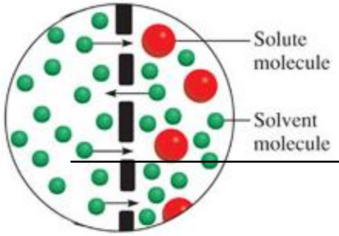
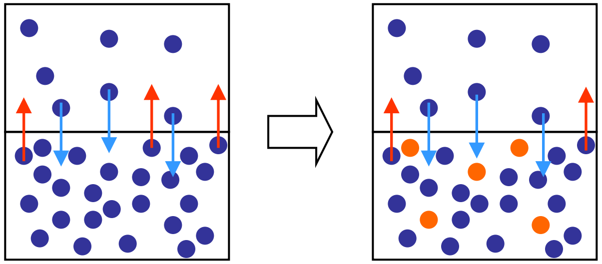
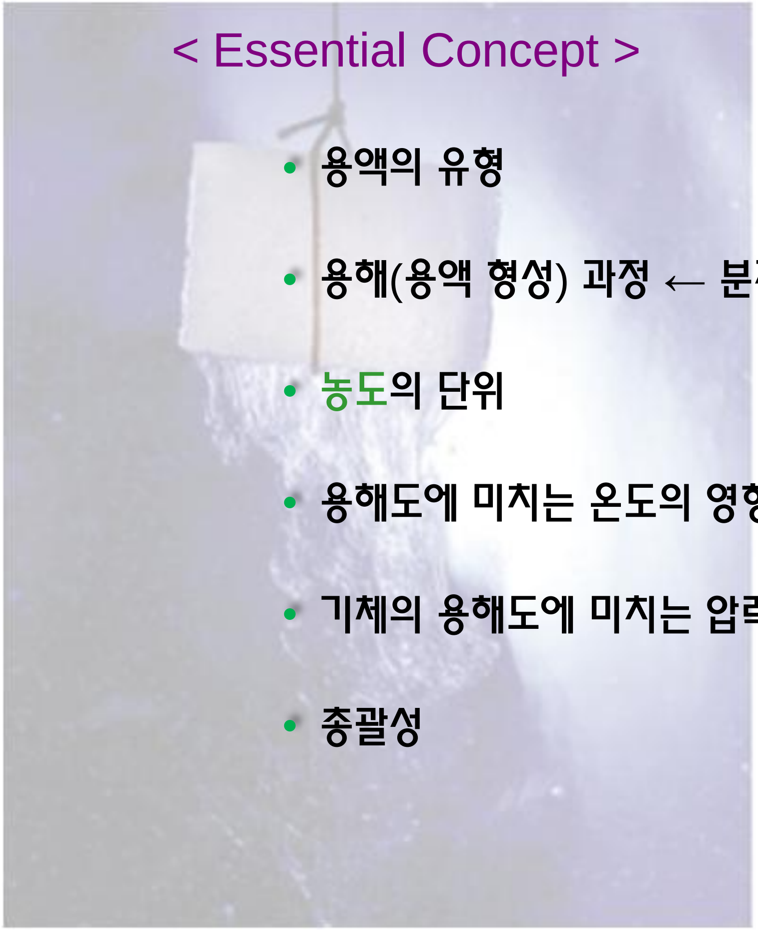


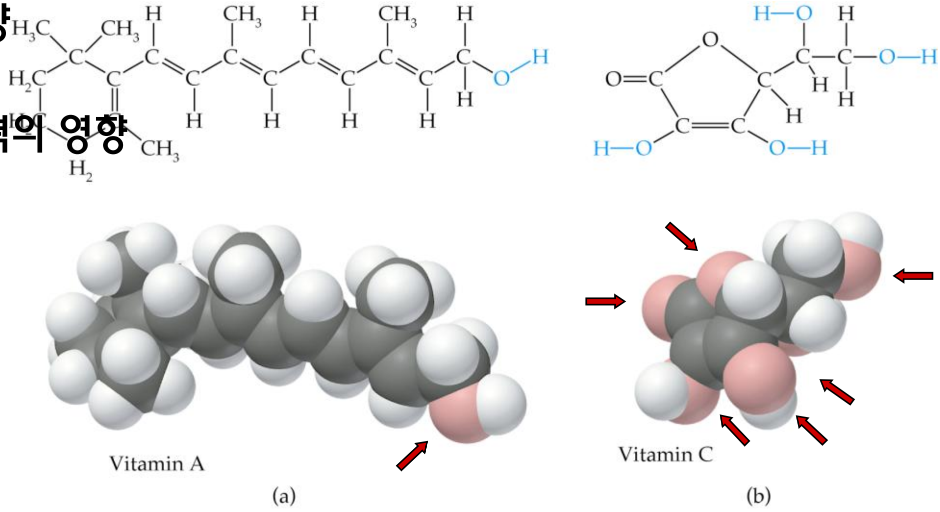
13. 용액의 물리적 성질





< Essential Concept >

- 용액의 유형
- 용해(용액 형성) 과정 ← 분자수준에서
- 농도의 단위
- 용해도에 미치는 온도의 영향
- 기체의 용해도에 미치는 압력의 영향
- 총괄성



■ 용액의 유형

↕

(균일혼합물)

(용매+용질)

