Ch.10 Solution

Solution: is a homogeneous mixture of solute distributed through a solvent.

Solute: Gas
Liquid
Solid

Solvent: Gas
Liquid
Solid

∴$3^2 = 9$ 大類 Solution

最重要者：Solvent：liquid 尤其是 H_2O

⇓

Aqueous solution

	真溶液	膠體溶液	懸浮液
d：	＜10Å	$10 \sim 10^4$Å	＞10^4Å

Ch. 10.1. Concentration units: M、m、N、X、mass percent

Ch. 10.2. Principles of solubility 極溶極、非極溶非極

Ch. 10.3. Colligative properties of nonelectrolytes

Colligative properties 依數性質:

Solution properties depend on the concentration of solution particles rather than their nature.

Colligative properties 包括：**沸點上升、凝固點下降、滲透壓、蒸氣壓下降.**

Ch. 10.4. Colligative properties of electrolytes. 1M = nN

§10-1. Concentration units

Molarity (M) 容積莫耳濃度

$$M=\frac{moles\quad solute}{liters\quad solution}$$

配置不同濃度之溶液：

n_{solute}(concentrated solution) = n_{solute}(dilute solution)

$$M_c \cdot V_c = M_d \cdot V_d$$

Ex 10.1: Copper sulfate is widely used as a dietary supplement for animal feed. A lab technician prepares a "stock" solution of $CuSO_4$ by adding 79.80 g of $CuSO_4$ to enough water to make 500.0 mL solution. An experiment requires a 0.1000 M solution of $CuSO_4$.

(a) What is the molarity of the $CuSO_4$ "stock" solution prepared by the technician？

(b) How would you prepare 1.500 L of 0.1000 M solution from the stock solution？

Ans：

$$(a)\quad MM_{CuSO_4} = 63.55 + 32.07 + 16.00 \times 4 = 159.6$$

$$M = \frac{79.80/159.6}{500/1000} = 1.000\ M$$

$$(b)\qquad M_c V_c = M_d V_d$$

$$1.000\ M \times V_c = 0.100\ M \times 1.500\ L$$

$$V_c = 0.1500\ L$$

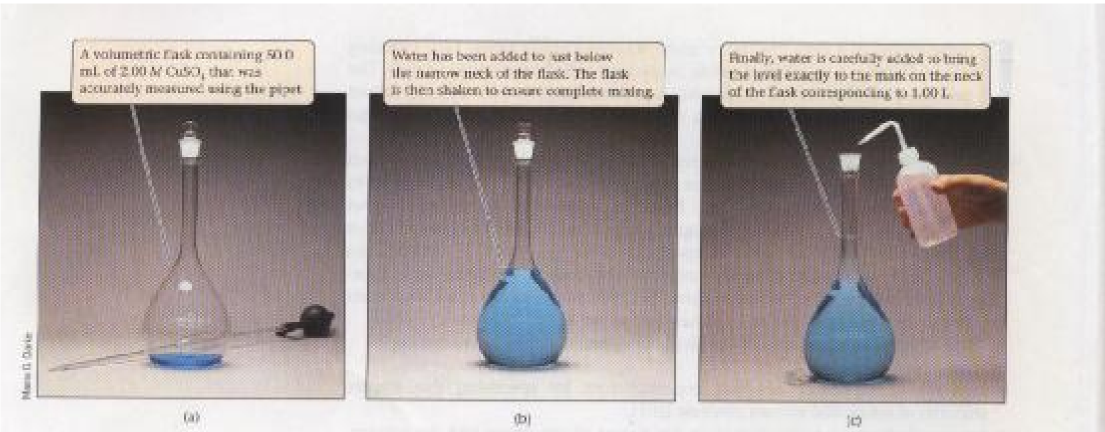


FIGURE 10.1
Preparation of one liter of 0.100 M $CuSO_4$ by dilution.

