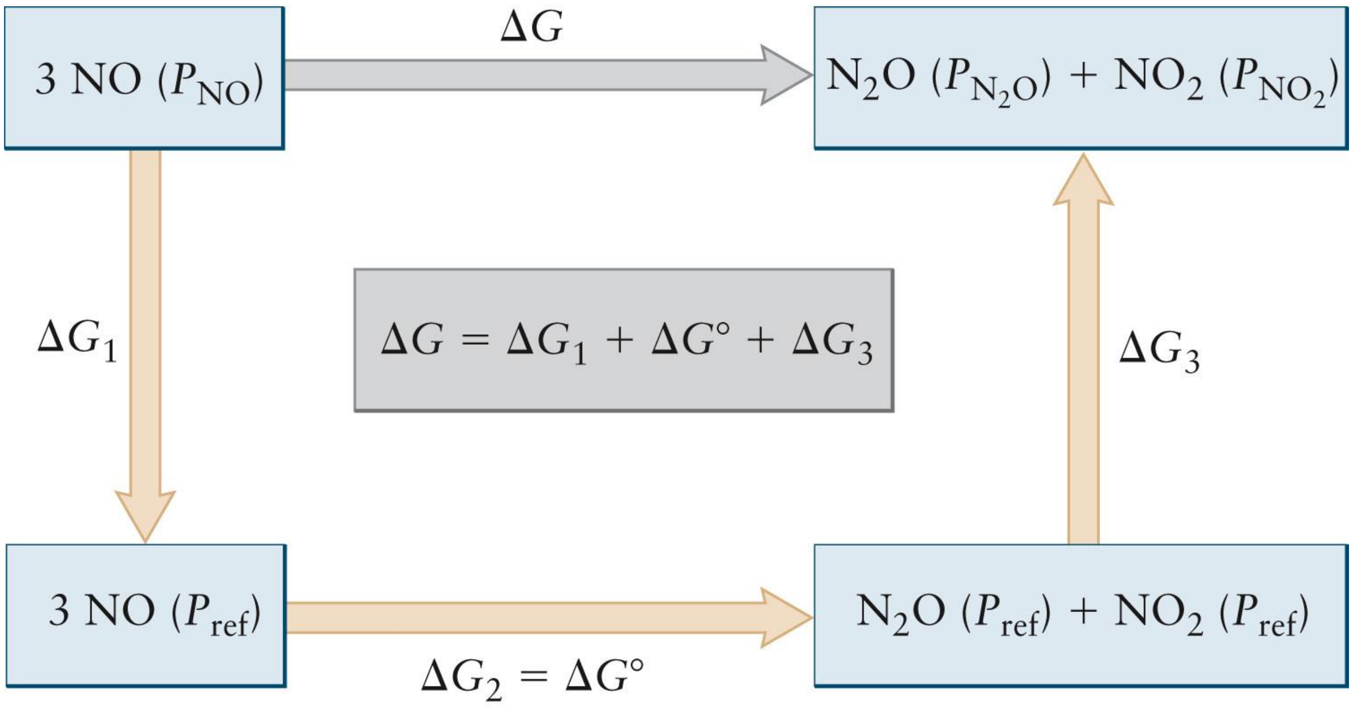


Fig. 14.4 A three-step process (red arrows) to calculate ΔG of a reaction (blue arrow) for which reactants and products are not in their standard states of 1 atm.

Step 1: $$\Delta G_1 = 3RT \ln\left(\frac{P_{ref}}{P_{NO}}\right) = RT \ln\left(\frac{P_{ref}}{P_{NO}}\right)^3$$

Step 2: $$\Delta G_2 = \Delta G^o$$

Step 3: $$\Delta G_3 = RT \ln\left(\frac{P_{N_2O}}{P_{ref}}\right) + RT \ln\left(\frac{P_{NO_2}}{P_{ref}}\right) = RT \ln\left[\left(\frac{P_{N_2O}}{P_{ref}}\right)\left(\frac{P_{NO_2}}{P_{ref}}\right)\right]$$

$$\Delta G = \Delta G_1 + \Delta G_2 + \Delta G_3 = \Delta G^o + RT \ln\left[\frac{(P_{N_2O}/P_{ref})(P_{NO_2}/P_{ref})}{(P_{NO}/P_{ref})^3}\right]$$

At equilibrium, $\Delta G = 0$ (const T & P).

$$-\Delta G^o = RT \ln\left[\frac{(P_{N_2O}/P_{ref})(P_{NO_2}/P_{ref})}{(P_{NO}/P_{ref})^3}\right] \equiv RT \ln K(T)$$

In other words, $\Delta G = 0$ as each species has its own equilibrium concentration that is given by ΔG^o

For the general reaction, $a\mathrm{A} + b\mathrm{B} \rightarrow c\mathrm{C} + d\mathrm{D}$

At equilibrium,

$$-\Delta G^{\mathrm{o}} = RT \ln\left[\frac{(P_{\mathrm{C}}/P_{\mathrm{ref}})^{c}(P_{\mathrm{D}}/P_{\mathrm{ref}})^{d}}{(P_{\mathrm{A}}/P_{\mathrm{ref}})^{a}(P_{\mathrm{B}}/P_{\mathrm{ref}})^{b}}\right] \equiv RT\ln K(T)$$

◆ Reactions in Ideal Solution

For the general reaction, $a\mathrm{A} + b\mathrm{B} \rightarrow c\mathrm{C} + d\mathrm{D}$

At equilibrium,

$$-\Delta G^{\mathrm{o}} = RT \ln\left[\frac{([\mathrm{C}]/c_{\mathrm{ref}})^{c}([\mathrm{D}]/c_{\mathrm{ref}})^{d}}{([\mathrm{A}]/c_{\mathrm{ref}})^{a}([\mathrm{B}]/c_{\mathrm{ref}})^{b}}\right] \equiv RT\ln K(T)$$

◆ Activity, *a*

$$\Delta G = nRT\ln\left(P/P_{\mathrm{ref}}\right) = nRT\ln P \quad \text{(ideal gas)}$$

$$= nRT\ln\left(c/c_{\mathrm{ref}}\right) = nRT\ln c \quad \text{(ideal solution)}$$

$$\Delta G = nRT\ln a \qquad \text{(nonideal system)}$$

- Activity coefficient, γ_i (γ_i = 1 for the reference state)

  $a_i = \gamma_i P_i / P_{\mathrm{ref}}$ (gas) $= \gamma_i c_i / c_{\mathrm{ref}}$ (solution)

- General expression for the equilibrium constant

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

14.4 THE LAW OF MASS ACTION FOR RELATED AND SIMULTANEOUS EQUILIBRIA

◆ Relationships among Equilibrium Expressions

- **Reversed reaction → Inversed *K***

$2\ H_2(g) + O_2(g) \leftrightarrows 2\ H_2O(g), \quad K_1 = P(H_2O)^2 / P(H_2)^2P(O_2)$

