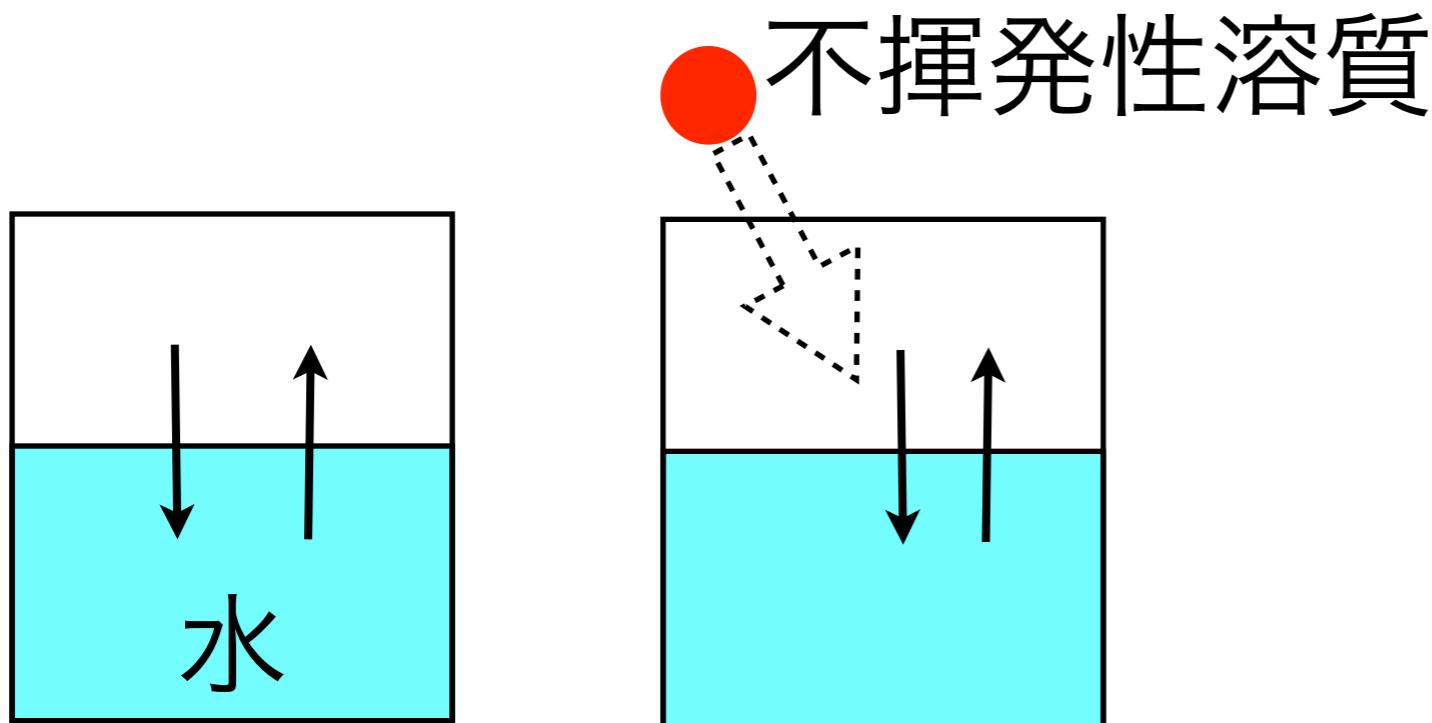


# 蒸気圧降下



$$d\mu^L(T,P,x) = \bar{V}dP - \bar{S}dT + RT(d\ln x), \quad d\mu_{T,P}^L = RTd(\ln x)$$

$$\mu^G(T,P) = \mu^{0,G}(T,P) + RT\ln(P/P^0), \quad d\mu_{T,P}^G = RTd(\ln P_x)$$

$$d\mu_{T,P}^L = d\mu_{T,P}^G, \quad \int_{\ln 1}^{\ln x} d(\ln x) = \int_{\ln P^0}^{\ln P_x} d(\ln P_x)$$