§ Mole Fraction：X 莫耳分率

$$X_A = \frac{n_A}{n_{tot}}$$

$X_A+X_B+\ldots\ldots=1$

Ex 10.2: Hydrogen peroxide is used by some water treatment systems to remove the disagreeable odor of sulfides in drinking water. It is available commercially in a 20.0% by mass aqueous solution. What is the mole fraction of H_2O_2？

Ans：

Basis: 100.0 g solution

$$n_{H_2O_2} = \frac{20.0}{34.02} = 0.588 \text{ mol}$$

$$n_{H_2O} = \frac{80.0}{18.02} = 4.44 \text{ mol}$$

$$X_{H_2O_2} = \frac{n_{H_2O_2}}{n_{tot}} = \frac{0.588}{0.588 + 4.44} = 0.117$$

§ Mass percent; Parts per Million (ppm); Parts per Billion (ppb)

$$\text{Mass percent of solute (\%)} = \frac{mass \quad of \quad solute}{total \quad mass \quad of \quad solution} \times 100$$

Ex: 24g of NaCl dissolve in 152g of water

$$\text{Mass percent of NaCl (\%)} = \frac{24}{24+152} \times 100$$
$$= 14\%$$

Ppm; ppb: when the amount of solute is very small; as the trace impurities in water.

$$\text{ppm solute} = \frac{wt. \quad of \quad solute}{wt. \quad of \quad solution} \times 10^6$$
$$= \text{Wt \%} \times 10^4$$

Ex: As 含量；USA lower than 5×10^{-8}g per gram of water.

$$\text{ppm As} = \frac{5\times10^{-8}}{1} \times 10^6 = 5\times10^{-2} = 0.05\, ppm$$

ppb As $= \frac{5\times10^{-8}}{1}\times10^{9} = 50\,ppb$

§ Molality (m) 重量莫耳濃度

Number of moles of solute per kilogram (1000g) of solvent.

Molality (m) = $\frac{moles \quad solute}{kilograms \quad solvent}$

Ex 10-3: Glucose, $C_6H_{12}O_6$, in water is often used for intravenous (靜脈注射) feeding. Sometimes sodium ions are added to the solution. A pharmacist prepares a solution by adding 2.0 mg of sodium ions (in the form of NaCl), 6.00 g of glucose, and 112 g of water.

(a) What is the molality of the glucose in solution？

(b) How many ppm of Na^+ does the solution contain？

Ans:

$$(a) \quad MM_{C_6H_{12}O_6} = 12.01 \times 6 + 1.008 \times 12 + 16.00 \times 6 = 180.16 \text{ g/mol}$$

$$m_{C_6H_{12}O_6} = \frac{moles \text{ solute}}{kilograms solvent} = \frac{6.00/180.16}{112/1000} = 0.297 \text{ m}$$

$$(b) \quad \text{ppm } Na^+ = \frac{wt. \text{ of solute}}{wt. \text{ of solution}} = \frac{2.0 \times 10^{-3} \text{ g}}{2.0\times10^{-3} + 6.00 + 112} \times 10^{6} = 17 \text{ ppm}$$