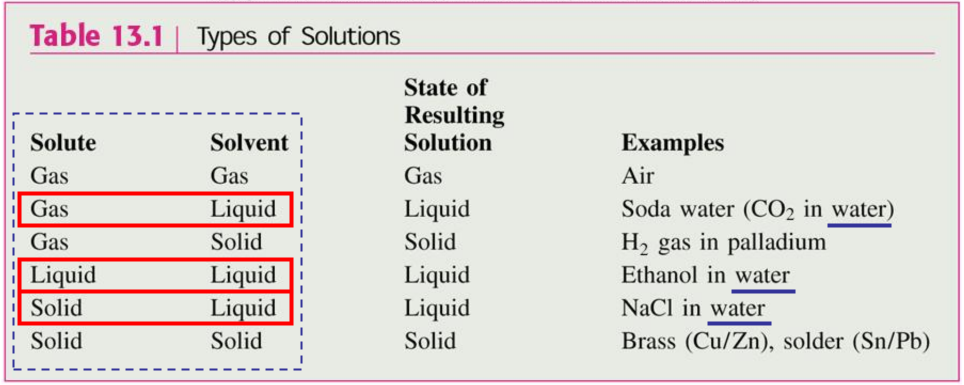


Table 13.1 | Types of Solutions

Solute	Solvent	State of Resulting Solution	Examples
Gas	Gas	Gas	Air
Gas	Liquid	Liquid	Soda water (CO_2 in water)
Gas	Solid	Solid	H_2 gas in palladium
Liquid	Liquid	Liquid	Ethanol in water
Solid	Liquid	Liquid	NaCl in water
Solid	Solid	Solid	Brass (Cu/Zn), solder (Sn/Pb)

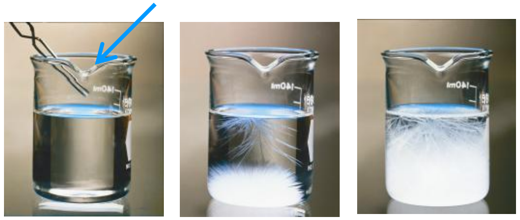
불포화 용액

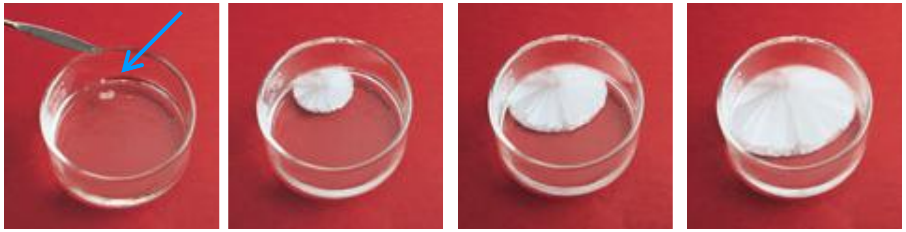
포화 용액

과포화 용액

침전 (precipitation)

결정화 (crystalization)





과포화된 아세트산나트륨 용액의 결정화

- 용해도 (solubility) → 일정한 양의 용매를 포화용액이 되게 하는데 필요한 용질의 양

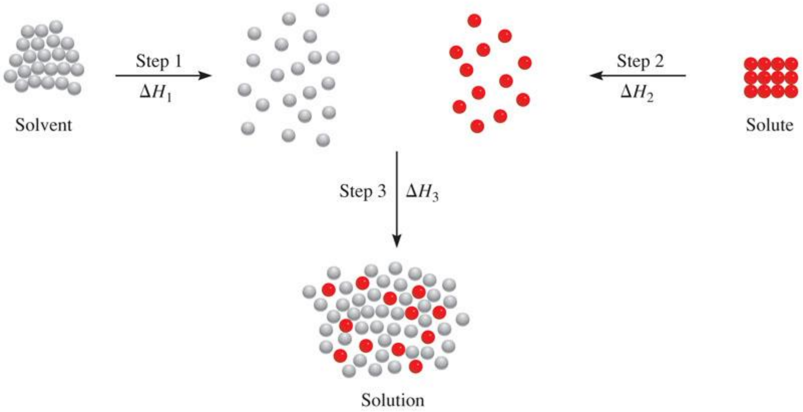
(예) 0℃, 물 100 mL당 NaCl 35.7 g

용해도 크다 ↔ 잘 녹는다 ↔ 잘 섞인다

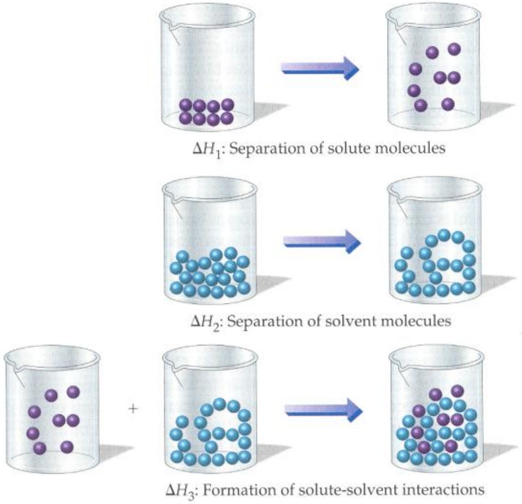
■ 용해 (용액 생성) 과정 ← 분자수준에서의 고찰

↑

분자간 힘 (용매-용매, 용질-용질, 용매-용질)



일반적으로 …



ΔH_1: Separation of solute molecules

ΔH_2: Separation of solvent molecules

ΔH_3: Formation of solute-solvent interactions

$\Delta H_1 > 0$

$\Delta H_2 > 0$

$\Delta H_3 < 0$

$$\Delta H_{\text{soln}} = \Delta H_1 + \Delta H_2 + \Delta H_3 < 0 \ \ ?$$

$\Delta H_{\text{soln}} < 0$ ⟷ **용액 형성 여부**

(섞임/녹음)