$$\ln x = \ln \frac{P_x}{P^0}, \quad x = \frac{P_x}{P^0}$$

$$P^0 - P_x = P^0 - xP^0 = (1-x)P^0 = x_{\text{solute}}P^0$$

vaper pressure of water / hPa

1000

980

960

940

920

900

880

0

1

2

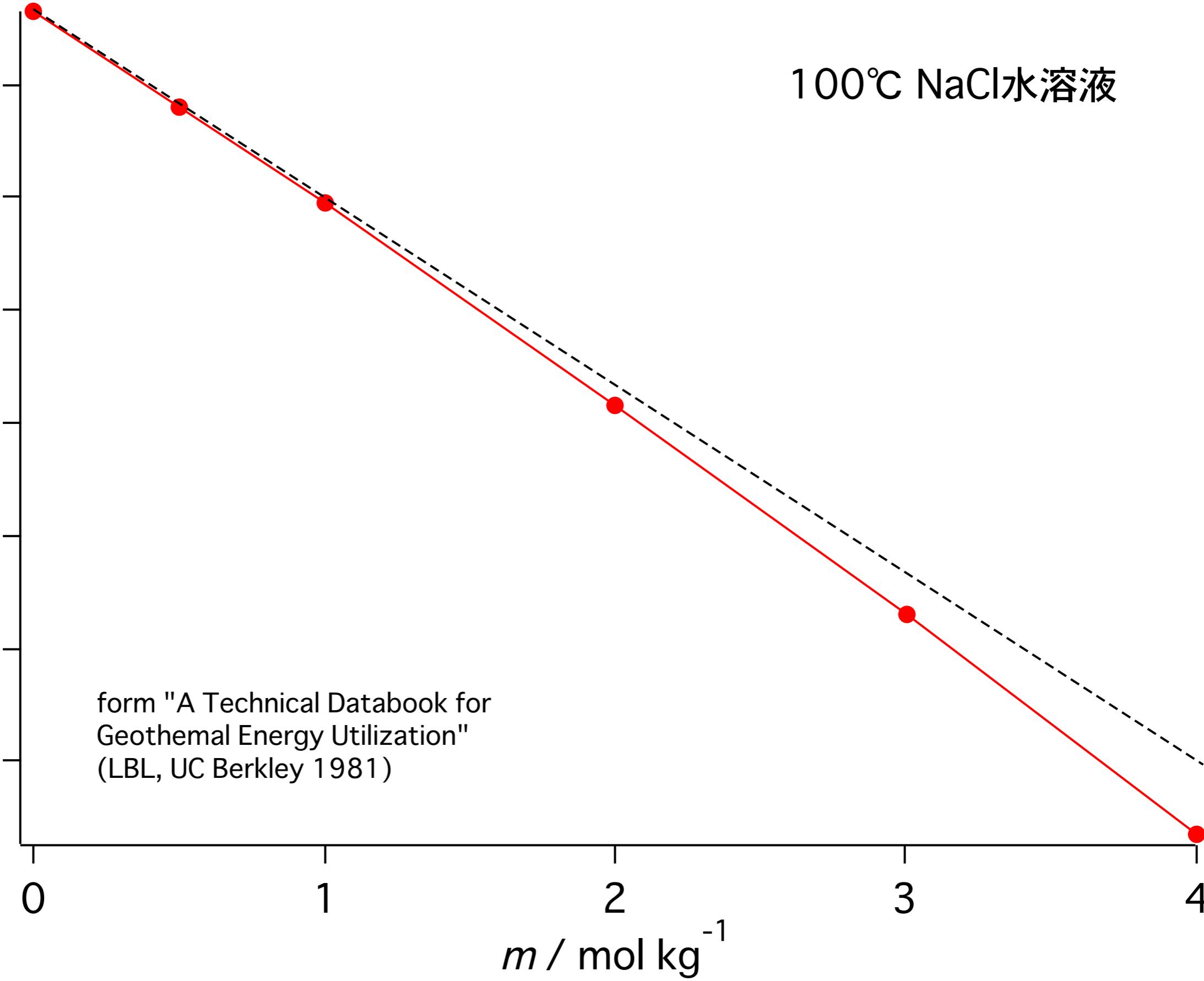
3

4

$m / \text{mol kg}^{-1}$

100°C NaCl水溶液

form "A Technical Databook for  
Geothermal Energy Utilization"  
(LBL, UC Berkley 1981)