§ Normality 當量濃度 N

$$N = \frac{溶質重量 / 溶質之當量}{溶質L數} \qquad 1M = nN$$

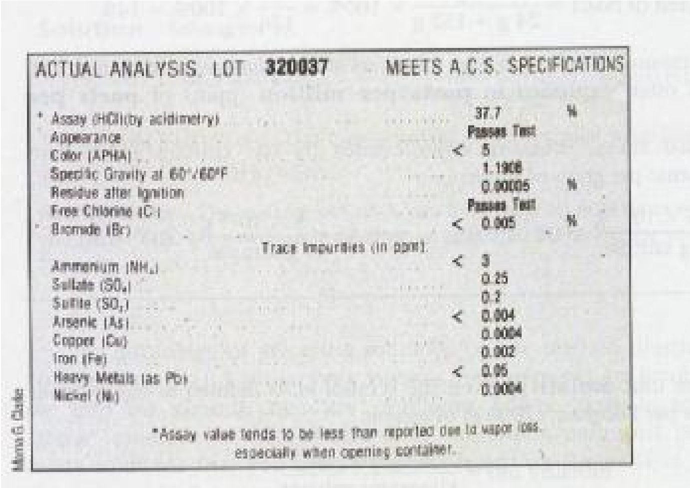
用途：1.氧化-還原作用

2.酸鹼中和

§ Conversions between concentration units

When the original concentration is	start with
Mass percent	100g solution
Molarity (M)	1.00L solution
Molality (m)	1000g solvent
Mole fraction(X)	1 mole (solution+solvent)

Ex 10-4: Using the information in Fig10.2, calculate



ACTUAL ANALYSIS LOT **320037** MEETS A.C.S. SPECIFICATIONS

* Assay (HCl)(by acidimetry)		37.7	%
Appearance		Passes Test	
Color (APHA)	<	5	
Specific Gravity at 60°/60°F		1.1906	
Residue after Ignition		0.00005	%
Free Chlorine (Cl)		Passes Test	
Bromide (Br)	<	0.005	%
Trace Impurities (in ppm):			
Ammonium (NH_4)	<	3	
Sulfate (SO_4)		0.25	
Sulfite (SO_3)		0.2	
Arsenic (As)	<	0.004	
Copper (Cu)		0.0004	
Iron (Fe)		0.002	
Heavy Metals (as Pb)	<	0.05	
Nickel (Ni)		0.0004	

*Assay value tends to be less than reported due to vapor loss, especially when opening container.

Marna G. Clarke

a) the mass percent of HCl and water in concentrated HCl
b) the molality of HCl (m)
c) the molarity of HCl (M)

Ans：

a) The mass percent of HCl = 37.7%
   Water = 100-37.7 = 62.3%

b) Basis：100.0g solution

$$m_{HCl} = 100 \times 37.7\,\% = 37.7\text{g}$$

$$n_{HCl} = \frac{37.7}{1.01+35.45} = \frac{37.7}{36.46} = 1.03\,mol$$

$$m = \frac{moles\ \ solute}{kilograms\ \ solvent} = \frac{1.03}{62.3/1000} = 16.5\,m$$

c) sp. gr. = 1.1906

$$\text{volume of 100.0g } HCl_{(aq)} = \frac{100}{1.1906} = 84.0\,mL$$

$$M = \frac{moles\ \ solute}{liter\ \ solvent} = \frac{1.03}{84.0/1000} = 12.3\text{M}$$

§10-2 Principles of solubility

Solubility 影響因素

- The nature of solvent and solute particles and the interaction between them.
- T
- P of gaseous solute.

Solute-solvent interaction:

"like dissolves like" 極溶極 非極溶非極

C_5H_{12} pentane(非極性) 與 hexane C_6H_{14}(非極性) → 互溶

C_5H_{12} 與 H_2O → 不互溶

TABLE 10.1 Solubilities of Alcohols in Water

Substance	Formula	Solubility (g solute/L H_2O)
Methyl alcohol	CH_3OH	Completely soluble
Ethyl alcohol	CH_3CH_2OH	Completely soluble
Propanol	$CH_3CH_2CH_2OH$	Completely soluble
Butanol	$CH_3CH_2CH_2CH_2OH$	74
Pentanol	$CH_3CH_2CH_2CH_2CH_2OH$	27
Hexanol	$CH_3CH_2CH_2CH_2CH_2CH_2OH$	6.0
Heptanol	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2OH$	1.7

Vitamin B、C(極性) → 水溶性

Vitamin A、D、E、K(非極性) → 脂溶性

離子固體在水中之溶解度 (Fig4.3) K_{sp}計算值＞K_{sp}理論值, 會生成沉澱.