(예) $MgSO_4$ … $\Delta H_{\text{soln}} = -91.2\ \text{kJ/mol} < 0$ ∴ 발열

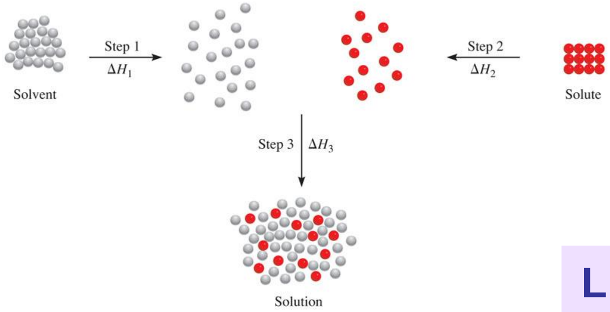
NH_4NO_3 … $\Delta H_{\text{soln}} = +26.4\ \text{kJ/mol} > 0$ ∴ 흡열

$CCl_4 + C_6H_{14}$ … $\Delta H_{\text{soln}} \approx 0$

무극성 (b.p. 77℃) 무극성 (b.p. 69℃)

- **자발적인 현상** ← ① 에너지 (energy) ② 무질서도 (entropy)

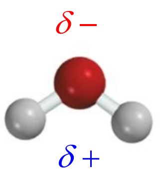
$\Delta H < 0$ $\Delta S > 0$



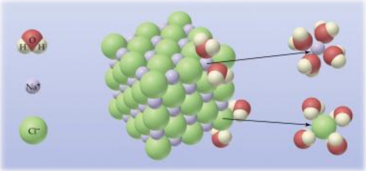
용해 ←← "무질서도" $\Delta S_{soln} > 0$

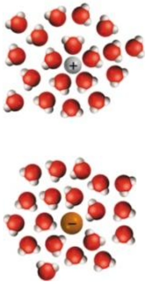
Like dissolves like.

극성 용질 + 극성 용매 → 용액
비극성 용질 + 비극성 용매 → 용액



H_2O



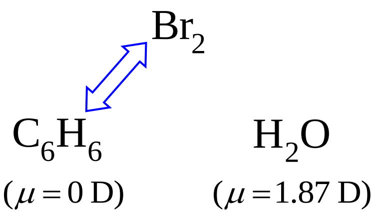


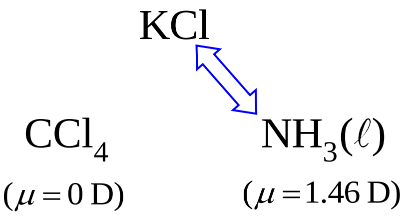
"aq"

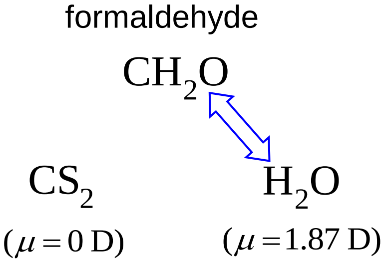
용매화(수화) ←-----→

CCl_4 / C_6H_6
C_2H_5OH / H_2O
$NaCl/H_2O$

[Ex 13.1] **상대적 용해도** (relative solubility, miscibility)



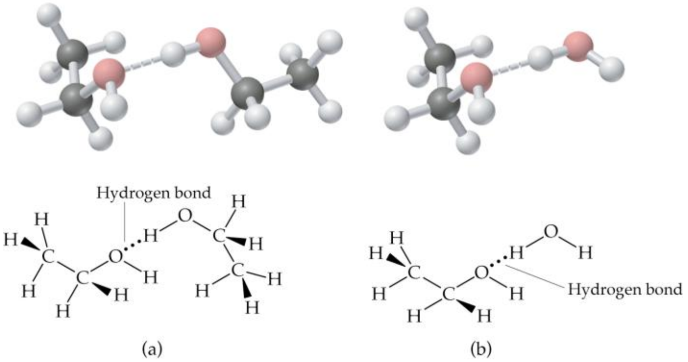




- 알코올 … C-O-H → 극성, 수소결합 가능

  탄소수↑ ⇒ 용해도 ↓

  O-H 결합수↑ ⇒ 용해도↑



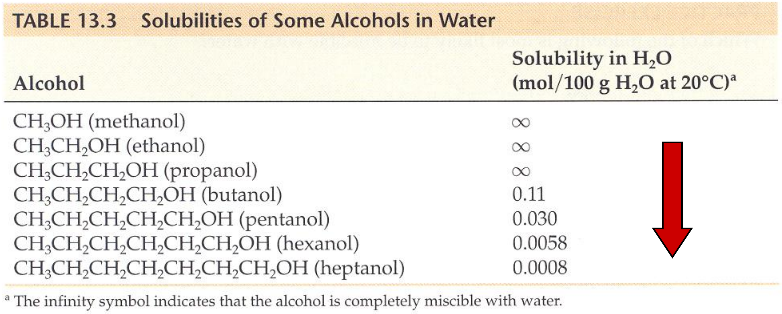
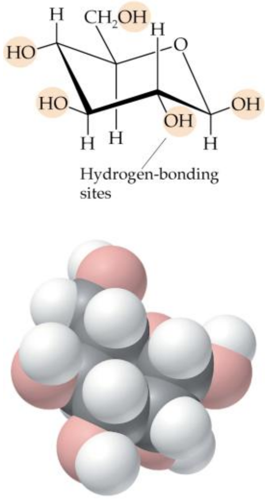