$2\ H_2O(g) \leftrightarrows 2\ H_2(g) + O_2(g), \quad K_2 = P(H_2)^2P(O_2) / P(H_2O)^2 = K_1^{-1}$

- **Multiplied by a constant → *K* raised to a power equal to the constant**

$H_2(g) + (1/2)\ O_2(g) \leftrightarrows H_2O(g), \quad K_3 = P(H_2O) / P(H_2)P(O_2)^{1/2} = K_1^{1/2}$

- **Addition (or Subtraction) of reactions**

  → Multiplication (or Division) of *K*'s

$2\ BrCl(g) \leftrightarrows Cl_2(g) + Br_2(g),\quad K_1 = P(Cl_2)P(Br_2) / P(BrCl)^2$

$Br_2(g) + I_2(g) \leftrightarrows 2\ IBr(g),\quad K_2 = P(IBr)^2 / P(Br_2)P(I_2)$

$2\ BrCl(g) + I_2(g) \leftrightarrows 2\ IBr(g) + Cl_2(g),\quad K_3 = ?$

$$K_3 = K_1K_2 = P(IBr)^2\, P(Cl_2) / P(BrCl)^2\, P(I_2)$$

EXAMPLE 14.7

At 25 °C,

$$NO(g) + \frac{1}{2}O_2(g) \rightleftharpoons NO_2(g) \qquad K_1 = 1.3 \times 10^6$$

$$\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \rightarrow NO\ (g) \qquad K_2 = 6.5 \times 10^{-16}$$

$$N_2(g) + 2\ O_2(g) \rightleftharpoons 2\ NO_2(g) \qquad K_3 = ?$$

$$K_3 = (K_1K_2)^2 = 7.1 \times 10^{-19}$$

14.5 EQUILIBRIUM CALCULATIONS FOR GAS-PHASE AND HETEROGENEOUS REACTIONS

- **Step 1** Balanced chemical **equation**
- **Step 2** Partial pressures; (a) **initial** (b) **changes** (c) **equilibrium**
- **Step 3** **Approximation** schemes of neglecting a very small quantity

◆ Evaluating Equilibrium Constants from Reaction Data

EXAMPLE 14.8 $CO(g) + Cl_2(g) \leftrightarrows COCl_2(g)$ ← phosgene

At 600 °C, $P_0(CO)$ = 0.60 atm, $P_0(Cl_2)$ = 1.10 atm, initially.

→ $P(COCl_2)$ = 0.10 atm at equilibrium. K = ?

	$CO(g)$	$Cl_2(g)$	$COCl_2(g)$
Initial	**0.60**	**1.10**	**0**
Change	–0.10	–0.10	+0.10
Equilibrium	0.50	1.00	**0.10**

$$K = \frac{P_{COCl_2}}{(P_{CO})(P_{Cl_2})} = \frac{(0.10)}{(0.50)(1.00)} = 0.20$$

◆ Calculating Equilibrium Compositions When K is known

EXAMPLE 14.10 $H_2(g) + I_2(g) \leftrightarrows 2\ HI(g)$

At 400 K, $P_0(H_2)$ = 1.320 atm, $P_0(I_2)$ = 1.140 atm, in a sealed tube.

→ At 600 K, K = 92.6. $P(H_2)$, $P(I_2)$, and $P(HI)$?

At 600 K, from the ideal gas law at const V,

$P_0(H_2)$ = 1.320 atm x (600 K / 400 K) = 1.980 atm

$P_0(I_2)$ = 1.140 atm x (600 K / 400 K) = 1.710 atm

	$H_2(g)$ +	$I_2(g)$ ⇆	$2\,HI(g)$
Initial	**1.980**	**1.710**	**0**
Change	–x	–x	+2x
Equilibrium	1.980-x	1.710-x	**2x**

$$K = \frac{(2x)^2}{(1.980 - x)(1.710 - x)} = 92.6$$

x = **1.504** or 2.352 (*unphysical* !)

$P(H_2)$ = 0.476 atm, $P(I_2)$ = 0.206 atm, $P(HI)$ = 3.009 atm

14 CHAPTER

CHEMICAL EQUILIBRIUM

14.6 The Direction of Change in Chemical Reactions: Empirical Description

14.7 The Direction of Change in Chemical Reactions: Thermodynamic Explanation

14.8 Distribution of a Single Species between Immiscible Phases: Extraction and Separation Processes

14.6 THE DIRECTION OF CHANGE IN CHEMICAL REACTIONS: EMPIRICAL DESCRIPTION

◆ The Reaction Quotient, *Q*

$$a\text{A} + b\text{B} \leftrightarrows c\text{C} + d\text{D}$$

$$Q = \frac{(P_\text{C})^c (P_\text{D})^d}{(P_\text{A})^a (P_\text{B})^b} \qquad K = \frac{(P_\text{C}^\text{eq})^c (P_\text{D}^\text{eq})^d}{(P_\text{A}^\text{eq})^a (P_\text{B}^\text{eq})^b}$$

Reaction quotient — Equilibrium constant

$$N_2(g) + 3\,H_2(g) \leftrightarrows 2\,NH_3(g), \qquad P(N_2) : P(H_2) = 1 : 3$$

$$K = \frac{P_{NH_3}^2}{P_{N_2} P_{H_2}^3} = \frac{P_{NH_3}^2}{(P_{H_2}/3) P_{H_2}^3} = \frac{P_{NH_3}^2}{(P_{H_2}^4)/3} \rightarrow P_{NH_3} \propto P_{H_2}^2$$