沉澱之影響因素:

1. 水與離子間之吸引力＞離子離子間吸引力

   ⇓

   完全溶解 例：NaCl、NaOH

2. 水與離子間之吸引力＜離子離子間吸引力

   ⇓

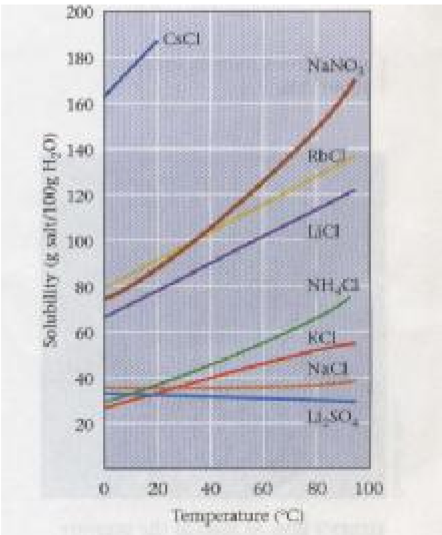
   沉澱 例：$CaCO_3$、$CaSO_4$

§ Effect of Temperature on Solubility

溶質：固體及液體 ⇒ 吸熱反應 T↑ Solubility↑

放熱反應 T↑ Solubility↓

氣體 ⇒ T↑ Solubility↓ ∵$\Delta H < 0$

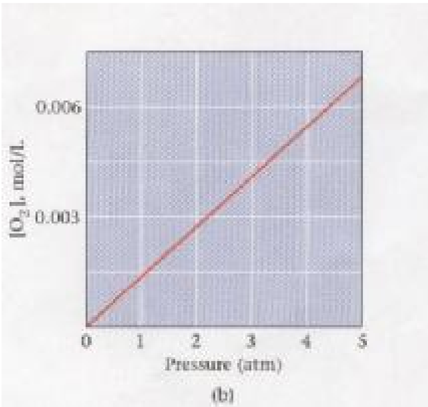


§ Effect of Pressure on Solubility

溶質：固體 ⇒ P 之影響少

液體 ⇒ P 之影響少

氣體 → P↑→ Solubility↑



Henry's law：

$C_g = k \cdot Pg$

C_g : gas 之 concentration

k : proportional constant

Pg : the partial pressure of the gas over the solution.

At low to moderate P，gas solubility is directly proportional to P.

Ex 10-5: The solubility of pure nitrogen in blood at body temperature, 37℃, and one atmosphere is 6.2×10^{-4}M. If a diver breathes air ($X_{N_2} = 0.78$) at a depth where the total pressure is 2.50atm, calculate the concentrating of nitrogen in his blood.

Ans：

$C_g = k \cdot P_g$

$k = \dfrac{C_g}{P_g} = \dfrac{6.2\times10^{-4}}{1.00} = 6.2\times10^{-4}\ M/atm$

$P_{N2} = X_{N2} \cdot P_{tot} = 0.78 \cdot 2.50 = 2.0$ atm

$[N_2] = C_{N2} = k \cdot P_g$
$=6.2\times10^{-4} \times 2.0$
$=1.2\times10^{-3}$ M

另解：$6.2\times10^{-4} : 1.00 = x : 2.0$
$x = 1.2\times10^{-3}$ M

"Bends" 水夫病

一人自深海(高壓)快速游上海平面(低壓)，造成氣體之溶解度降低，使氣體由 blood 及其他 body fluids 以 bubble 析出，損及血液循環系統及神經系統.

⇒潛水夫以 He-O_2 取代 N_2-O_2，∵He 之溶解度僅為 N_2 之 1/3∴減壓時較少氣體析出.

§10-3 Colligative properties of nonelectrolytes

Colligative properties(依數性質)：

Solution properties depend primary on the concentration of solute particles rather than their nature.

依數性質包含：vapor pressure lowering 蒸氣壓下降
osmotic pressure 滲透壓
boiling point elevation 沸點上升
freezing point depression 凝固點下降

For nonelectrolytes：

低濃度(＜1M) deviations 小於 few percent
高濃度 deviations 則較大

§ Vapor pressure lowering

The vapor pressure of water over the solution is less than that of pure water.