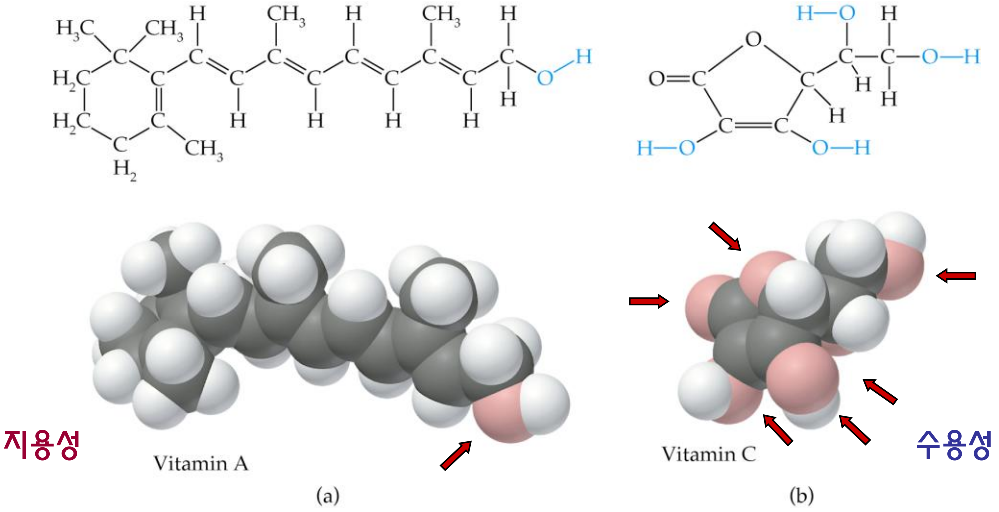
TABLE 13.3 Solubilities of Some Alcohols in Water

Alcohol	Solubility in H_2O (mol/100 g H_2O at 20°C)[a]
CH_3OH (methanol)	∞
CH_3CH_2OH (ethanol)	∞
$CH_3CH_2CH_2OH$ (propanol)	∞
$CH_3CH_2CH_2CH_2OH$ (butanol)	0.11
$CH_3CH_2CH_2CH_2CH_2OH$ (pentanol)	0.030
$CH_3CH_2CH_2CH_2CH_2CH_2OH$ (hexanol)	0.0058
$CH_3CH_2CH_2CH_2CH_2CH_2CH_2OH$ (heptanol)	0.0008

[a] The infinity symbol indicates that the alcohol is completely miscible with water.

(예) 글루코오스 (glucose, $C_6H_{12}O_6$) … 5 O-H → 83g/100mL H2O





지용성

수용성

농도(concentration)의 단위

① **질량백분율**(%), ppm, ppb

$$\% \Rightarrow \frac{\text{(성분)용질의 질량}}{\text{용액의 총질량}} \times 100$$

(예) 36g HCl / 100g 용액 → 36% HCl 용액

$$\text{ppm} \Rightarrow \frac{\text{(성분)용질의 질량}}{\text{용액의 총질량}} \times 10^{6}$$

(예) 1mg 용질 / 1kg 용액

1mg 용질 / 수용액 1L → 1 ppm

② **몰농도**(M)

$$\text{M} \Rightarrow \frac{\text{용질의 몰수}}{\text{용액의 부피 (L)}}$$

③ **몰랄농도**(m)

$$\text{m} \Rightarrow \frac{\text{용질의 몰수}}{\text{용매의 질량 (kg)}}$$

[Ex 13.2] 황산 24.4g / 물 198g (황산: 98.08 g/mol)

$$\frac{24.4\,\text{g}}{98.08\,\text{g}/\text{mol}} = 0.249\,\text{mol}$$

$$\text{몰랄농도(molality)} = \frac{0.249\,\text{mol H}_2\text{SO}_4}{0.198\,\text{kg H}_2\text{O}} = 1.26\,m$$

몰농도: 용액의 부피 → 용질의 몰수

질량백분율: 온도에 무관, 몰질량에 무관

몰랄농도: 온도에 무관, 용액 제조시 편리

1.0 M (25℃) ⟶ 0.97 M (45℃)

$$\text{몰농도} \xleftrightarrow{\text{용액의 밀도}} \text{몰랄농도}$$

[Ex 13.3] 2.45 *M* (몰농도) 메탄올 수용액: 밀도 = 0.976 g/mL, (메탄올 몰질량: 32.04 g/mol)

용액 1L의 질량 = 976 g

용액 1L에 들어있는 메탄올의 질량 = $2.45\,\text{mol} \times 32.04\,\text{g/mol} = 78\,\text{g}$

용액 1L에 들어있는 물(용매)의 질량 = $976\,\text{g} - 78\,\text{g} = 898\,\text{g}$

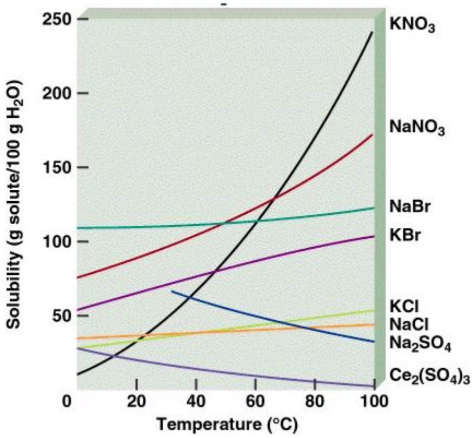
용액의 몰랄농도 = $\dfrac{2.45\,\text{mol}}{0.898\,\text{kg}} = 2.73\,m$

■ 용해도 ⟷ 온도

(예) NaCl: 35.7 g / 100mL water, 0℃

(특정 온도에서 주어진 양의 용매에 녹을 수 있는 용질의 최대 양)