# 海水パンツ問題

- 海水を含んだ水の蒸気圧はさがる
- 海水パンツが乾燥するにつれて、 塩分濃度は増加し、 蒸気圧はさらに減少する

$$\begin{aligned}
x_{\text{solute}} &= n_{\text{solute}} / (n_{\text{solute}} + n_{\text{solvent}}) \\
&= mW_{\text{solvent}} / (mW_{\text{solvent}} + 1000W_{\text{solvent}} / M_{\text{solvent}}) \\
&= m / (m + 1000 / M_{\text{solvent}}) \approx mM_{\text{solvent}} / 1000
\end{aligned}$$

$$P^0 - P_x = P^0 - xP^0 = (1 - x)P^0 = x_{\text{solute}}P^0$$

$$= P^0 \frac{M_{\text{solvent}}}{1000} m$$

$$\frac{P^0 - P_x}{P^0} = \frac{M_{\text{solvent}}}{1000} m$$

理論値 :  $2 \times 18 / 1000 = 0.036 \text{ kg mol}^{-1}$

実験値(最初の 2 点)  $0.034 \text{ kg mol}^{-1}$

沸点上升

# 束一的性質(colligative property)

$$\Delta T_b = K_b m$$

[K] [K mol<sup>-1</sup> kg][mol kg<sup>-1</sup>]

モル沸点上昇定数  
ebullioscopic constant

# モル沸点上昇定数 ebullioscopic constant

| Compound             | Boiling point in °C | Ebullioscopic constant $K_b$ in units of [(°C·kg)/mol] or [°C/molal] |
|----------------------|---------------------|--|
| Acetic acid          | 118.1               | 3.07   |
| Benzene              | 80.1                | 2.53   |
| Carbon disulfide     | 46.2                | 2.37   |
| Carbon tetrachloride | 76.8                | 4.95   |
| Naphthalene          | 217.9               | 5.8  |
| Phenol               | 181.75              | 3.04   |
| Water                | 100                 | 0.512  |

束一的性質(colligative property)

$$d\mu^L(T, P, x) = \bar{V}dP - \bar{S}dT + RT(d\ln x)$$

$$d\mu_P^L = -\bar{S}^LdT + RTd(\ln x)$$

$$d\mu_P^{0,G} = -\bar{S}^GdT$$

$$d\mu_P^L = d\mu_P^{0,G}$$

$$RTd(\ln x) = -(\bar{S}^G - \bar{S}^L)dT = -(\Delta_{\text{vap}}\bar{S})dT = -\frac{\Delta_{\text{vap}}\bar{H}}{T_b}dT$$

$$\frac{\Delta_{\text{vap}}\bar{H}}{T_b} \int_{T_b}^{T_b + \Delta T_b} dT = -RT_b \int_{\ln 1}^{\ln x} d(\ln x)$$

$$\frac{\Delta_{\text{vap}}\bar{H}}{T_b} \Delta T_b = -RT_b \ln x$$

$$\ln x = \ln(1 - x_{\text{solute}}) \simeq -x_{\text{solute}}$$

$$\frac{\Delta_{\text{vap}}\bar{H}}{T_b} \Delta T_b = RT_b x_{\text{solute}}$$

$$\Delta T_b = \frac{RT_b^2}{\Delta_{\text{vap}}\bar{H}} x_{\text{solute}}$$

$$\begin{aligned}
x_{\text{solute}} &= n_{\text{solute}} / (n_{\text{solute}} + n_{\text{solvent}}) \\
&= mW_{\text{solvent}} / (mW_{\text{solvent}} + 1000W_{\text{solvent}} / M_{\text{solvent}}) \\
&= m / (m + 1000 / M_{\text{solvent}}) \approx mM_{\text{solvent}} / 1000
\end{aligned}$$

$$\Delta T_b = \frac{RT_b^2}{\Delta_{\text{vap}}\bar{H}} x_{\text{solute}} = \frac{RT_b^2 M_{\text{solvent}}}{1000 \Delta_{\text{vap}} \bar{H}} m$$

理論値  $0.512 \text{ K kg mol}^{-1}$

実験値  $0.515 \text{ K kg mol}^{-1}$

## 束一的性質(colligative property)

$$\Delta T_f = K_f m$$

[K]

[K mol<sup>-1</sup> kg][mol kg<sup>-1</sup>]

モル凝固点降下定数  
molal freezing-point-depression constant

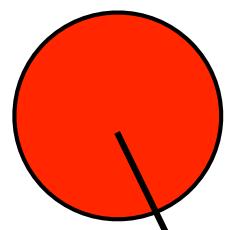
# 束一的性質(colligative property)

| 溶媒         | 凝固点 / °C | $K_f / \text{K mol}^{-1} \text{ kg}$ |
|------------|----------|--------------------------------------|
| 水          | 0        | 1.853                                |
| ニトロベンゼン    | 5.76     | 6.852                                |
| t-ブチルアルコール | 25.82    | 8.37                                 |
| 四塩化炭素      | -22.95   | 29.8                                 |