$P_1 = X_1 P_1^\circ$

P_1：vapor pressure of solvent over the solution
P_1°：at same T，vapor pressure of pure solvent
X_1：mole fraction of solvent

$\Delta P = (1- X_1)\ P_1°$ ΔP：vapor lowering

$= X_2\ P_1°$ X_2：mole fraction of solute

Ex10-6: A solution contains 82.0 g of glucose, $C_6H_{12}O_6$ (MM=180.16g/mol), in 322 g of water. Calculate the vapor pressure lowering at 25℃(vapor pressure of pure water, $P°_{H2O}$ = 23.76 mmHg)

Ans：

$$\Delta P = X_2 P_1°$$

$$n_{C_6H_{12}O_6} = \frac{82.0}{180.16} = 0.455 mol$$

$$n_{H_2O} = \frac{322}{18.02} = 17.9 mol$$

$$X_{C_6H_{12}O_6} = \frac{0.455}{17.9 + 0.455} = 0.0248$$

$$\Delta P = X_{C_6H_{12}O_6} P^0{}_{H_2O}$$

$= 0.0248 \times 23.76$

$= 0.589$ mmHg

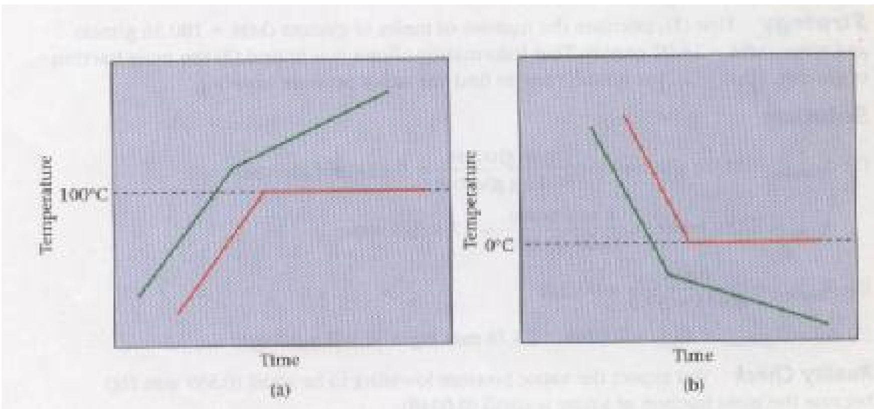
§ Boiling Point Elevation and Freezing Point Lowering

$\Delta T_b = T_b - T_b°$ $\Delta T_b = k_b \cdot m$ 沸點上升

水 k_b=0.52℃/m

$\Delta T_f = T_f° - T_f$ $\Delta T_f = k_f \cdot m$ 凝固點下降

如此 k_f 爲”+”值 水 k_f=1.86℃/m



Ex10-7: An anti freeze solution (抗凍劑) is prepared containing 50.0 cm^3 of ethylene glycol, $C_2H_6O_2$ (MM = 62.07 g/mol, d = 1.12 g/mL), in 50.0g of water. Calculate the freezing point of this 50-50 volume ratio mixture.