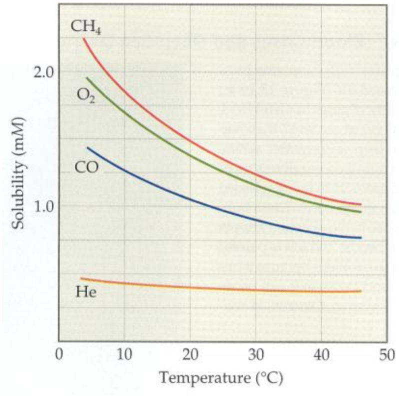
- 고체



온도↑ ⇒ 용해도↑

물에 대한 설탕의 용해도 → 캔디 제조시

- 기체

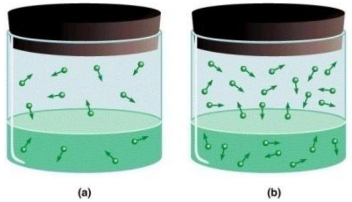


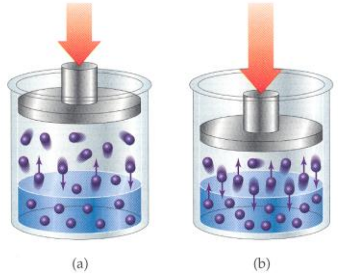
온도↑ ⇒ 용해도↓

탄산음료: T↑ ⇒ CO_2(g)↑ (cold tap water in a glass)

강, 호수: T↑ ⇒ O_2(g)↑ (thermal pollution)

■ 기체 용해도 ↔ 압력





헨리의 법칙 p↑ ⇨ 기체의 용해도 ↑

Henry

$$c_g = k\,P_g$$

기체의 용해도(mol/L ≡ M)

용액에 작용하는
기체의 (부분)압력

Henry 법칙 상수 ← (용매, 용질), 온도

(예) N_2 / water, 0℃, 1 atm: $c_{N_2(g)} = 6.8\times10^{-4}$ mol/L

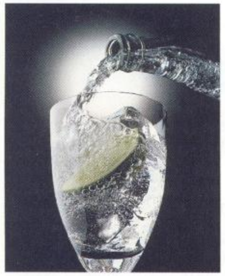
$$k = \frac{c_{N_2(g)}}{P_{N_2(g)}} = \frac{6.8\times10^{-4}\,\text{mol/L}}{1\ \text{atm}} = 6.8\times10^{-4}\,\text{mol/L}\cdot\text{atm}$$

대기압 하에서 질소의 (부분)압력은 0.78 atm

$$c = k\,P_{N_2(g)} = (6.8\times10^{-4}\,\text{mol/L}\cdot\text{atm})(0.78\,\text{atm})$$

$$= 5.3\times10^{-4}\,\text{mol/L} = 5.3\times10^{-4}\,M$$

탄산음료 (carbonated beverages) --------▸



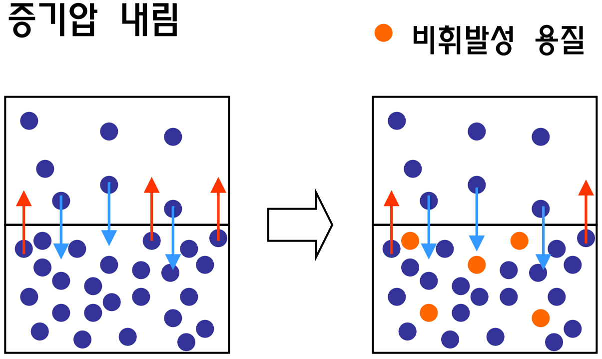
총괄성*** (Colligative properties) ◀-------- 증기압 내림 (끓는점 오름, 어는점 내림), 삼투압

← 순수한 용매와 용액의 물리적 성질의 차이

← 용질의 종류에 관계 없이 농도(용질의 입자수)에만 의존 (< 0.2M)

← (예) 부동액 (물 + 에틸렌글리콜) ⇒ T_f↓, T_b↑

① 증기압 내림

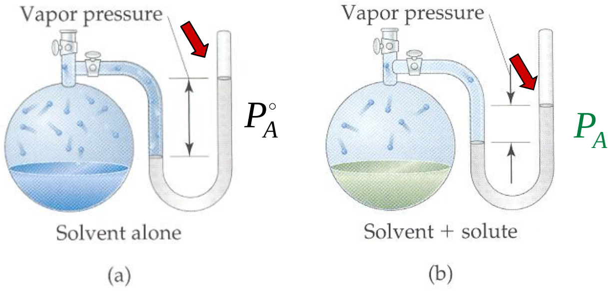


순수한 용매　　　용액

증발 속도 ↓

⇩

증기압 ↓



$P_A^\circ > P_A$

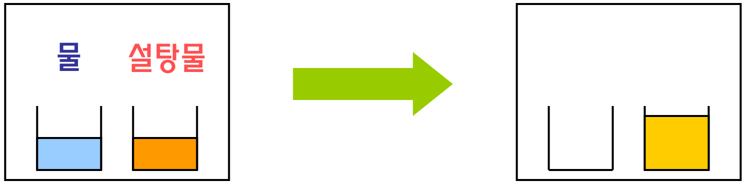
(순수한) 용매의 증기압 > 용액의 증기압

- **라울의 법칙** Raoult　$P_A = x_A P_A^\circ$

↑ 용매의 몰분율

(예) H_2O … 20℃, $P^\circ_{H_2O} = 17.5\,\text{torr}$

$$x_{H_2O} = 0.80,\quad x_{\text{glucose}} = 0.20 \longrightarrow p_{H_2O} = 0.80 \times 17.5 = 14\,\text{torr}$$



- A(용매), B(용질)

↑

"비휘발성"

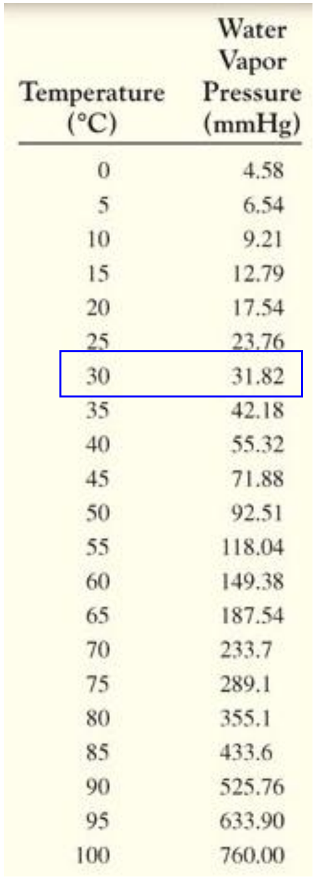
$$P_A = x_A P_A^{\circ} \Longrightarrow P_A = (1 - x_B) P_A^{\circ}$$

$$P_A^{\circ} - P_A \equiv \Delta P = x_B P_A^{\circ}$$

증기압 내림

용질(용액)의 농도

(몰분율 ∝ 몰랄농도)



