Recap

- ❑ Vapor pressure in mixed binary system
- ❑ Gas-liquid and solid-liquid solutions
- ❑ Colligative properties, molality

Find the molality of sucrose, $C_{12}H_{22}O_{11}$, in 1.06 M $C_{12}H_{22}O_{11}$(aq), which is known to have density 1.14 g.mL^{-1}.

$$\text{molality} = \frac{n_{solute} \text{ (mol)}}{m_{solvent} \text{ (kg)}}$$

342.3 g·mol^{-1} $C_{12}H_{22}O_{11}$

Calculating the molality, given the molarity:

m_{solute} (g) = n_{solute} (mol) M_{solute} (g·mol^{-1}) =
$\quad\quad$ molarity (mol·L^{-1})× 1L × M_{solute} (g·mol^{-1})

$m_{solvent}$ (g) = $m_{solution}$ (g) − m_{solute} (g)

Find the molality of sucrose, $C_{12}H_{22}O_{11}$, in 1.06 M $C_{12}H_{22}O_{11}$(aq), which is known to have density 1.14 g.mL^{-1}.

Mass of solvent must be calculated per liter because we're working with molarity:

1.14 g.mL^{-1} × 1000 mL = 1140 g of solution (we use this in the second equation to find the mass of solvent).

Next, mass of solute = molarity × (1L) × M$_{solute}$,
(1.06 mol·L^{-1}) × 1L × 342.3 g·mol^{-1} = 363 g

$m_{solvent}$ (g) = $m_{solution}$ (g) - m_{solute} (g),
         1140 g solution - 363 g solute = 780 g or 0.78 kg

$$n_{surose} = \frac{1 \text{ mol } C_{12}H_{22}O_{11}}{342.3 \text{ g}} \times \frac{363g}{1} = 1.06 \text{ mol}, \qquad m = \frac{1.06 \text{ mol}}{0.78 \text{ kg}} =$$

$$1.4 \text{ mol·kg}^{-1}$$

Boiling-Point Elevation and Freezing-Point Depression

A **nonvolatile solute** lowers the vapor pressure of the solvent, therefore increasing the boiling point and therefore it is called **boiling-point elevation**.

The **effect of the solute** on the **entropy** of the solvent increases more than in the pure solvent, thus the boiling point is higher in the presence of the solute.

Boiling-Point Elevation and Freezing-Point Depression

The increased boiling temperature is usually quite small and is of **little practical importance in science**. A 0.1 m aqueous sucrose solution, for instance, boils at 100.05°C.
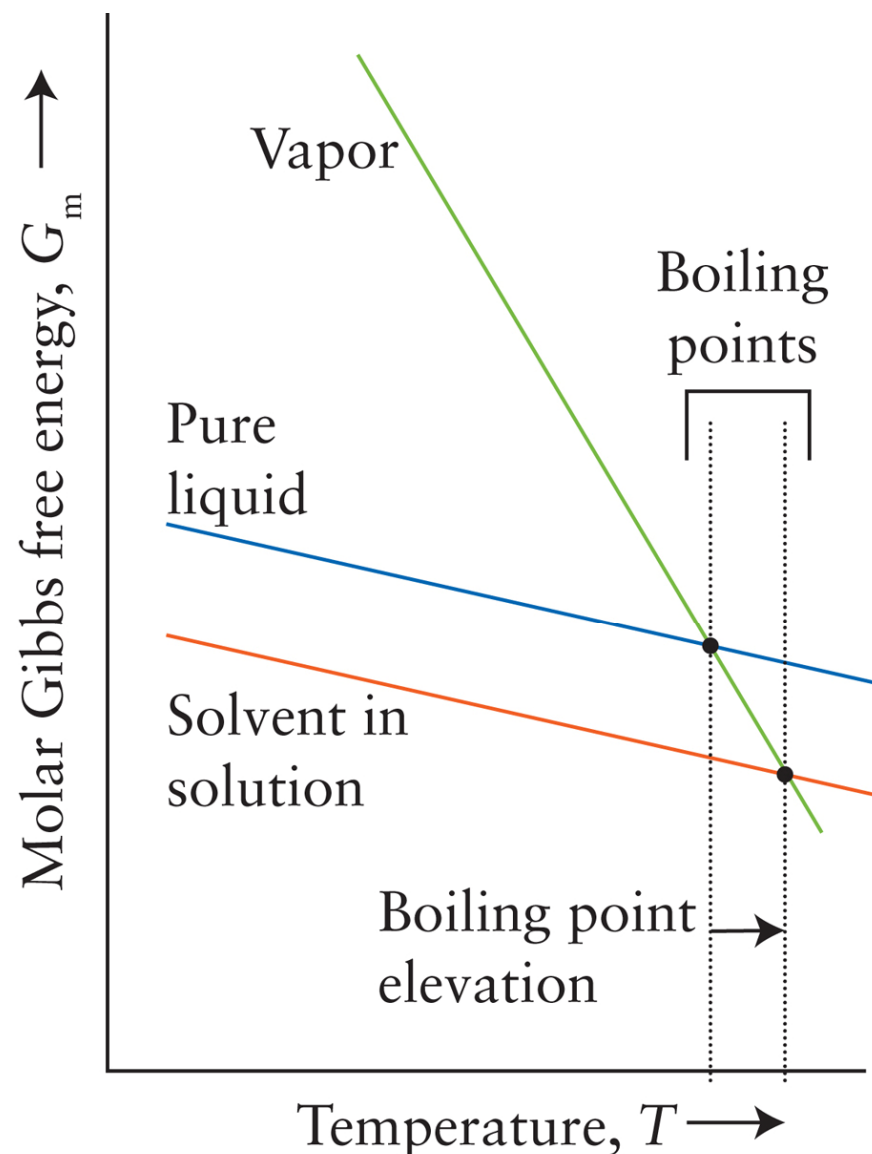

Figure 5F.1
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Boiling-Point Elevation and Freezing-Point Depression

Freezing-point depression is more significant. An added solute lowers of the freezing point of a solvent.