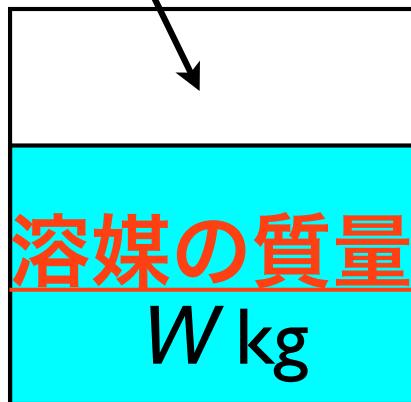
$m$ : 質量モル濃度 **molality** [mol kg<sup>-1</sup>]

溶質の質量

$w$  g



溶質のモル質量  
 $M$  g mol<sup>-1</sup>

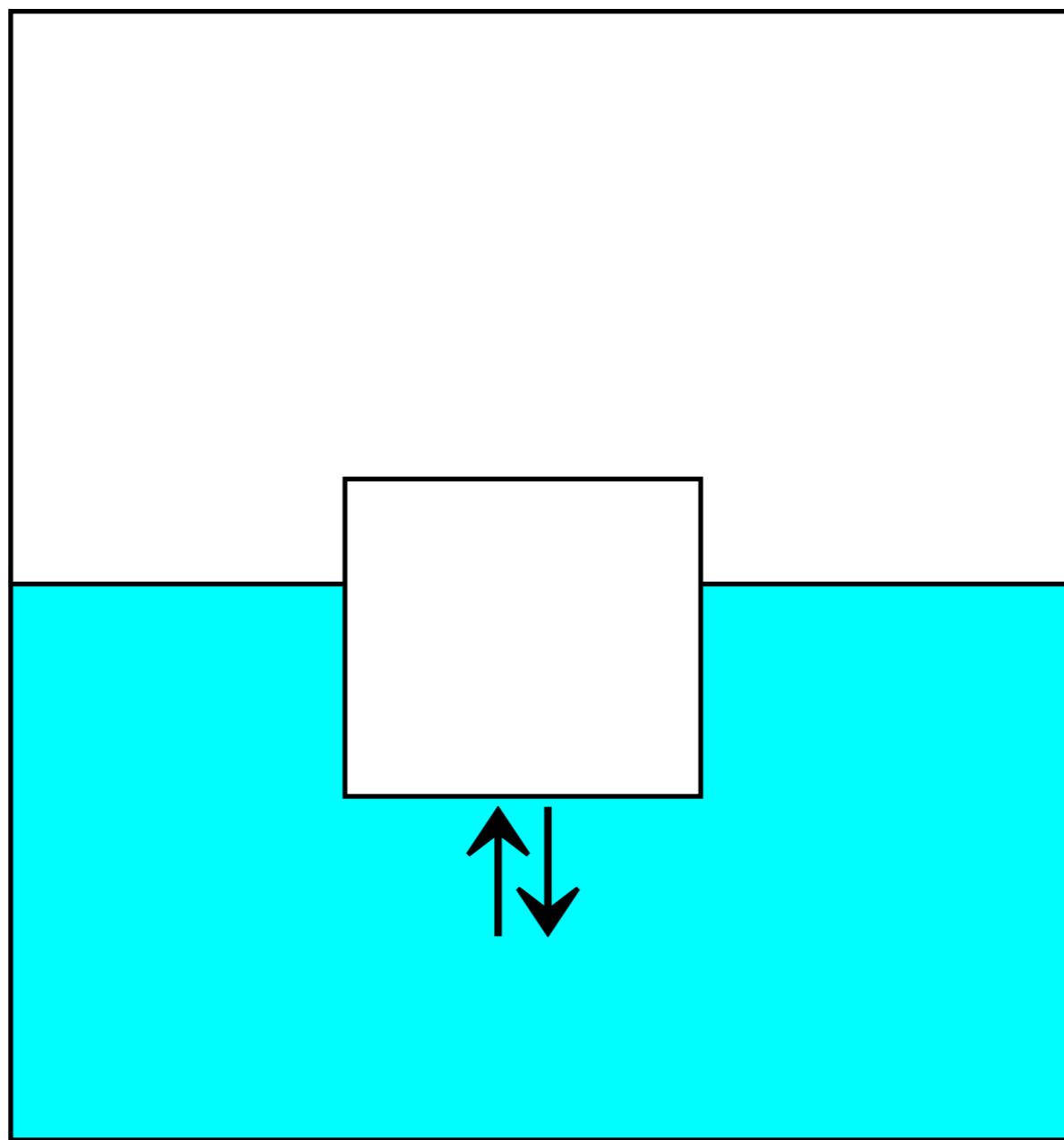


$$m = \frac{w}{M} \frac{1}{W}$$

凝固点降下では  
こちらを使う！Why？

# 相平衡の問題として

化学ポテンシャル=1分子増加したときのギブズエネルギー変化



## 化学ポテンシャル=1分子増加したときのギブズエネルギー変化

氷中の水分子

$$\mu_{\text{water}}^{\text{ice}}(T, a_{\text{water}}) =$$

$$\mu_{\text{water}}^{\text{ice}}(T) =$$

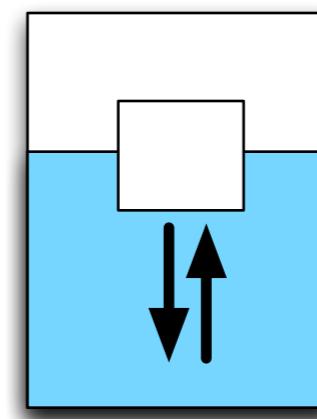
$$\mu_{\text{water}}^{\text{liq}}(T, a_{\text{water}}) =$$

水溶液中の水分子

$$\mu_{\text{water}}^{\text{liq}}(T, a_{\text{water}})$$

$\mu_{\text{water}}^{0,\text{ice}}(T)$  : 氷は水分子のみ

$$\mu_{\text{water}}^{0,\text{liq}}(T) + RT \ln a_{\text{water}}$$