Temperature (°C)	Water Vapor Pressure (mmHg)
0	4.58
5	6.54
10	9.21
15	12.79
20	17.54
25	23.76
30	31.82
35	42.18
40	55.32
45	71.88
50	92.51
55	118.04
60	149.38
65	187.54
70	233.7
75	289.1
80	355.1
85	433.6
90	525.76
95	633.90
100	760.00

[Ex 13.6] 218 g glucose (m.w. 180.2 g/mol) / 460 mL water at 30℃

$$P_A,\ \Delta P = ?$$

218 g glucose: $\dfrac{218\,\text{g}}{180.2\,\text{g/mol}} = 1.21\,\text{mol}$

460 mL water: $\dfrac{460\,\text{g}}{18.02\,\text{g/mol}} = 25.5\,\text{mol}$

$$x_A = \frac{25.5}{1.21 + 25.5} = 0.955, \quad x_B = 1 - 0.955 = 0.045$$

$$\begin{cases} P_A = x_A P_A^o = 0.955 \times 31.82 = 30.4\,\text{mmHg} \\ \Delta P = P_A^o - P_A = x_B P_A^o = 0.045 \times 31.82 = 1.4\,\text{mmHg} \end{cases}$$

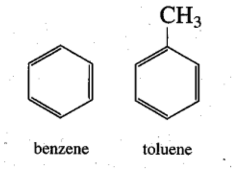
- **휘발성 용질(B)**

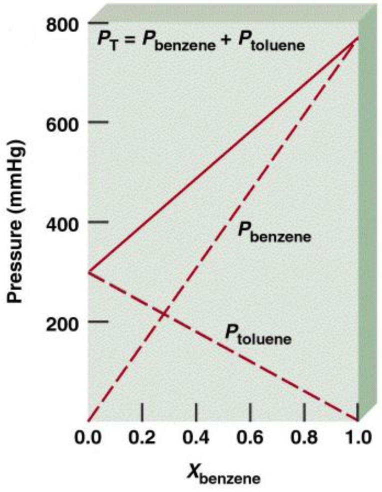
$$\left.\begin{aligned} P_A &= x_A P_A^\circ \\ P_B &= x_B P_B^\circ \end{aligned}\right\} \quad P_T = P_A + P_B = x_A P_A^\circ + x_B P_B^\circ = x_A P_A^\circ + (1-x_A) P_B^\circ$$

$$= (P_A^\circ - P_B^\circ) x_A + P_B^\circ$$

- 이상용액 ← 농도에 관계 없이 ✓ 라울의 법칙 만족 (용매, 용질)

(예) 벤젠 / 톨루엔 (휘발성이 더 큰 물질은?)





② 끓는점 오름

→ 증기압이 외부압력(대기압)과 같아지는 온도 (정상 끓는점: 증기압 = 1 기압)

순수한 용매 $\xrightarrow{\text{비휘발성 용질}}$ 증기압↓ $\xrightarrow{T\uparrow}$ 증기압 = 1기압

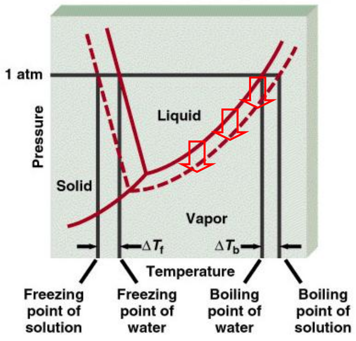
끓는점 오름

$$\Delta T_b = T_b - T_b^\circ$$

$$\Delta T_b \propto m \rightarrow \Delta T_b = \boxed{K_b}\, m$$

몰랄농도

몰랄 끓는점 오름 상수



③ 어는점 내림

순수한 용매 (무질서도↓) $\xrightarrow{-E^{\circ}}$ 고 체

용 액 (무질서도↑) $\xrightarrow{-E}$ 고 체

$$E^{\circ} < E$$

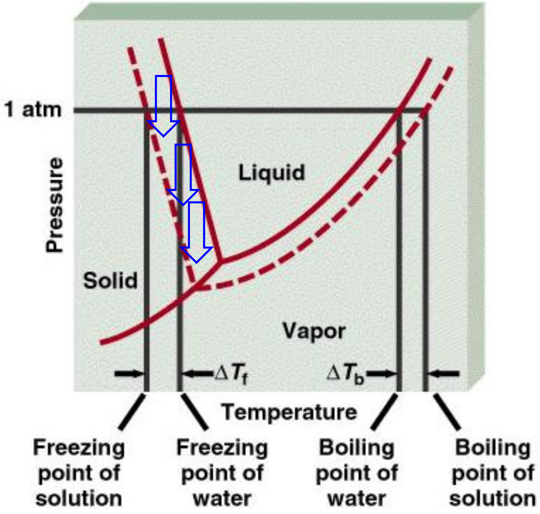
$$\downarrow$$

어는점 내림

$$\Delta T_f = T_f - T_f^{\circ}$$

$$\Delta T_f \propto m \;\rightarrow\; \Delta T_f = \underbrace{K_f}_{\uparrow} m$$