Seawater freezes about 1°C *lower* than fresh water.

Salting walkways and roads lowers the water's freezing point melting it.

Melting point are also a method for determining the **purity of a solid.**
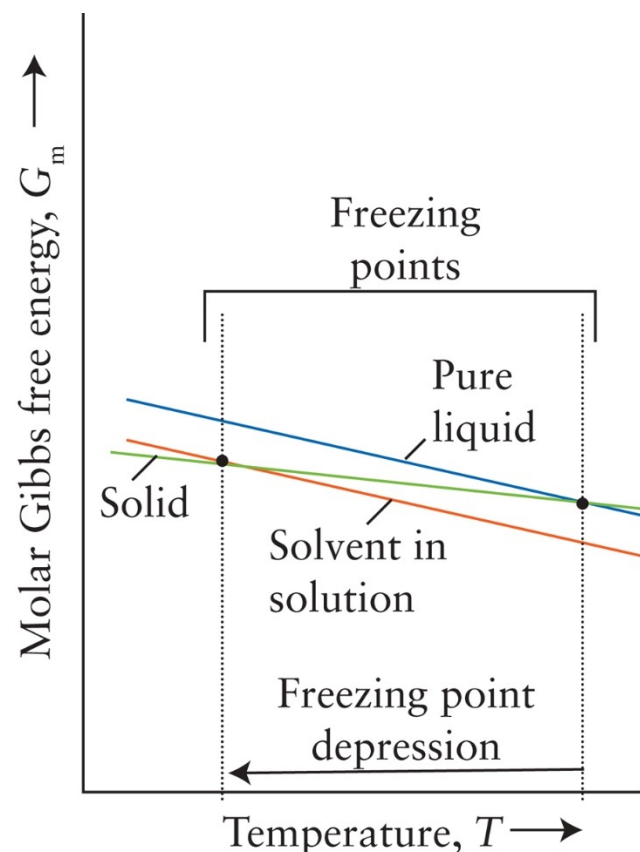

Figure 5F.2
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Boiling-Point Elevation and Freezing-Point Depression

Freezing-point depression = k_f × molality, <u>temperature</u> <u>decreases</u>.

Boiling-point elevation = k_b × molality, <u>temperature</u> <u>increases</u>.

TABLE 5F.1 Boiling-Point and Freezing-Point Constants				
Solvent	Freezing point/°C	k_f/ (K·kg·mol^{-1})	Boiling point/°C	k_b/ (K·kg·mol^{-1})
acetone	−95.35	2.40	56.2	1.71
benzene	5.5	5.12	80.1	2.53
camphor	179.8	39.7	204	5.61
carbon tetrachloride	−23	29.8	76.5	4.95
cyclohexane	6.5	20.1	80.7	2.79
naphthalene	80.5	6.94	217.7	5.80
phenol	43	7.27	182	3.04
water	0	1.86	100.0	0.51

Table 5F.1
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W. H. Freeman & Company, © 2016 by P. W. Atkins, L. L. Jones, and L. E. Laverman

Boiling-Point Elevation and Freezing-Point Depression

TABLE 5F.1 Boiling-Point and Freezing-Point Constants

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naphthalene	80.5	6.94	217.7	5.80
phenol	43	7.27	182	3.04
water	0	1.86	100.0	0.51

Table 5F.1

The effect is small. For a 0.1 M $C_{12}H_{22}O_{11}$ (aq) (sucrose) solution:

Freezing-point depression = (1.86 K·kg·mol^{-1}) × (0.1 mol·kg^{-1}) = 0.2 K, therefore water would freeze at -0.2°C.

Self-test 5F.1B Use the data in Table 5E.1 to determine at what temperature a 0.050 mol·kg^{-1} solution of the insecticide malathion, $C_{10}H_{19}O_6PS_2$, in camphor will freeze.

Solve for freezing point = k_f × molality. We need both k_f and molality$_{malathion}$

The freezing point for pure camphor is 179.8°C.

k_f for camphor is 39.7 K·kg·mol^{-1}.

Molality of $C_{10}H_{19}O_6PS_2$ = 0.050 mol·kg^{-1}.

Freezing-point depression = (39.7 K·kg·mol^{-1}) × (0.050 mol·kg^{-1}) = 1.99 K (K is not the new temperature, it is the amount the temperature will decrease by), therefore camphor would freeze at 179.8°C - 1.99°C = 177.8°C

Boiling-Point Elevation and Freezing-Point Depression, a New Variable: van 't Hoff i Factor

In an *electrolyte solution*, each formula unit contributes two or more ions. Sodium chloride gives Na^+ and Cl^- ions and both ions contribute to the depression of the freezing point.

Solve for freezing point = $ik_f \times$ molality

The van't Hoff i factor, is determined experimentally.

In very dilute solution, less than 0.001 M, where all ions are independent, $i = 2$ for MX salts such as NaCl, and for MX_2 salts such as $CaCl_2$, $i = 3$.

Of the following five materials, which has the lowest freezing point and the highest boiling point in water?

A. 1.0 m magnesium phosphate
B. 1.0 m sodium chloride
C. 1.0 m calcium chloride
D. 1.0 m aluminum nitrate

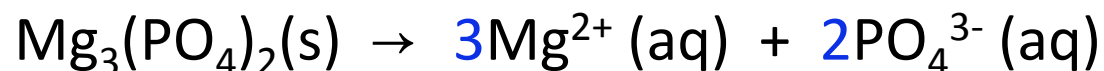Which has the lowest freezing point and the highest boiling point in water?