Ans：

$m_{C_2H_6O_2}$ = 50.0 × 1.12 = 56.0g

$$n_{C_2H_6O_2} = \frac{56.0}{62.07} = 0.902mol$$

$$m = \frac{\text{質 mol數}}{\text{劑 kg數}} = \frac{0.902}{50.0/1000} = 18.0m$$

$\Delta T_f = k_f \cdot m$

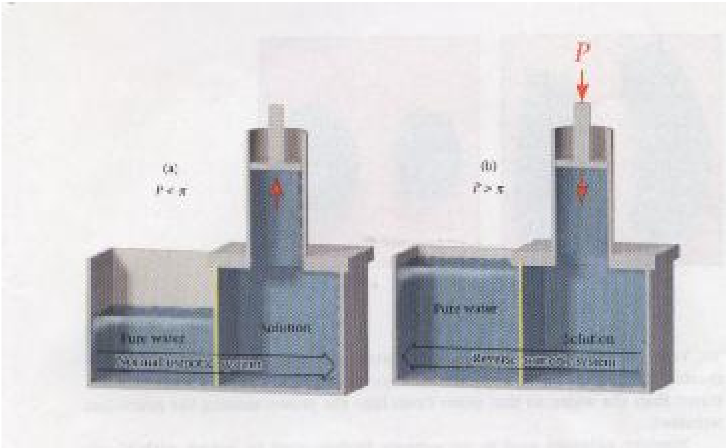
$= 1.86 \cdot 18.0 = 33.5℃$

$T_f = T°_f - \Delta T_f$

$= 0- 33.5$

$= -33.5℃$

§Osmotic Pressure 滲透壓



滲透壓：濃度低的向濃度高的滲透

$$p = \frac{nRT}{V} = M \times RT$$

Ex: 0.10M solution at 25℃下之 Osmotic Pressure

$\pi = M \cdot R \cdot T$

$= 0.10 \cdot 0.0821 \cdot (25+273) = 2.4$ atm

Ex 10-8: Calculate the osmotic pressure at 15℃ of a solution prepared by dissolving 50.0g of sugar, $C_{12}H_{22}O_{11}$, in enough water to form one liter of solution

Ans：

MM=12.01×12+1.008×22+16.00×11=342.3 g/mol

$$n = \frac{50.0}{342.3} = 0.146mol$$

$$M = \frac{\text{質莫耳數}}{\text{液L數}} = \frac{0.146}{1} = 0.146\text{M}$$

$\pi = M \cdot R \cdot T$

$= 0.146 \cdot 0.0821 \cdot (15+273)$

$= 3.45$ atm

§ Determination of Molar Masses from Colligative Properties

Ex10-9: A laboratory experiment on colligative properties directs students to determine the molar mass of an unknown solid. Each student receives 1.00 g of solute, 225 mL of solvent and information that may be pertinent to the unknown.

(a) Student A determines the freezing point of her solution to be 6.18℃. She is told that her solvent is cyclohexane, which has density 0.779 g/mL, freezing point 6.50℃ and k_f = 20.2℃/m.

(b) Student B determines the osmotic pressure of his solution to be 0.846 atm at 25℃. He is told that his solvent is water (d= 1.00 b/mL) and that the density of the solution is also 1.00 g/mL.

Ans：

$$(a)\quad \Delta T_f = T_f^0 - T_f = 6.50 - 6.18 = 0.32°C$$

$$\Delta T_f = m \times k_f$$

$$m = \frac{\Delta T_f}{k_f} = \frac{0.32}{20.2} = 0.016\ m = \frac{moles\ \text{solute}}{kg\ \text{solvent}}$$

$$m_{solvent} = 225\ \text{mL} \times \frac{0.779\ \text{g}}{mL} = 175\ \text{g} = 0.175\ \text{kg}$$

$$n_{solute} = m \times \text{kg solvent} = 0.016 \times 0.175 = 2.8 \times 10^{-3}\ \text{mol}$$

$$MM_{solute} = \frac{1.00}{2.8 \times 10^{-3}} = 357 = 3.6 \times 10^2\ \text{g/mol}$$

$$(b)\quad p = MRT$$

$$M = \frac{p}{RT} = \frac{0.846}{0.0821 \times 298} = 0.0346\ \text{mol/L} = \frac{moles\ \text{solute}}{L\ \text{solution}}$$

$$m_{solution} = 1 + 225 = 226\ \text{g}$$

$$V_{solution} = \frac{226\ \text{g}}{1.00\ \text{g/mL}} = 226\ \text{mL} = 0.226\ \text{L}$$

$$n_{solute} = M_{solute} \times V_{solution} = 0.0346 \times 0.226 = 7.82 \times 10^{-3}\ \text{mol}$$