몰랄 어는점 내림 상수



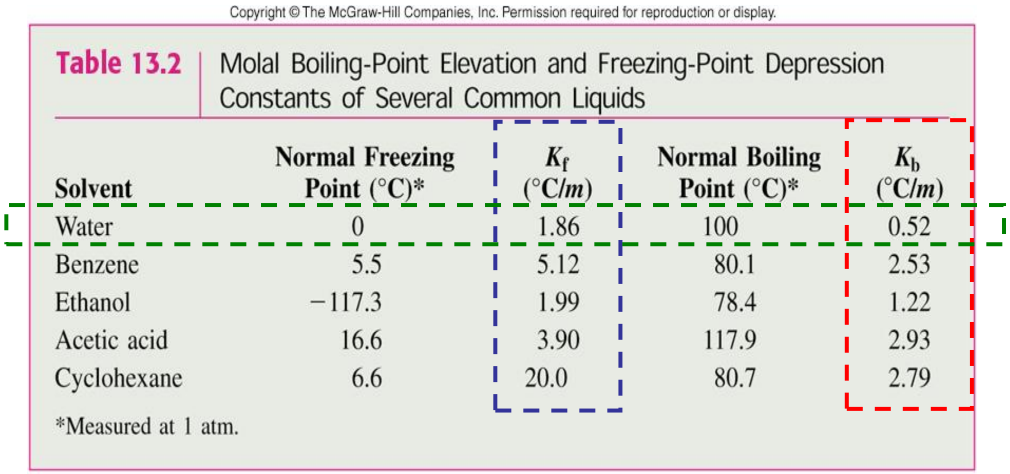

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Table 13.2 Molal Boiling-Point Elevation and Freezing-Point Depression Constants of Several Common Liquids

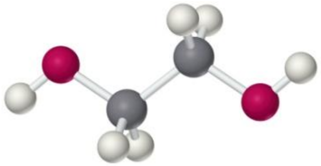
Solvent	Normal Freezing Point (°C)*	K_f (°C/m)	Normal Boiling Point (°C)*	K_b (°C/m)
Water	0	1.86	100	0.52
Benzene	5.5	5.12	80.1	2.53
Ethanol	−117.3	1.99	78.4	1.22
Acetic acid	16.6	3.90	117.9	2.93
Cyclohexane	6.6	20.0	80.7	2.79

*Measured at 1 atm.

[Ex 13.7] **에틸렌 글라이콜** [EG]: $CH_2(OH)CH_2(OH)$

물에 녹고 비휘발성 (b.p. 197℃) ← **자동차 부동액**

EG 651g / water 2505g **용액의 어는 점**?



Ethylene glycol

mw = 62.01 g/mol

(i) **용액의 몰랄 농도 결정**

$$\frac{651}{62.01}\times\frac{1}{2.505}=4.19\,m$$

(ii) **어는점 내림**, ΔT_f

$$\Delta T_f = K_f \times m = (1.86)(4.19) = 7.79\ ^\circ\mathrm{C}$$

$$T_f^\circ = 0 \;\rightarrow\; T_f = -7.79\ ^\circ\mathrm{C}$$

(iii) **끓는점 오름**, ΔT_b

$$\Delta T_b = K_b \times m = (0.52)(4.19) = 2.18\ ^\circ\mathrm{C}$$

$$T_b^\circ = 100 \;\rightarrow\; T_b = 102.2\ ^\circ\mathrm{C}$$

[활용]

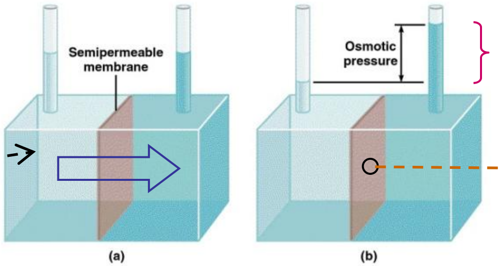
어는점 내림

끓는점 오름

→ **몰랄 농도 결정** → **몰질량 결정**

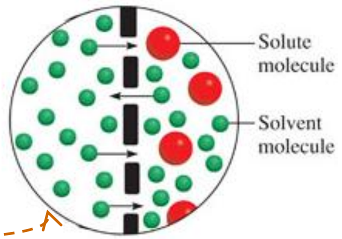
④ 삼투압

삼투현상(osmosis)