A. 1.0 m magnesium phosphate
B. 1.0 m sodium chloride
C. 1.0 m calcium chloride
D. 1.0 m aluminum nitrate

Magnesium phosphate, $i = 5$

$Mg_3(PO_4)_2(s) \rightarrow 3Mg^{2+} (aq) + 2PO_4^{3-} (aq)$

Sodium chloride: NaCl, $i = 2$
Calcium Chloride: $CaCl_2$, $i = 3$
Aluminum nitrate: $Al(NO_3)_3$, $i = 4$

Example 5F.1 The addition of 0.24 g of sulfur to 100 g of the solvent carbon tetrachloride lowers the solvent's freezing point by 0.28°C. What is the molar mass and molecular formula of sulfur?

$$\text{Molality} = \frac{\text{freezing point}}{ik_f} , \frac{0.28\,K}{(1) \times (29.8\ K \cdot kg \cdot mol^{-1})}$$

$$\text{mol} = \frac{0.28\,K}{(1) \times (29.8\ K \cdot kg \cdot mol^{-1})} \times 0.100\ kg$$

$$\text{First part, g·mol}^{-1} = \frac{0.24\ g}{\dfrac{0.28\,K}{(1) \times (29.8\ K \cdot kg \cdot mol^{-1})} \times 0.100\ kg} =$$

$$2.6 \times 10^2\ g \cdot mol^{-1}$$

$$\text{Second part, } M_{solute}/\text{atomic mass} , \frac{2.6 \times 10^2\ g \cdot mol^{-1}}{32.1\ g \cdot mol^{-1}} = 8.1, \text{ so } S_8$$

Osmosis

Osmosis is the flow of solvent through a membrane into a more concentrated solution.

The membrane permits only certain types of molecules or ions to pass through.

Cellulose acetate, for instance, *allows* water molecules to pass through it, but *not* bulky solute molecules or ions coated with hydrated water molecules.
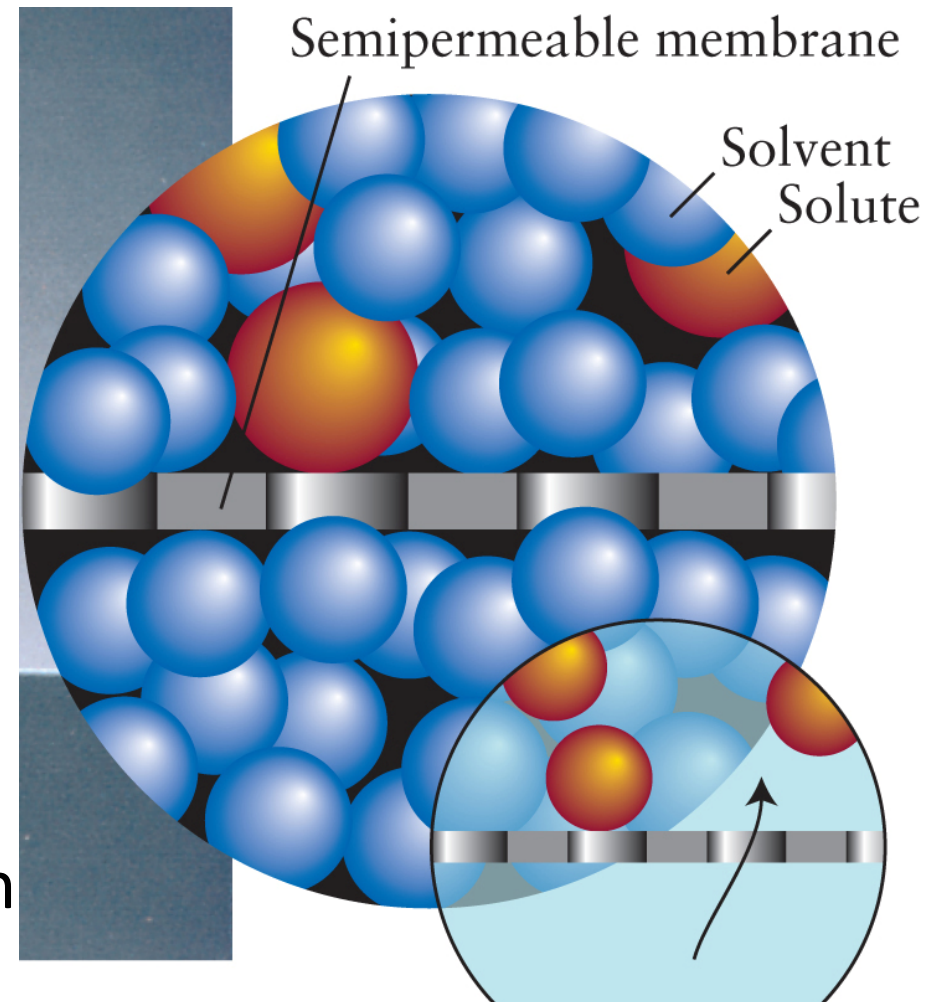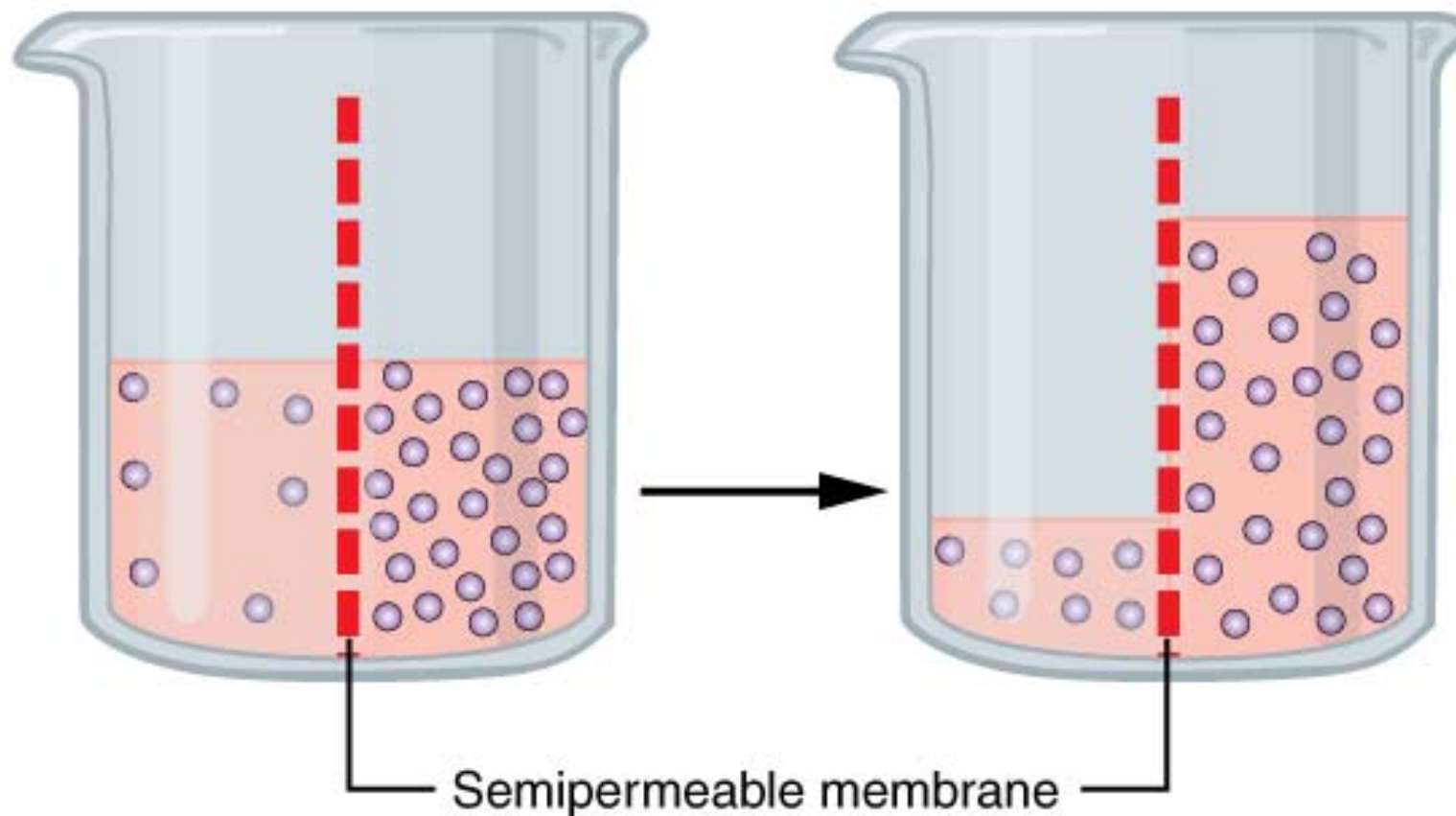