$$MM = \frac{m}{n} = \frac{1.00}{7.82 \times 10^{-3}} = 128\ \text{g/mol}$$

Osmotic Pressure 測得之數值較大；較 ΔT_b、ΔT_f 易得準確之結果

↓

Q值一般太小

例：0.0010M 水溶液；π = 0.024atm = 18mmHg

$\Delta T_f = 1.86\times10^{-3}$℃

$\Delta T_b = 5.2\times10^{-4}$℃

§ Colligative Properties of electrolytes

An electrolyte should have a greater effect on Colligative Properties than those of a nonelectrolytes.

One mole glucose dissolves in water，one mole of solute molecules is obtained.
One mole NaCl dissolves in water，two mole of solute ions is obtained.
One mole $CaCl_2$ dissolves in water，three mole of solute ions is obtained.

1.0M solution of glucose，NaCl and $CaCl_2$ at 25℃

	Glucose	NaCl	$CaCl_2$
ΔP	0.42mmHg	0.77mmHg	1.3mmHg

$\Delta T_f = i \times k_f \cdot m$

$\Delta T_b = i \times k_b \cdot m$

$\pi = i \times M \cdot RT$

i：the number of moles of ions formed per mole of electrolyte

Ex10-10: Estimate the freezing points of 0.20m water solutions of
a). KNO_3 b). $Cr(NO_3)_3$

Ans：

a) $KNO_{3(s)} \xrightarrow{H_2O} K^+{}_{(eq)} + NO_3^-{}_{(eq)}$

i = 2

$\Delta T_f = 2 \times k_f \cdot m$

$= 2 \cdot 1.86 \cdot 0.20 = 0.74$

$T_f = T_f^\circ - \Delta T_f = 0 - 0.74 = -0.74$℃

b) $Cr(NO_3)_3 \xrightarrow{H_2O} Cr^{3+}{}_{(eq)} + 3NO_3^-{}_{(eq)}$

i = 4

$\Delta T_f = 4 \times k_f \cdot m$

$= 4 \cdot 1.86 \cdot 0.20 = 1.5$℃

$T_f = -1.5$℃

TABLE 10.3 Freezing Point Lowerings of Solutions				
	ΔT_f Observed (°C)		i (Calc from ΔT_f)	
Molality	NaCl	$MgSO_4$	NaCl	$MgSO_4$
0.00500	0.0182	0.0160	1.96	1.72
0.0100	0.0360	0.0285	1.94	1.53
0.0200	0.0714	0.0534	1.92	1.44
0.0500	0.176	0.121	1.89	1.30
0.100	0.348	0.225	1.87	1.21
0.200	0.685	0.418	1.84	1.12
0.500	1.68	0.995	1.81	1.07

i 值只有在稀薄溶液中，其值接近於理論值

m↑→ i↓

其理由爲：

1. 靜電吸引力，濃度高時離子完全分離之效果較差
2. 正、負離子生成離子對而非獨立之陽離子、陰離子

Ex10-11: The freezing point of a 0.5m solution of oxalic acid, $H_2C_2O_4$, in water is -1.12℃. Which of the following equations best represents what happen when oxalic acid dissolves in water？

a) $H_2C_2O_{4(s)} \rightarrow H_2C_2O_{4(eq)}$ i = 1

b) $H_2C_2O_{4(s)} \rightarrow H^+_{(eq)} + HC_2O_4^-{}_{(eq)}$ i = 2

c) $H_2C_2O_{4(s)} \rightarrow 2H^+_{(eq)} + C_2O_4^{2-}{}_{(eq)}$ i = 3

Ans：

$\Delta T_f = T_f° - T_f$

$= 0-(-1.12) = 1.12$℃

$\Delta T_f = i \times k_f \cdot m$

$1.12 = i \cdot 1.86 \cdot 0.5$

i = 1.2 →較接近 1 ∴ a.

i 值與解離度成正比.