pure water : freezing point  $T = T_f^0$

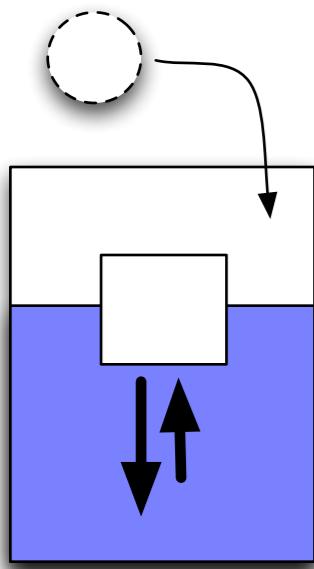
$$\mu_{\text{water}}^{0,\text{ice}}(T_f^0) = \mu_{\text{water}}^{0,\text{liq}}(T_f^0) + RT_f^0 \underbrace{\ln 1}_{=0} \quad (*)$$

dilute solution

## 希薄溶液

$$\ln a_{\text{water}} \simeq \ln x_{\text{water}} = \ln(1 - x_{\text{solute}}) \simeq -x_{\text{solute}}$$

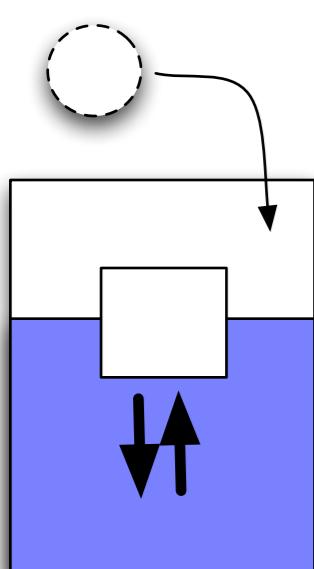
$$\ln(1 - x) \simeq \ln(1 - 0) + \frac{-1}{1 - x} \Big|_{x=0} x + \frac{1}{2} \frac{(-1)^3}{(1 - x)^2} \Big|_{x=0} x^2 + \dots = -x - \frac{1}{2}x^2$$



純水の凝固点では氷が溶け出でるので

$$\text{dilute solution : } T = T_f^0$$

$$\mu_{\text{water}}^{0,\text{ice}}(T_f^0) < \mu_{\text{water}}^{0,\text{liq}}(T_f^0) - RT_f^0 x_{\text{solute}}$$