Semipermeable membrane

Solvent
Solute

Figure 5F.3
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W. H. Freeman photo by Ken Karp

A net movement of solvent → equal concentration of solutions

Semipermeable membrane

The pressure needed to stop the flow of solvent is called the
osmotic pressure, Π

Biological cell walls act as **semipermeable membranes** that **allow water**, **small molecules**, and hydrated ions to pass, yet **block the passage** of the enzymes and proteins.

Water passes into the more concentrated solution in the interior of the cell, carrying small nutrient molecules with it.

This influx of water also keeps the cell **turgid** (swollen). When the water supply is cut off, the turgidity is lost and the cell becomes dehydrated.

Salted meat is preserved from bacterial attack by osmosis; high concentrated salt solution **dehydrates** and kills the bacteria by causing water to flow out of them.

Osmosis

Osmosis is a thermodynamic property ($G = H - TS$).

Pure solvent | Solution

H_m H_m

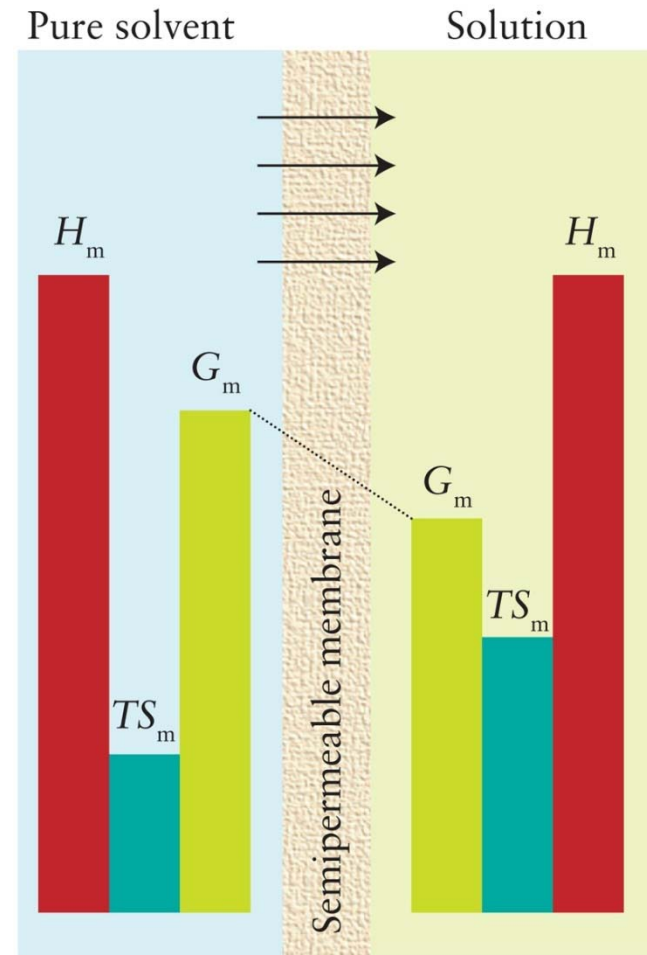G_m

G_m

TS_m

TS_m

Semipermeable membrane

Figure 5F.5
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Solvent flows until the molar Gibbs free energy of the solvent is the same on each side of the membrane.

The same van 't Hoff *i* factor appears in osmotic pressure:

$\Pi = iRTc$ (also $\Pi = iRTM$, where *M* is molarity)

c is molarity,
R is the gas constant,
T is temperature.

Osmometry is the technique used to determine the molar mass of a solute from osmotic pressure measurements.

Example 5F.2 The osmotic pressure due to 2.20 g of polyethylene (PE) dissolved in enough benzene to produce 100 mL of solution was 1.10×10^{-2} atm at 25°C. Calculate the average molar mass of the polymer, which is a nonelectrolyte.