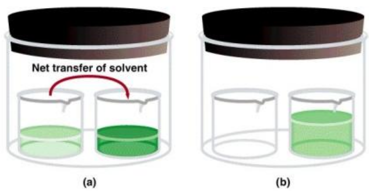


반투막

삼투압 ← 삼투현상이 일어나지 못하게 하는데 필요한 압력



Solvent Transfer



$$\pi = M\,RT$$

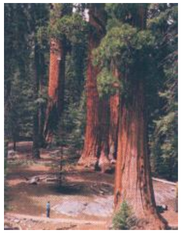
용액의 몰농도

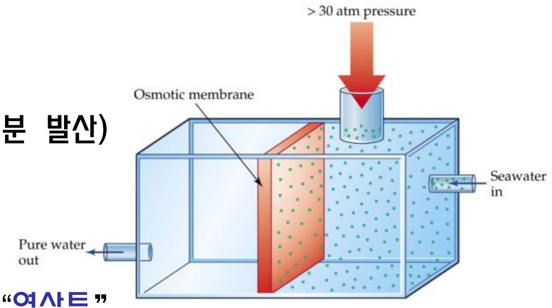
기체상수

절대온도

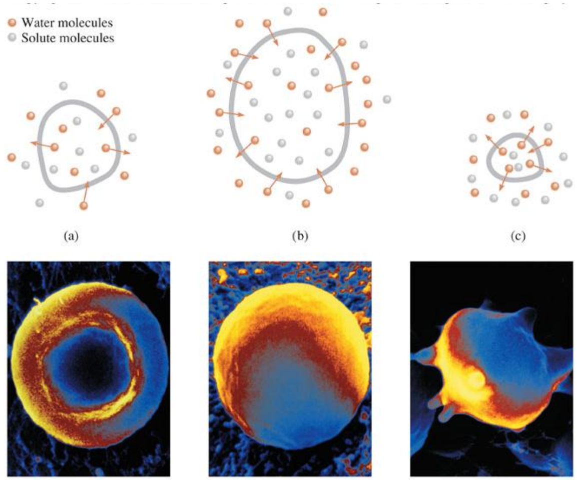
[예] 삼투현상

- 세포
- 소금(육류), 설탕(과일) 첨가 → 박테리아에 의한 부패 방지 (c)
- 피클 (c)
- 물렁물렁해진 당근 (b)
- 소금기 많은 음식 섭취 (b)
- 식물의 수분 흡수 (잎에서 수분 발산)
- 노폐물 배출 (세포)
- 해수의 탈염





“역삼투”



등장성 (isotonic)

저장성 (hypotonic)

고장성 (hypertonic)

적혈구

● 총괄성을 이용한 몰질량의 결정 ←———— 증기압 내림, 끓는점 오름, ① 어는점 내림, ② 삼투압

[Ex 13.8] **실험식** [C_5H_4] 7.85g / C_6H_6 301g → ΔT_f = 1.05 ℃

$$\text{몰랄농도} = \frac{\Delta T_f}{K_f} = \frac{1.05}{5.12} = 0.205\,m \qquad 7.85 \times \frac{1000}{301} = 0.205 \times M \rightarrow M = 127\text{ g/mol}$$

$$[C_5H_4] \rightarrow 12\times5+1\times4=64 \rightarrow C_{10}H_8 \text{ (나프탈렌)}$$

[Ex 13.9] **헤모글로빈**(Hb) 35.0g / 1L **수용액** → π = 10.0 mmHg

$$\pi = M\,RT$$

$$M = \frac{\pi}{RT} = \frac{\frac{10.0}{760.0}}{(0.08206)(298)} = 5.38\times10^{-4}\,M \qquad \text{몰질량} = \frac{35.0}{5.38\times10^{-4}} = 65{,}000\text{ g/mol}$$

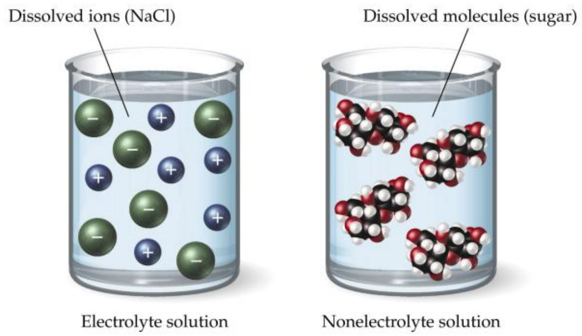
$$\Delta T_f = K_f\,m = (1.86)(5.38\times10^{-4}) = 0.001\,^\circ C$$

어는점 내림 →
- 몰질량 < 500
- 용해도 큰 분자

전해질의 총괄성

"전해질" → "해리" → 입자의 수 증가 → van't Hoff factor (i)

$$i = \frac{\Delta T_f(\text{측정})}{\Delta T_f(\text{예상})}$$ ← 비전해질이라 가정



$$\pi = i\,M\,RT$$

$$\Delta T_f = i\,K_f\,m$$

[예] 이론적인 van't Hoff factor

비전해질 : $i = 1$

NaCl, KNO3 : $i = 2$

Na2SO4, MgCl2 : $i = 3$

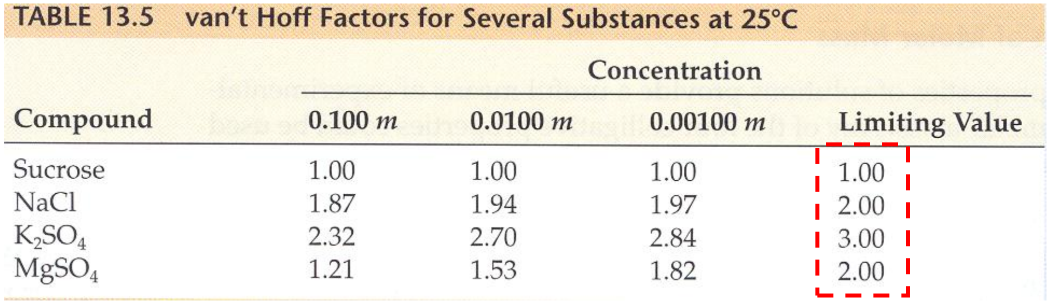
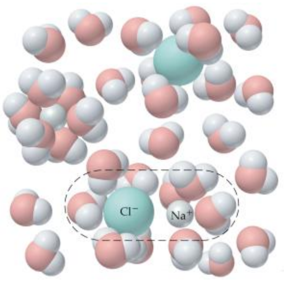


TABLE 13.5 van't Hoff Factors for Several Substances at 25°C

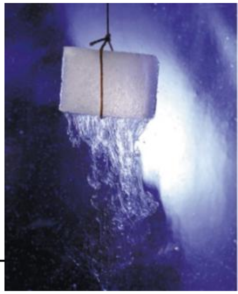
Compound	Concentration 0.100 m	0.0100 m	0.00100 m	Limiting Value
Sucrose	1.00	1.00	1.00	1.00
NaCl	1.87	1.94	1.97	2.00
K_2SO_4	2.32	2.70	2.84	3.00
$MgSO_4$	1.21	1.53	1.82	2.00

Why?



이온쌍 (ion pair)

13. 용액의 물리적 성질 — 연습문제



78 / 80 / 82 / 86 / 88 / 92 /

94 / 96 / 100 / 102 / 104 / 106