温度が低下すると、バランスする。

$$\text{dilute solution : freezing point } T = T_f$$

$$\mu_{\text{water}}^{0,\text{ice}}(T_f) \simeq \mu_{\text{water}}^{0,\text{liq}}(T_f) - RT_f x_{\text{solute}} \quad (**)$$

$$-x_{\text{solute}} = \frac{1}{RT_f} (\mu_{\text{water}}^{0,\text{ice}}(T_f) - \mu_{\text{water}}^{0,\text{liq}}(T_f)) \quad (**)$$

$$\ln 1 = \frac{1}{RT_f^0} (\mu_{\text{water}}^{0,\text{ice}}(T_f^0) - \mu_{\text{water}}^{0,\text{liq}}(T_f^0)) \quad (*)$$

$$\begin{aligned} -x_{\text{solute}} - \ln 1 &= \frac{\mu_{\text{water}}^{0,\text{ice}}(T_f) - \mu_{\text{water}}^{0,\text{liq}}(T_f)}{R} \frac{1}{T_f} - \frac{\mu_{\text{water}}^{0,\text{ice}}(T_f^0) - \mu_{\text{water}}^{0,\text{liq}}(T_f^0)}{R} \frac{1}{T_f^0} \\ &\approx \frac{\mu_{\text{water}}^{0,\text{ice}}(T_f) - \mu_{\text{water}}^{0,\text{liq}}(T_f)}{R} \frac{T_f^0 - T_f}{T_f T_f^0} \\ &\approx \frac{\mu_{\text{water}}^{0,\text{ice}}(T_f) - \mu_{\text{water}}^{0,\text{liq}}(T_f)}{R} \frac{T_f^0 - T_f}{(T_f^0)^2} \end{aligned}$$

$$T_f - T_f^0 = \frac{R(T_f^0)^2}{\mu_{\text{water}}^{0,\text{ice}}(T_f) - \mu_{\text{water}}^{0,\text{liq}}(T_f)} x_{\text{solute}}$$

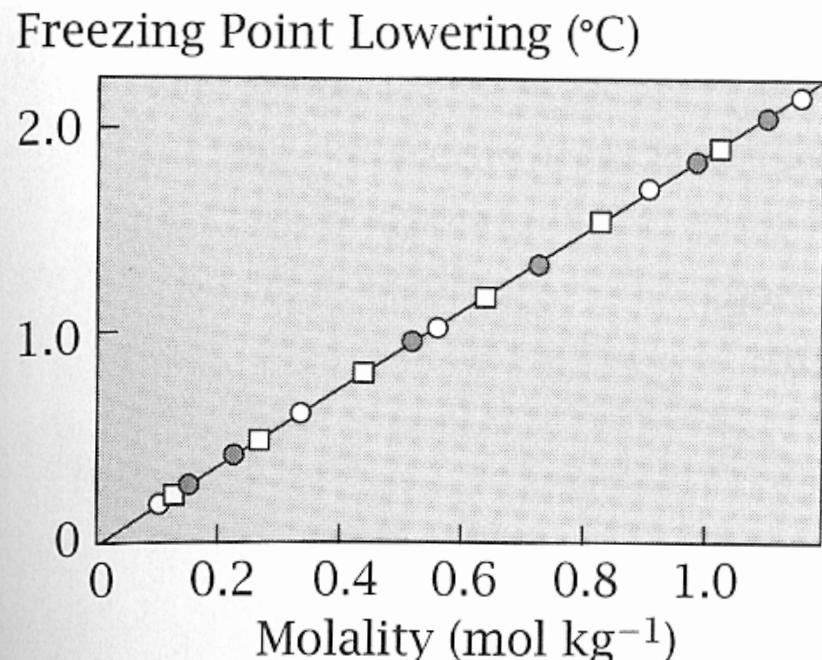
$$\mu_{\text{water}}^{0,\text{ice}}(T_f) - \mu_{\text{water}}^{0,\text{liq}}(T_f) < 0 \rightarrow T_f - T_f^0 < 0$$

$$K_f = \frac{R(T_f^*)^2 M_{\text{water}}}{1000 \Delta H_f}$$

溶質分子の種類ではなく数できる:  
束一的性質 **colligative property**

$R$ : 気体定数  $\text{J mol}^{-1} \text{K}^{-1}$ ,  $T_f^*$ : 純溶媒の凝固点 / K

$M_{\text{water}}$ : 水の分子量 /  $\text{g mol}^{-1}$ ,  $\Delta H_f$ : 凝固のエンタルピー /  $\text{J mol}^{-1}$