We are asked to find $g \cdot mol^{-1}$. We have g, so we need mole. From $\Pi = iRTc$ we can isolate "c" or molarity, $mol \cdot L^{-1}$, which has mole.

100 mL = 0.1000 L

(273.15 + 25°C)K = 298 K

$$mol \cdot L^{-1} = c = \frac{\Pi}{iRT}, \quad \frac{1.10 \times 10^{-2} \text{ atm}}{(1) \times (0.08206 \text{ atm} \cdot L \cdot mol^{-1} \cdot K^{-1}) \times (298 \text{ K})}$$

$mol \cdot L^{-1} \times L = mol =$

$$\frac{1.10 \times 10^{-2} \text{ atm}}{(1) \times (0.08206 \text{ atm} \cdot L \cdot mol^{-1} \cdot K^{-1}) \times (298 \text{ K})} \times 0.1000 \text{ L}$$

Example 5F.2 The osmotic pressure due to 2.20 g of polyethylene (PE) dissolved in enough benzene to produce 100 mL of solution was 1.10×10^{-2} atm at 25°C. Calculate the average molar mass of the polymer, which is a nonelectrolyte.

$$g \cdot mol^{-1} = \frac{2.20 \text{ g}}{\dfrac{1.10 \times 10^{-2} \text{ atm}}{(1) \times (0.08206 \text{ atm·L·mol}^{-1}\cdot K^{-1}) \times (298 \text{ K})} \times 0.1000 \text{ L}} =$$

4.89×10^4 g·mol^{-1}

or 48,900 g·mol^{-1}

Chemical Equilibria

Figure 5J.1
Atkins, *Chemical Principles: The Quest for Insight*, 7e
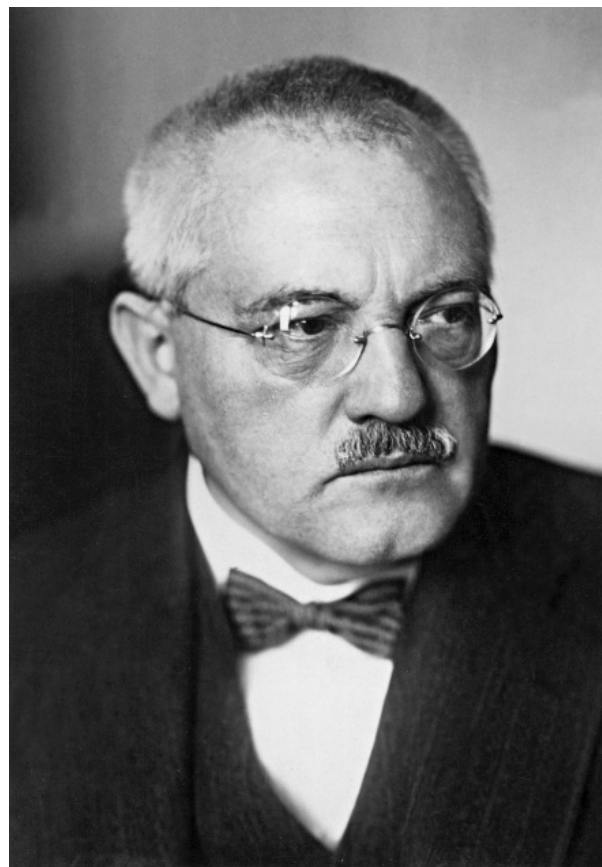ullstein bild/The Granger Collection, NYC.

Figure 5J.2
Atkins, *Chemical Principles: The Quest for Insight*, 7e
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Fritz Haber
1918 Nobel in Chemistry

Carl Bosch
1931 Nobel in Chemistry
High-pressure Chemistry

N$_2$ fixation

Even though nitrogen is common, 70% of air is N$_2$, twentieth century methods were unable to convert nitrogen into **nitrates** and ammonia.

Finally a German chemist, **Fritz Haber,** and a chemical engineer, **Carl Bosch,** found a way to **improve the yield** by **changing the reaction conditions**.

Fritz Haber and **Carl Bosch** were the *first* to produce ammonia, originally thought *impossible to make* on a large scale, by **changing the reaction conditions**.

Instead of following "normal stoichiometry" rules, they
1. added **overwhelming** quantities of reactants, *and*
2. continually **starved** the reaction by removing product.

$$3\ H_2(g)\ +\ N_2(g)\ \rightleftharpoons\ 2\ NH_3(l) + heat$$
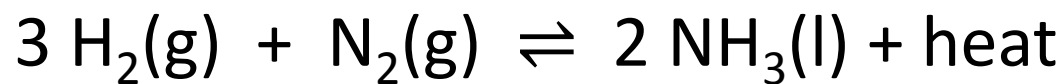
This feat was possible by understanding the nature of equilibrium reactions.