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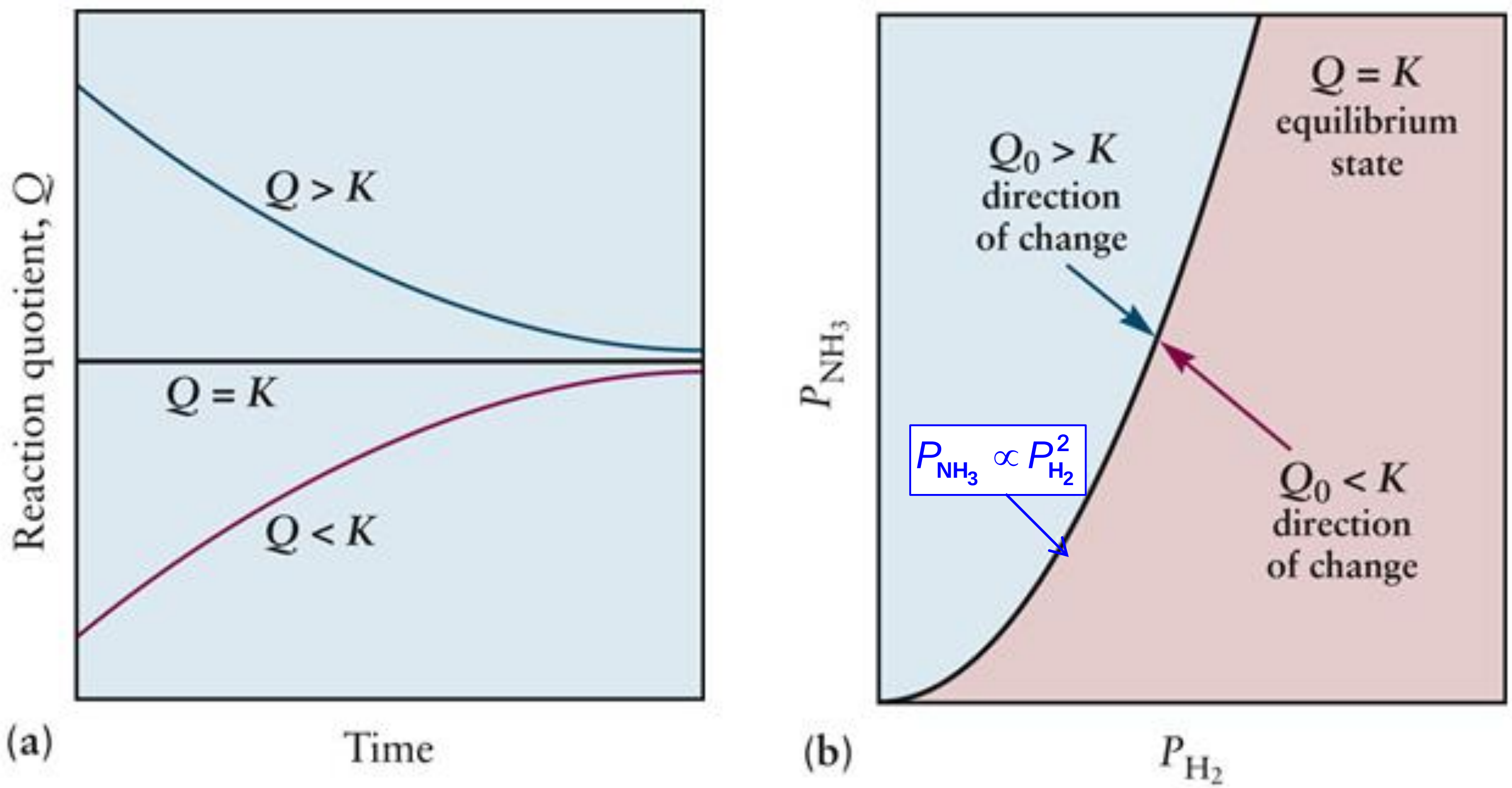


Fig. 14.5 $N_2(g) + 3\ H_2(g) \leftrightarrows 2\ NH_3(g)$

(a) $Q < K$: Q must increase, ***forward*** reaction,

$Q > K$: Q must decrease, ***reverse*** reaction

(b) From initial nonequilibrium conditions on either side of the parabola, the partial pressures approach equilibrium along lines with slope –2/3, because three moles of H_2 are consumed to produce two moles of NH_3.

◆ Free Energy Changes and the Reaction Quotient

aA + bB ⇆ cC + dD

$\Delta G = \Delta G° + RT \ln Q$

$$Q = \frac{\left(P_C / P_{ref}\right)^c \left(P_D / P_{ref}\right)^d}{\left(P_A / P_{ref}\right)^a \left(P_B / P_{ref}\right)^b}$$

At equilibrium, $\Delta G = 0$

and $Q \rightarrow K$.

$\therefore \quad \Delta G° = - RT \ln K$

$\Delta G = -RT \ln K + RT \ln Q$

$= RT \ln (Q/K)$

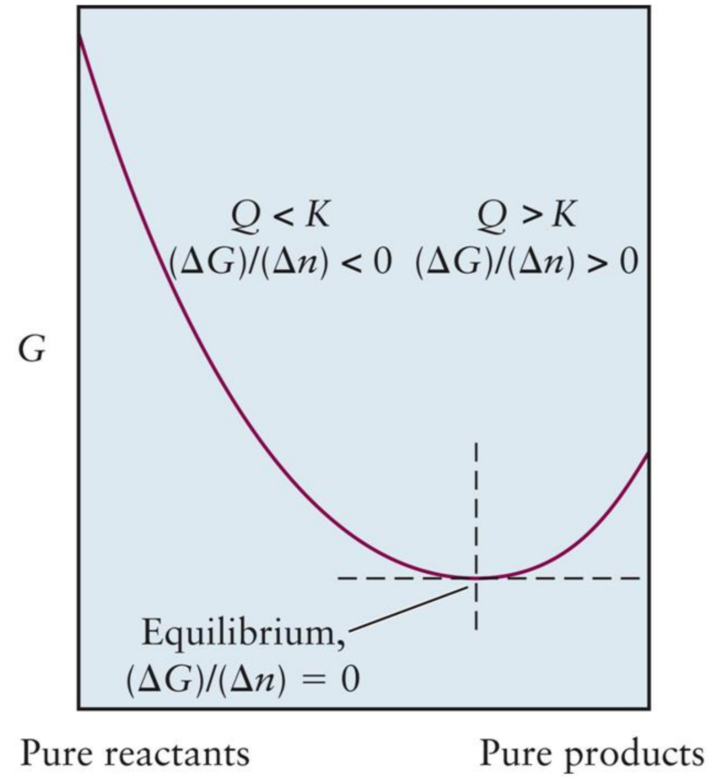


Fig. 14.10 The free energy of a reaction system is plotted against its progress from pure reactants(left) to pure products (right).

◆ External Effects on *K*: Principle of Le Châtelier

Fig. 14.6 Partial pressure versus time for the equilibrium:

$$H_2(g) + I_2(g) \leftrightarrows 2\,HI(g)$$

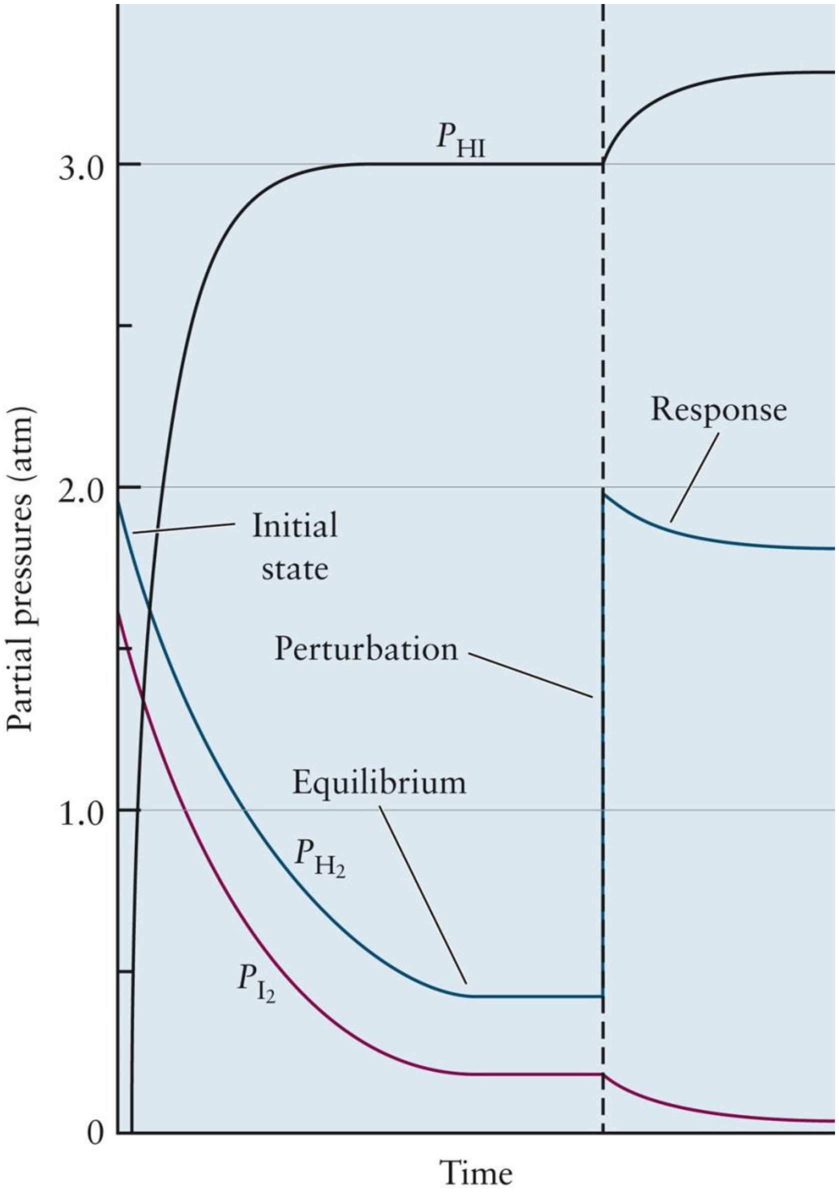
(1) LHS of the dashed line:
Approach to equilibrium (Ex. 14.10)

(2) Abrupt perturbation by increasing $P(H_2)$ to 2.0 atm.

(3) Le Châtelier principle works on the RHS of the dashed line:

Decrease in $P(I_2)$ and increase in $P(HI)$, resulting in the decrease in $P(H_2)$ to counteract the perturbation.

(4) Approach to a new equilibrium!



◆ ***Le Châtelier's principle*** (1884)

*A system in equilibrium that is subject to a stress will react in a way that tends to **counteract** the stress.*

Le Châtelier's principle predicts the direction of change of a system under an external perturbation.

Henry Le Châtelier
(Fra, 1850-1936)

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◆ Effects of Changing the Concentration of a Reactant or Product

EXAMPLE 14.15 $H_2(g) + I_2(g) \leftrightarrows 2\,HI(g)$

An equilibrium mixture at 600 K (Ex. 14.10):

$P(H_2) = 0.4756$ atm, $P(I_2) = 0.2056$ atm, $P(HI) = 3.009$ atm

$K(600\text{ K}) = 92.6$

➢ *External perturbation* (addition of H_2)

Abrupt increase of $P(H_2)$ to 2.000 atm

→ New equilibrium reached

→ New equilibrium partial pressures?

	$H_2(g)$ +	$I_2(g)$ ⇆	$2\,HI(g)$
Initial	**2.000**	**0.2056**	**3.009**
Change	–x	–x	+ 2x
Equilibrium	2.000–x	0.2056–x	3.009+2x

$$K = \frac{(3.009 + 2x)^2}{(2.000 - x)(0.2056 - x)} = 92.6$$

x = **0.1425** or 2.299 (*unphysical* !)

At new equilibrium,

$P(H_2)$ = 1.86 atm, $P(I_2)$ = 0.063 atm, $P(HI)$ = 3.29 atm

KAIST CHEMISTRY

◆ Effects of Changing the Volume

$$2\,P_2(g) \rightleftarrows P_4(g) \qquad Q = P_{P_4} / \left(P_{P_2}\right)^2$$

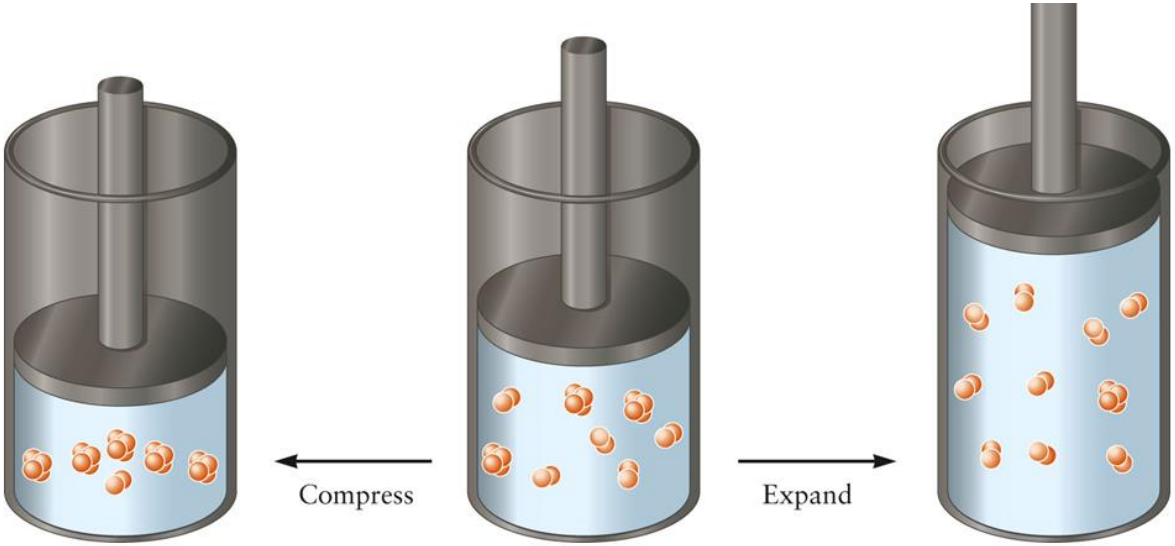


Fig. 14.7 An equilibrium mixture of P_2 and P_4 (center) is compressed (left) or expanded (right).

- Compression → Equilibrium shifts toward the forward direction.
- Expansion → Equilibrium shifts toward the backward direction.