millennium essay

Detonator of the population explosion

WIthout ammonia, there would be no inorganic fertilizers, and nearly half the world would go hungry. Of all the century's technological marvels, the Haber–Bosch process has made the most difference to our survival.
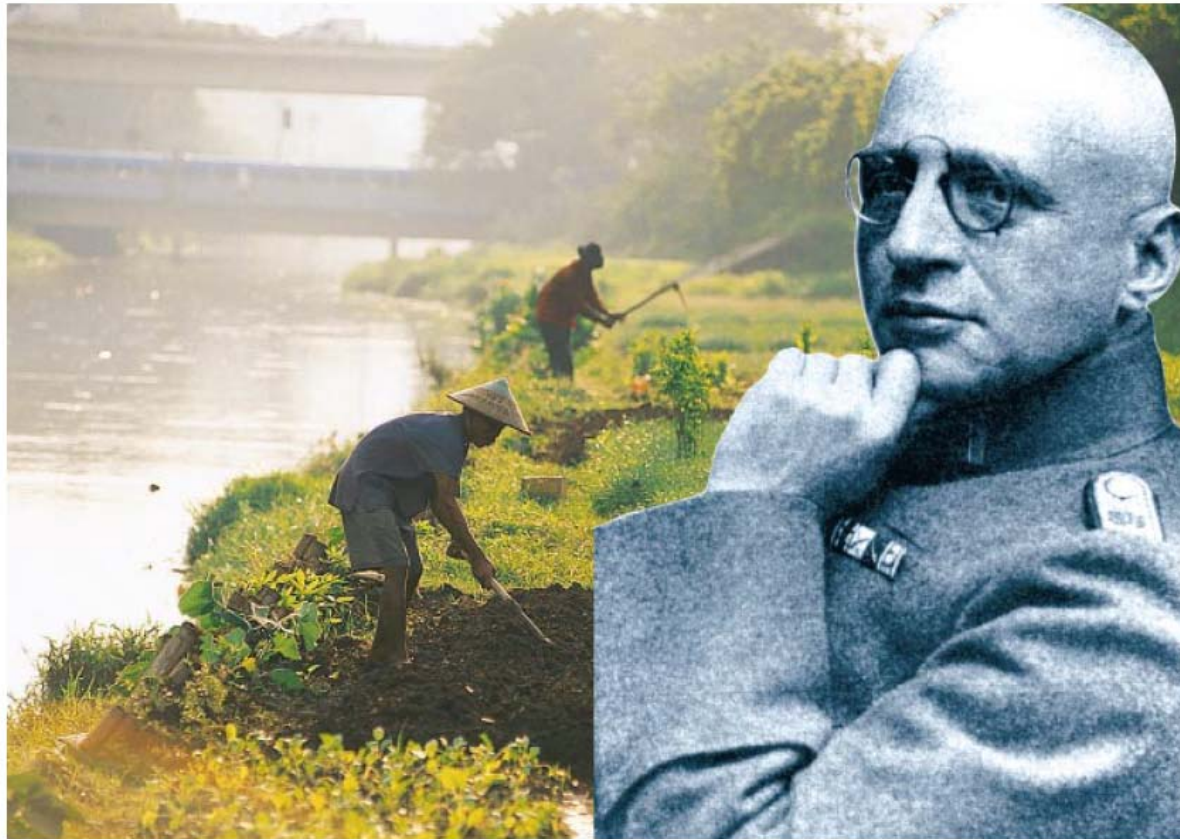

Haber (right) invented the process while Bosch brought the necessary engineering skills.

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Both forward and reverse reactions occur at the same rate.

As fast as reactants make products, products will react to make reactants, all at the same *speed*.
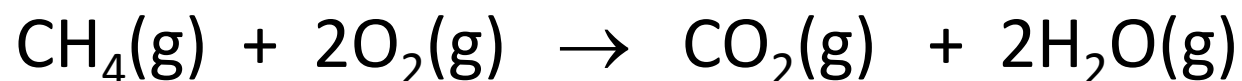
Though this appears to be a static reaction, in reality the reaction races to make both *reactants and products.*
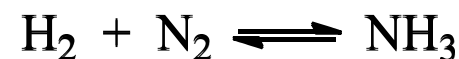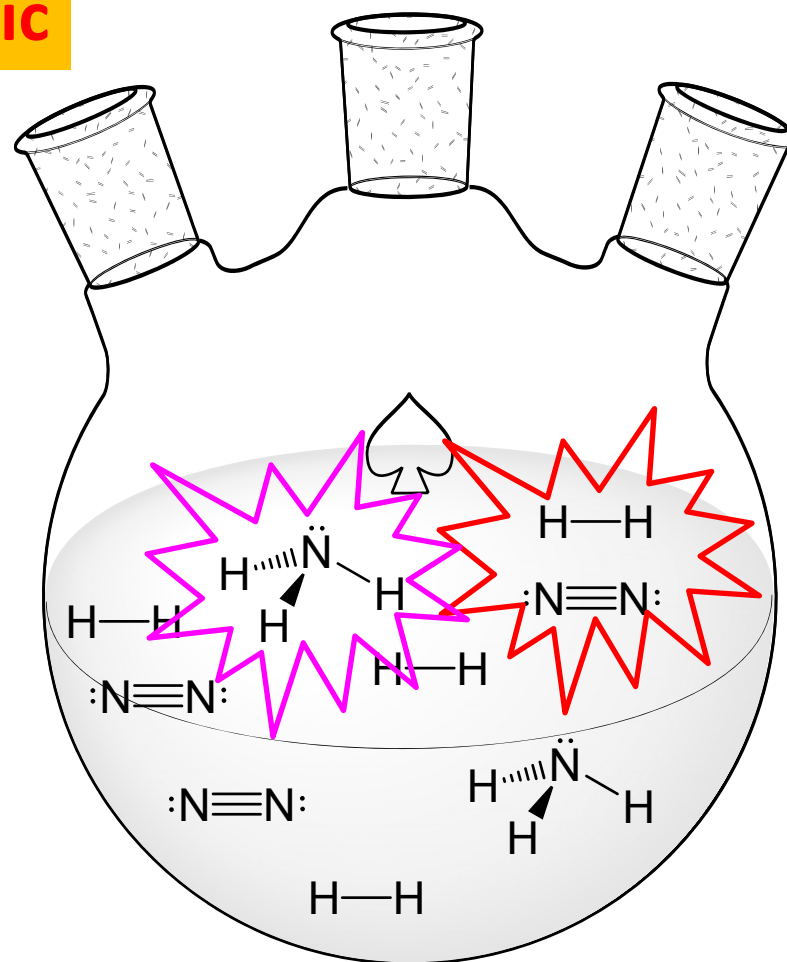
$$H_2 + N_2 \rightleftharpoons NH_3$$

Use of a new symbol "$\rightleftharpoons$" means chemical equilibria.

Burning methane, CH_4, in oxygen is a one-way reaction,

$$CH_4(g) \ + \ 2O_2(g) \ \rightarrow \ CO_2(g) \ + \ 2H_2O(g)$$

Here we only make products.