◆ Effects of Changing the Temperature

$2\ NO_2(g) \leftrightarrows N_2O_4(g)$

high T low T

Exothermic

$\Delta H\ (25^oC) = -58.02\ kJ\ mol^{-1}$

$$K = \frac{P_{N_2O_4}}{\left(P_{NO_2}\right)^2}$$

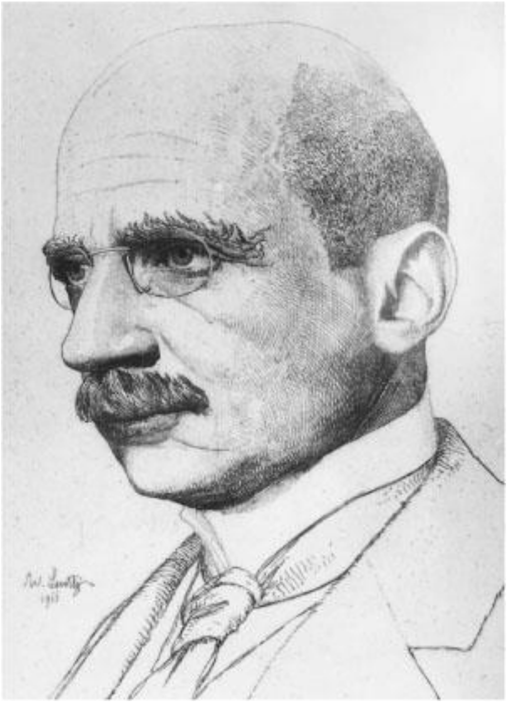
$K(25^oC) = P(N_2O_4)/P^2(NO_2) = 8.8$

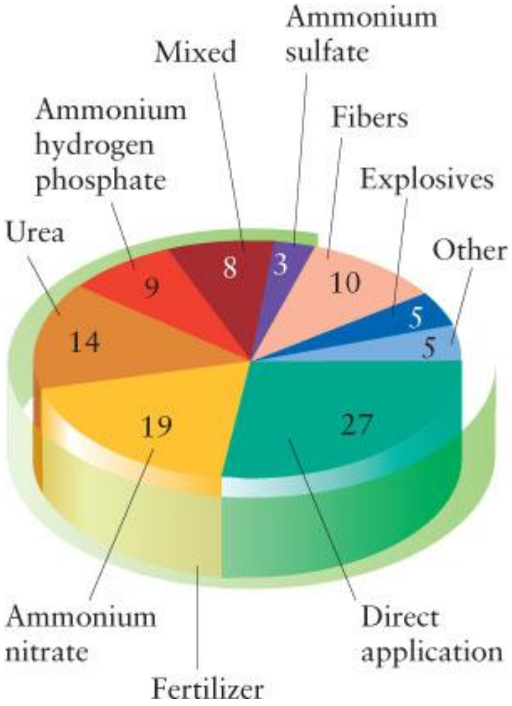
Fig. 14.8 Equilibrium between N_2O_4 and NO_2 depends on temperature.
Right: Ice bath at 0^oC, Mostly N_2O_4, Pale color
Left: Water bath at 50^oC, Mostly NO_2, Deep color

- **The Haber process**

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

Iron oxide catalyst





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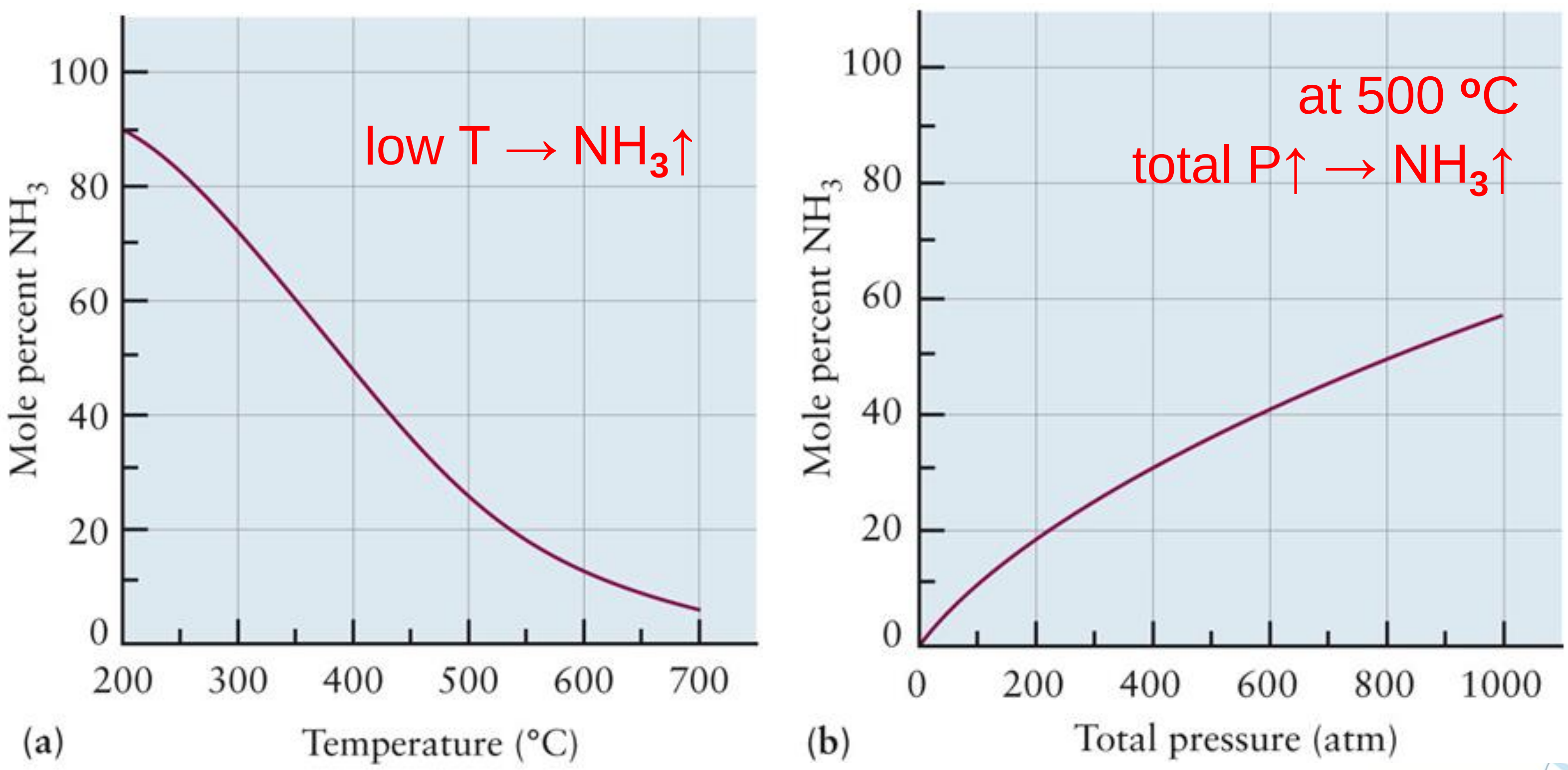
◆ Maximizing the Yield of a Reaction

➢ **Haber-Bosch** process: Fixation of N_2 from air

$N_2(g) + 3\,H_2(g) \leftrightarrows 2\,NH_3(g)$, $\Delta H < 0$ (exothermic)

Large *K* at low *T* (slow reaction) and at high *P*

→ 500°C, 200 atm, catalyst, continuous NH_3 removal



14.7 THE DIRECTION OF CHANGE IN CHEMICAL REACTIONS: THERMODYNAMIC EXPLANATION

◆ The Magnitude of the Equilibrium Constant

$$\ln K = \frac{-\Delta G^{o}}{RT} = \frac{\Delta S^{o}}{R} - \frac{\Delta H^{o}}{RT}$$

$$K = \exp\left[\frac{-\Delta G^{o}}{RT}\right] = \exp\left[\frac{\Delta S^{o}}{R}\right]\exp\left[\frac{-\Delta H^{o}}{RT}\right]$$

Large value of *K*

→ For ΔS^{o} positive and large and ΔH^{o} negative and large

→ Increasing the number of microstates ($\Delta S^{o} > 0$)

and decreasing enthalpy ($\Delta H^{o} < 0$)

◆ Free Energy Changes and the Reaction Quotient

aA + bB ⇆ cC + dD

$\Delta G = \Delta G° + RT \ln Q$

$$Q = \frac{(P_C / P_{ref})^c (P_D / P_{ref})^d}{(P_A / P_{ref})^a (P_B / P_{ref})^b}$$

At equilibrium, $\Delta G = 0$

and $Q \rightarrow K$.

$\therefore\ \Delta G° = -RT \ln K$

$$\Delta G = -RT \ln K + RT \ln Q$$
$$= RT \ln (Q/K)$$

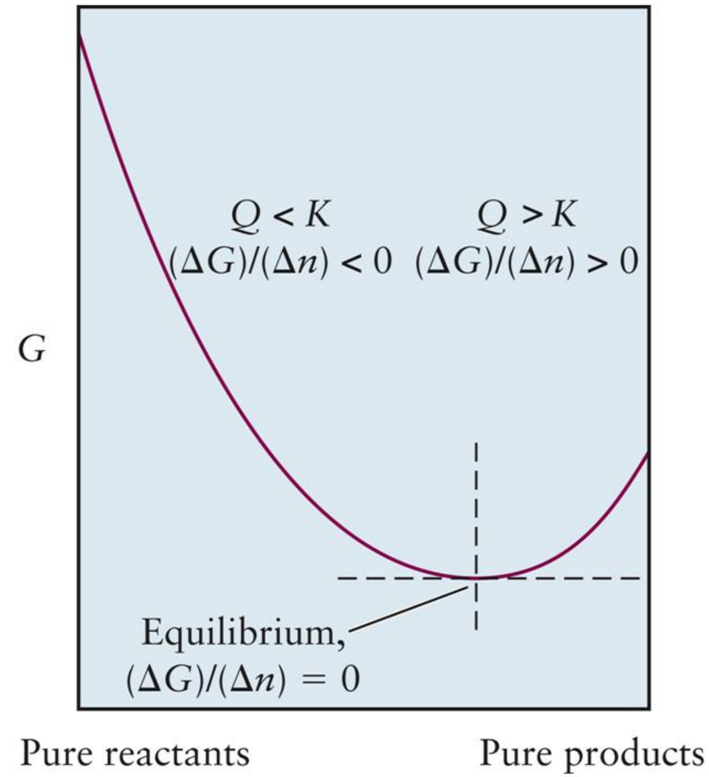


Fig. 14.10 The free energy of a reaction system is plotted against its progress from pure reactants(left) to pure products (right).

◆ Temperature Dependence of Equilibrium Constants

$$-RT\ln K = \Delta G^{o} = \Delta H^{o} - T\Delta S^{o}$$

$$\ln K = -\Delta G^{o} / RT$$

$$= -\Delta H^{o} / RT + \Delta S^{o} / R$$

$$\ln K_1 = -\frac{\Delta H^{o}}{RT_1} + \frac{\Delta S^{o}}{R}$$

$$\ln K_2 = -\frac{\Delta H^{o}}{RT_2} + \frac{\Delta S^{o}}{R}$$

$$\ln\left(\frac{K_2}{K_1}\right) = -\frac{\Delta H^{o}}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

Van't Hoff equation

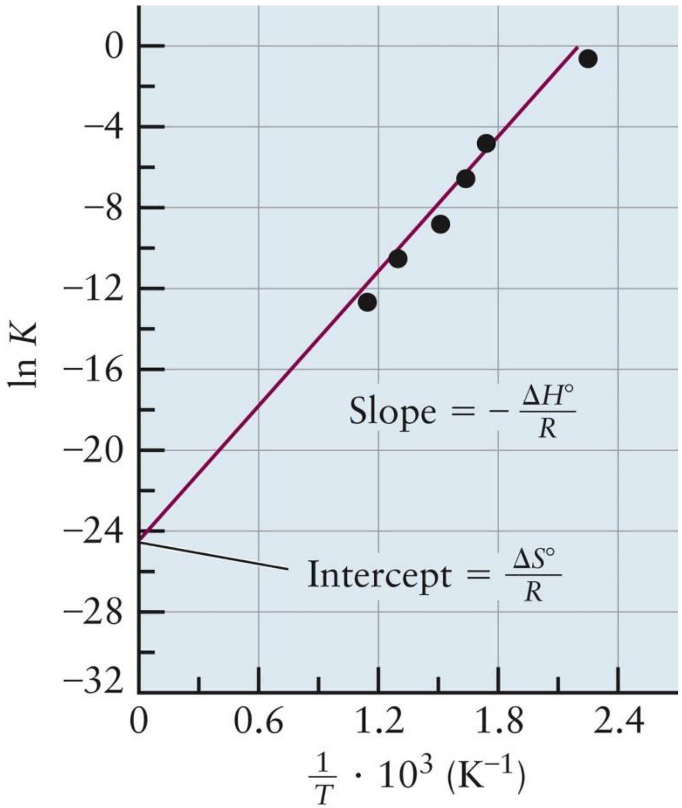


Fig. 14.11 Temperature dependence of the equilibrium constant for the reaction $N_2(g) + 3\,H_2(g) \leftrightarrows 2\,NH_3(g)$

◆ Effect of temperature change on *K*

→ Depends on the sign of $\Delta H°$

$\Delta H° < 0$ (exothermic) $K\downarrow$ as $T\uparrow$

$\Delta H° > 0$ (endothermic) $K\uparrow$ as $T\uparrow$

$$\ln\left(\frac{K_2}{K_1}\right) = -\frac{\Delta H^o}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