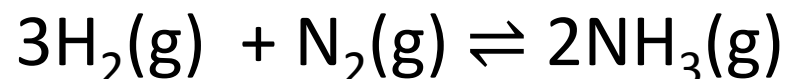Time only moves in one direction (as we experience it).

Reactions at Equilibrium

The *criteria* for dynamic chemical equilibrium are:

1. The forward and reverse reactions are both taking place.
2. The forward rate equals the reverse rate (so there appears to be no net change in speed).

Rates of breaking and making bonds are the same.

Forward **rate** $\rightleftharpoons$ Reverse **rate**

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

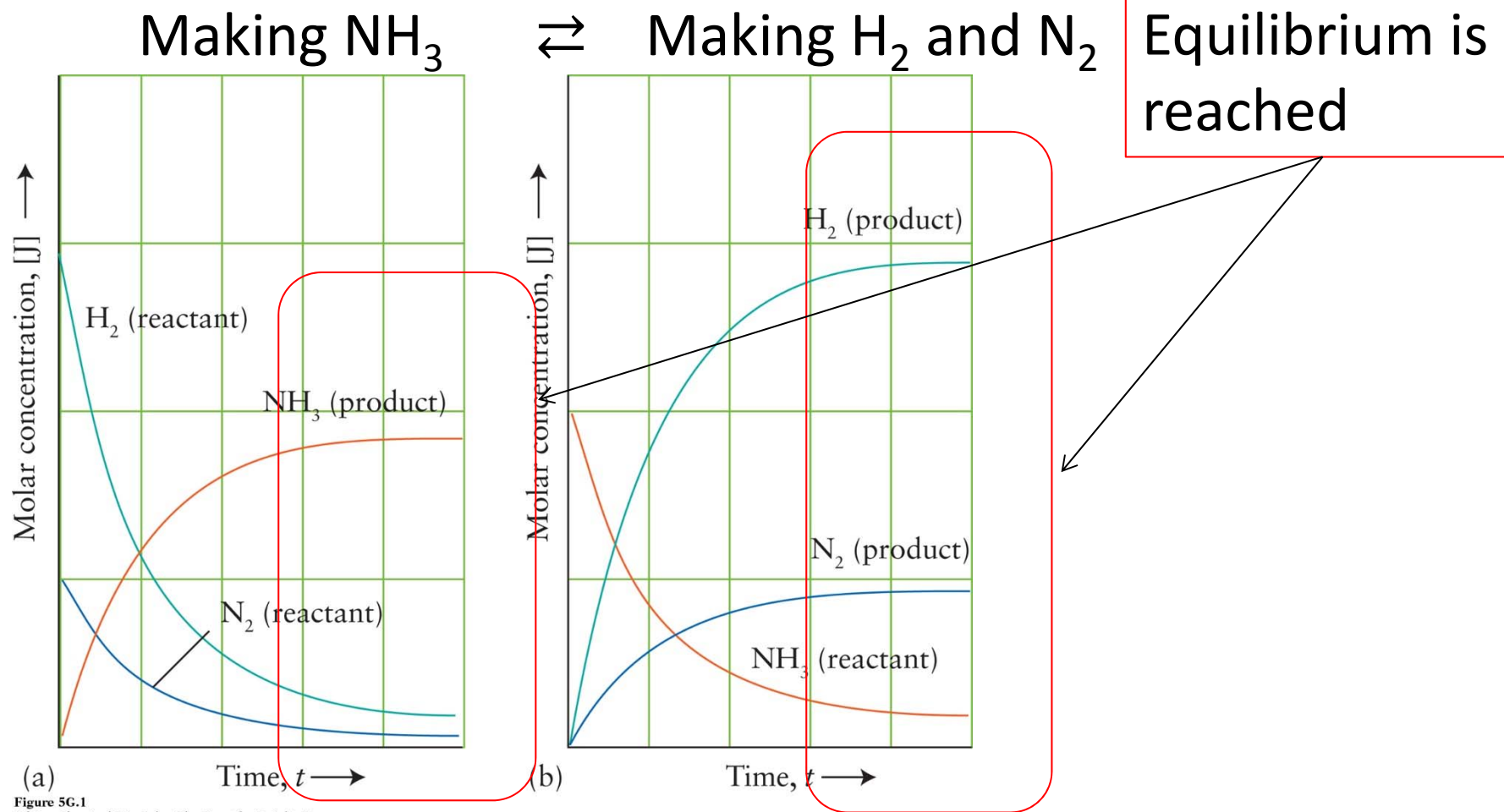Use of a new symbol "$\rightleftharpoons$" means chemical equilibria.

Figure 5G.1
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Note, it's **impossible** to make more product when at equilibrium. The reaction just **appears to have stopped moving**.

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Cato Guldberg (mathematician), and Peter Waage (Chemist), discovered in 1864 the mathematical equilibrium relationship

$$2 SO_2(g) + O_2(g) \rightleftharpoons 2 SO_3(g)$$
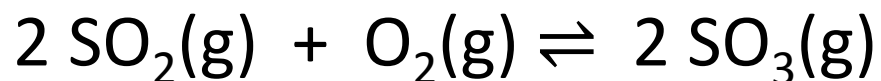
	P_{SO_2} (bar)	P_{O_2} (bar)	P_{SO_3} (bar)	K
Exp 1	0.660	0.390	0.0840	0.0415
Exp 2	0.110	0.0110	0.00750	0.0423
Exp 3	1.44	1.98	0.410	0.0409

Exp 1: $\cong$ = 0.0415

Exp 2: = 0.0423   Exp 3: = 0.0409

Equilibrium and the Law of Mass Action

This is known as the **equilibrium constant** (**K**) and summarizes the law of mass action as:

$$K = \left\{ \frac{partial\ pressure\ of\ \textbf{Products}}{partial\ pressure\ of\ \textbf{Reactants}} \right\}_{equilbrium}$$

In general for a A(g) + b B(g) $\rightleftharpoons$ c C(g) + d D(g)

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

here $\underline{P}$ means partial pressure

Notice (3):

1. Products over reactants.

2. The powers are the stoichiometric coefficients.

3. is "**multiplied**" same for.