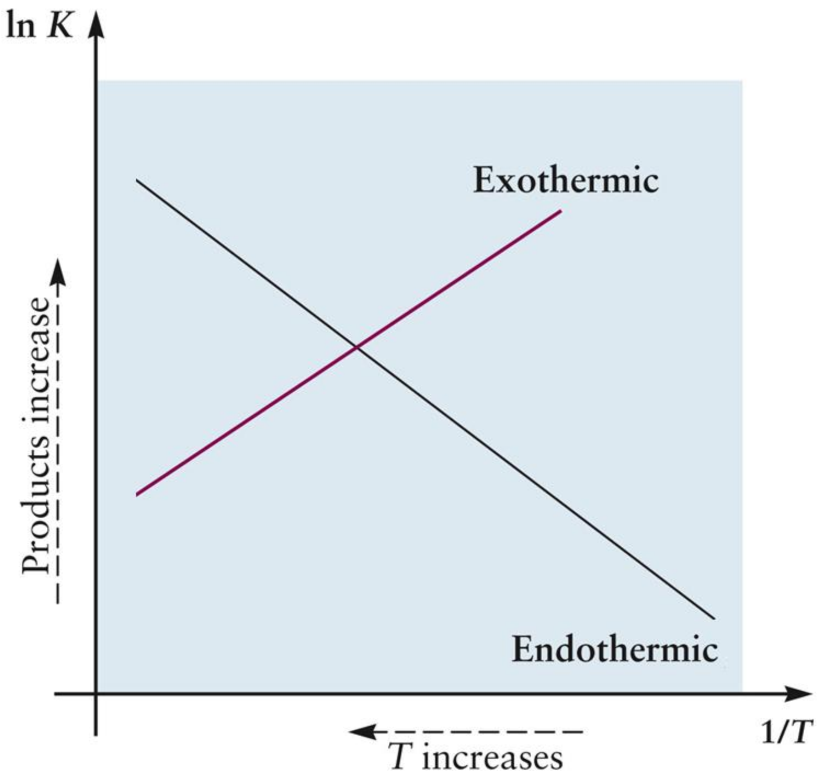


Fig. 14.12 Sketch of ln *K* against 1/*T* for an exothermic and for an endothermic reaction as predicted by thermodynamics.

EXAMPLE 10.13

The equilibrium constant K for the synthesis of ammonia is 6.8×10^5 at 298 K. Predict its value at 400 K. $\Delta H_f^0(NH_3(g)) = -46.11\ kJmol^{-1}$

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

$$\Delta H_r^\circ = 2\Delta H_f^\circ(NH_3, g) = 2(-46.11\ kJ\cdot mol^{-1})$$
$$= -92.22\ kJ\cdot mol^{-1} \text{ or } -92.22 \times 10^3\ J\cdot mol^{-1}$$

$$\ln K_1 - \ln K_2 = -\frac{\Delta H_r^\circ}{R}\left\{\frac{1}{T_1} - \frac{1}{T_2}\right\} = \frac{\overbrace{-9.222 \times 10^4\ J\cdot mol^{-1}}^{-92.22\ kJ\cdot mol^{-1}}}{8.3145\ J\cdot K^{-1}\cdot mol^{-1}} \times \left\{\frac{1}{298\ K} - \frac{1}{400.\ K}\right\}$$
$$= -9.49$$

$$K_2 = K_1 e^{-9.49} = (6.8 \times 10^5) \times e^{-9.49} = 51$$

◆ Temperature Dependence of Vapor Pressure

$$H_2O(l) \rightleftharpoons H_2O(g) \qquad P_{H_2O(g)} = K$$

$$\ln\left(\frac{K_2}{K_1}\right) = \ln\left(\frac{P_2}{P_1}\right) = -\frac{\Delta H_{vap}}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

At the normal boiling point, $T_1 = T_b$ at $P_1 = 1$ atm.

$$\ln P = -\frac{\Delta H_{vap}}{R}\left[\frac{1}{T} - \frac{1}{T_b}\right]$$

14.8 DISTRIBUTION OF A SINGLE SPECIES BETWEEN IMMISCIBLE PHASES: EXTRACTION AND SEPARATION PROCESSES

◆ Heterogeneous equilibrium

Partitioning a solute species between two immiscible solvent phases

I_2 in H_2O and CCl_4 $I_2(aq) \leftrightarrows I_2(CCl_4)$

➢ Partition coefficient, *K*

$$K = \frac{[I_2]_{CCl_4}}{[I_2]_{aq}} = 85 \ \ (\text{at } 25^{\circ}\text{C}) \ > 1$$

~ I_2 more soluble in CCl_4 than in H_2O

➢ Shifting the equilibrium

Add I^- in the water. $I_2(aq) + I^-(aq) \rightarrow I_3^-(aq)$

More $I_2(aq)$ in the water consumed.

Le Châtelier's principle causes more I_2 to move from CCl_4 to H_2O.

◆ Extraction Processes

EXAMPLE 14.18 $[I_2(aq)]_i = 2.00 \times 10^{-3}$ M. 0.100 L of this aq solution is extracted with 0.050 L of CCl_4 at 25°C. $[I_2(aq)]_f$ = ?

$n(I_2) = (2.00 \times 10^{-3}\ \text{mol L}^{-1})(0.100\ \text{L})$

$= 2.00 \times 10^{-4}$ mol

Let y moles remain in aqueous solution.

$$K = \frac{[I_2]_{CCl_4}}{[I_2]_{aq}} = 85 = \frac{(2.00 \times 10^{-4} - y)/0.050}{y/0.100}$$

$y = 4.6 \times 10^{-6}$ mol or 2.3%

Fig. 14.13. (a) $I_2(aq)$ on CCl_4 in a separatory funnel.
(b) After shaking.

◆ Chromatographic Separations

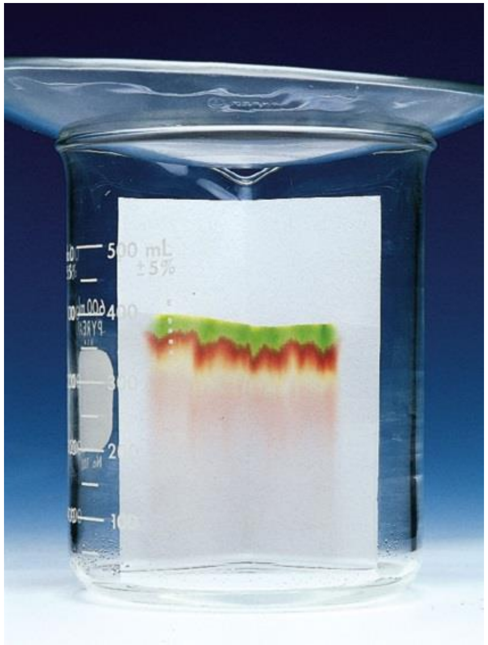
- Separation technique based on partition equilibria
- Continuous extraction process

Exchange of solute species between mobile and stationary phases

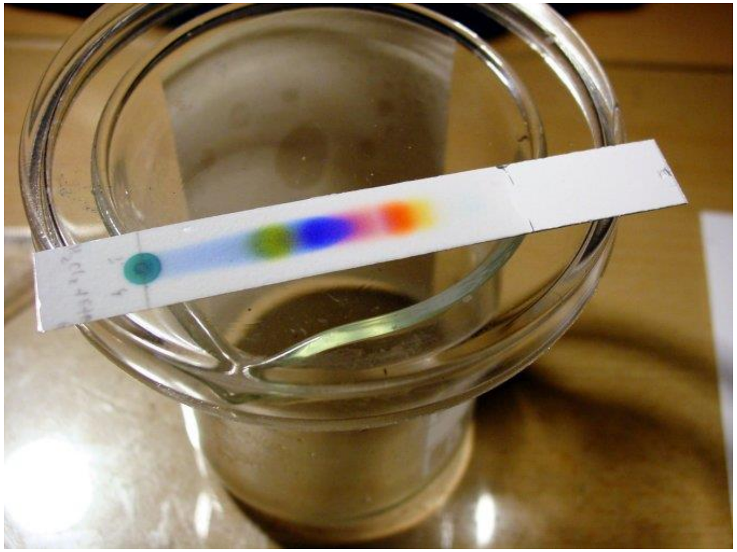
Partition ratio, $K = \dfrac{[A]_{stationary}}{[A]_{mobile}}$

TABLE 14.1 Chromatographic Separation Techniques†

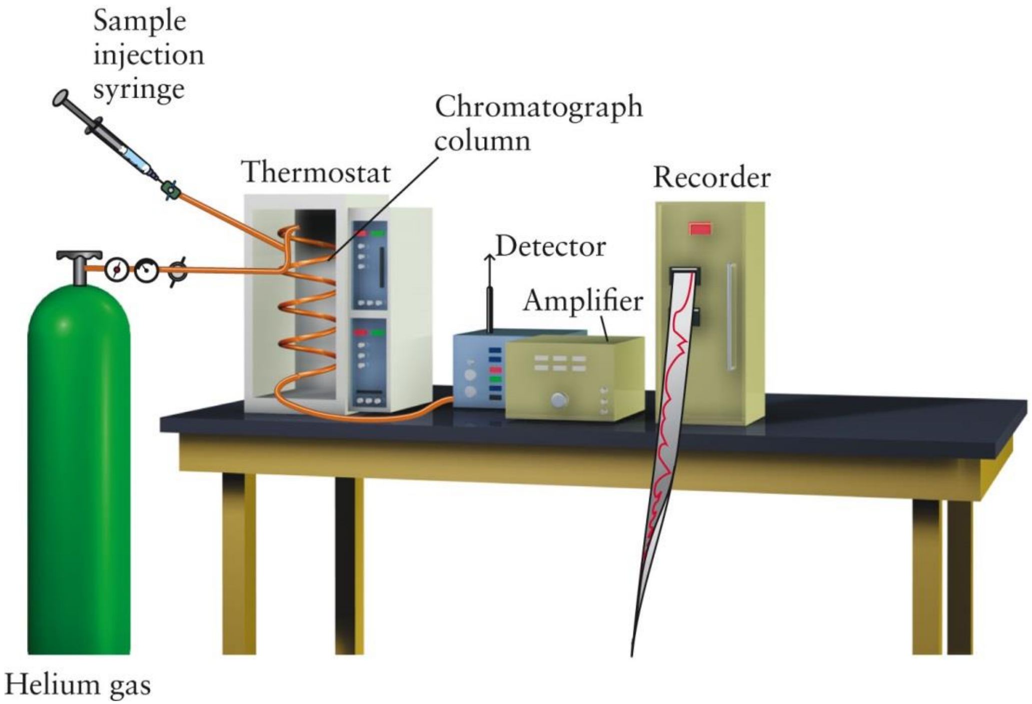
Name	Mobile Phase	Stationary Phase
Gas–liquid	Gas	Liquid adsorbed on a porous solid in a tube
Gas–solid	Gas	Porous solid in a tube
Column	Liquid	Liquid adsorbed on a porous solid in a tubular column
Paper	Liquid	Liquid held in the pores of a thick paper
Thin layer	Liquid	Liquid or solid; solid is held on glass plate and liquid may be adsorbed on it
Ion exchange	Liquid	Solid (finely divided ion-exchange resin) in a tubular column



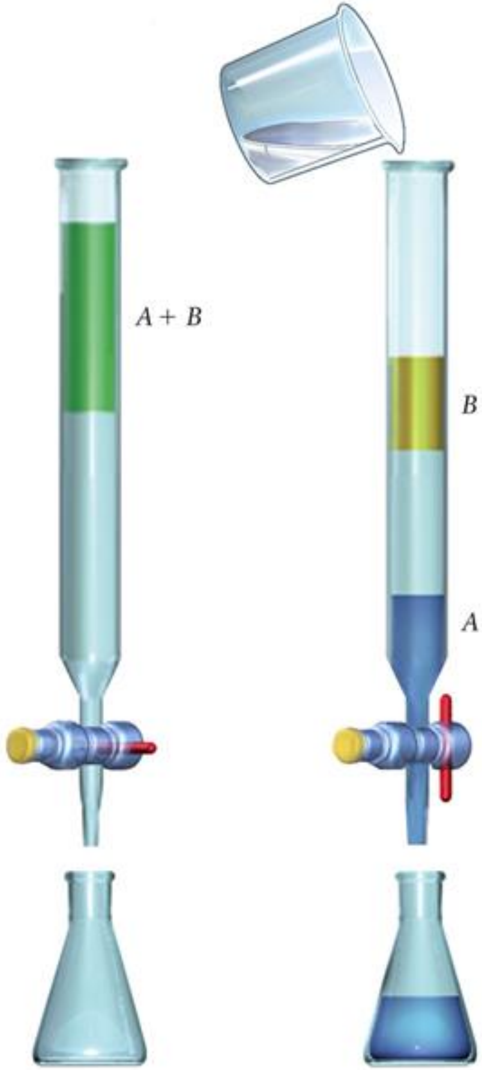
Paper chromatography



Thin layer chromatography (TLC)



Gas-liquid chromatography



Column chromatography

For Chapter 14,

- Problem Sets

  : 9, 26, 53, 74, 105

- Chapter Summary (Choose one)

  : Chemical Equilibrium,
  The direction of chemical reactions