Example 5G.1 Write the equilibrium constant for the ammonia synthesis reaction, $3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$.

Using the general form:

$$K = \frac{(products)}{(reactants)}$$

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

We get:

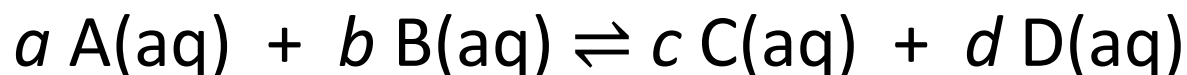$$K = \frac{(P_{NH3})^2}{(P_{H_2})^3 P_{N_2}}$$

P, partial pressure, since the reactants and products are **gases**.

Equilibrium Measurements: Aqueous Solutions

From thermodynamics we know there is a relationship between pressure and concentration of liquids.

Changing from (g) to (aq)

a A(aq) + b B(aq) $\rightleftharpoons$ c C(aq) + d D(aq)

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

Note the change to brackets, [ ], signifying, c, or molarity, mol·L^{-1}

Equilibrium Measurements

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

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

Notice that the P in the K_P stands for equilibrium constant in terms of pressure, and in K_C, the C means concentration in terms of $mol \cdot L^{-1}$.

Also, $K_p \neq K_c$, something we'll look at shortly.

Equilibrium Measurements

It can be shown empirically or thermodynamically that pure **liquids** or **solids** **do not** appear in K.

For example the equilibrium expression for

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

Both $CaCO_3(s)$ and $CaO(s)$ do not appear in the equilibrium expression:

$$K = P_{CO_2}$$

Activity: It is common when deriving equations to simplify expressions without units, so the **empirical form** of partial pressure, P_B or concentration [B], are reported as the activity of partial pressure $a_B = P_B$, or the activity of concentration a_B = [B] (empirical is just a pure number without units).

Summary: Simplified form:

Ideal gas $a_J = P_J$

Solute in a dilute solution a_J = [J]

pure solid or **pure liquid**,   **$a = 1$** (unchanging throughout the reaction) so are not included in an equilibrium expression.

Each reaction has its own characteristic equilibrium constant at its own temperature.

The *extraordinary empirical result* is that, regardless of the initial composition, the *reaction adjusts* so that the activities give **the same characteristic value of *K*** for each reaction at that temperature.

	T(K)	K
$H_2(g) + Cl_2(g) \rightleftharpoons 2\,HCl(g)$	300	4.0×10^{31}
	500	4.0×10^{18}
	1000	5.1×10^{8}
$I_2(g) \rightleftharpoons 2I^-(g)$	800	2.1×10^{-3}
	1000	0.26
	1200	6.8

The Thermodynamic Origin of Equilibrium Constants

The fully derived equations are in your text for $\Delta G_r° = -RT \ln K$.

In Chapter 9, Gibbs free energy tells us the tendency "if," **not** how fast, the reaction reaches equilibrium:

When $\Delta G < 0$, is spontaneous
When $\Delta G > 0$, is nonspontaneous
When $\Delta G = 0$, is at equilibrium

$$\text{Reactants} \quad \overset{-\Delta G}{\underset{+\Delta G}{\rightleftarrows}} \quad \text{Products}$$
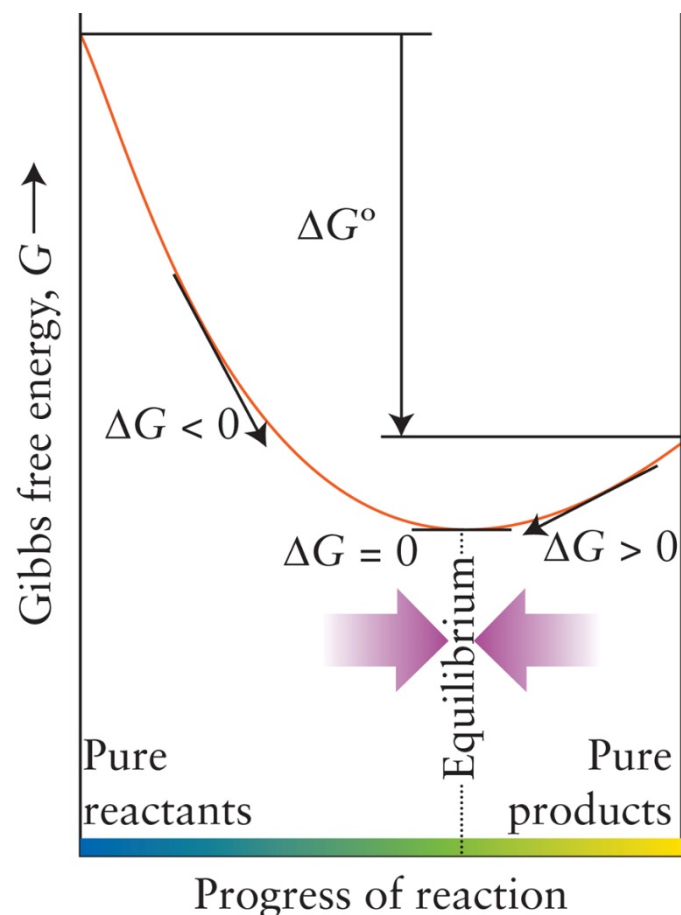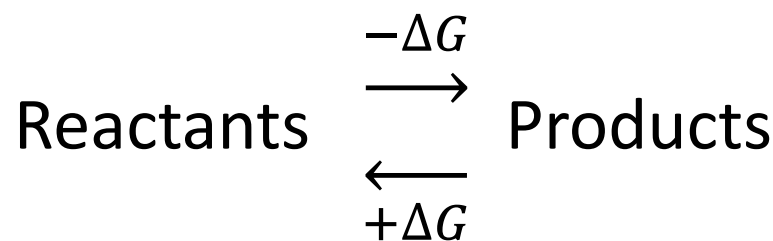

Figure 5G.4
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