**Figure 16.7** The depression of the freezing temperature of water is a linear function of the concentration of glycerol (○), dextrose (●), and sucrose (□).  
Source: CH Langford and RA Beebe, *The Development of Chemical Principles*, Dover Publications, New York, 1969.

$$\chi_{\text{solute}} = n_{\text{solute}} / (n_{\text{solute}} + n_{\text{solvent}})$$

$$\begin{aligned}
 &= mW_{\text{solvent}} / (mW_{\text{solvent}} + 1000W_{\text{solvent}} / M_{\text{solvent}}) \\
 &= m / (m + 1000 / M_{\text{solvent}}) \approx mM_{\text{solvent}} / 1000
 \end{aligned}$$

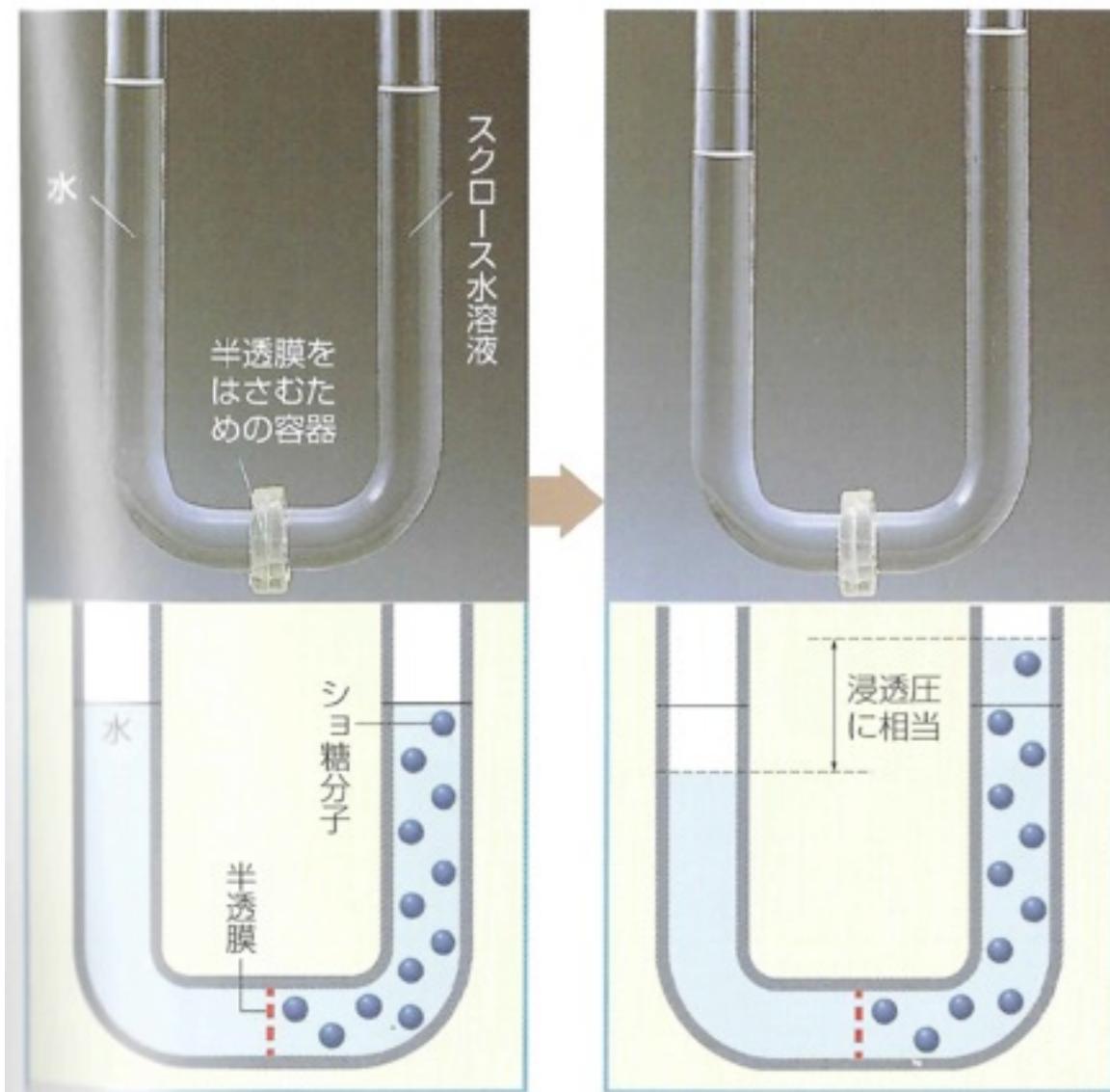
# 浸透圧

## Osmotic Pressure

van't Hoff's  
equation

$$\Pi = \frac{n}{V} RT$$

$\underbrace{V}_{=c}$



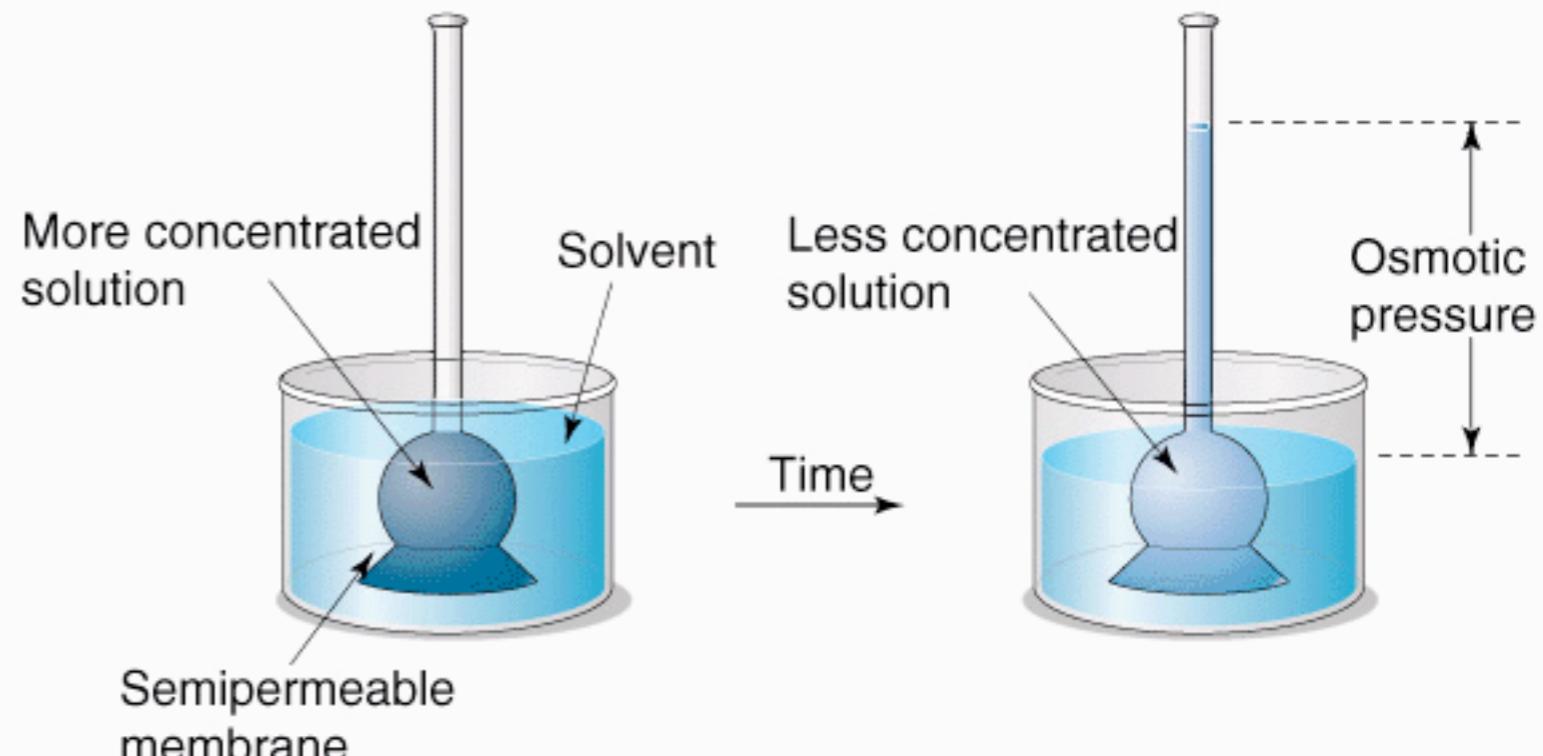
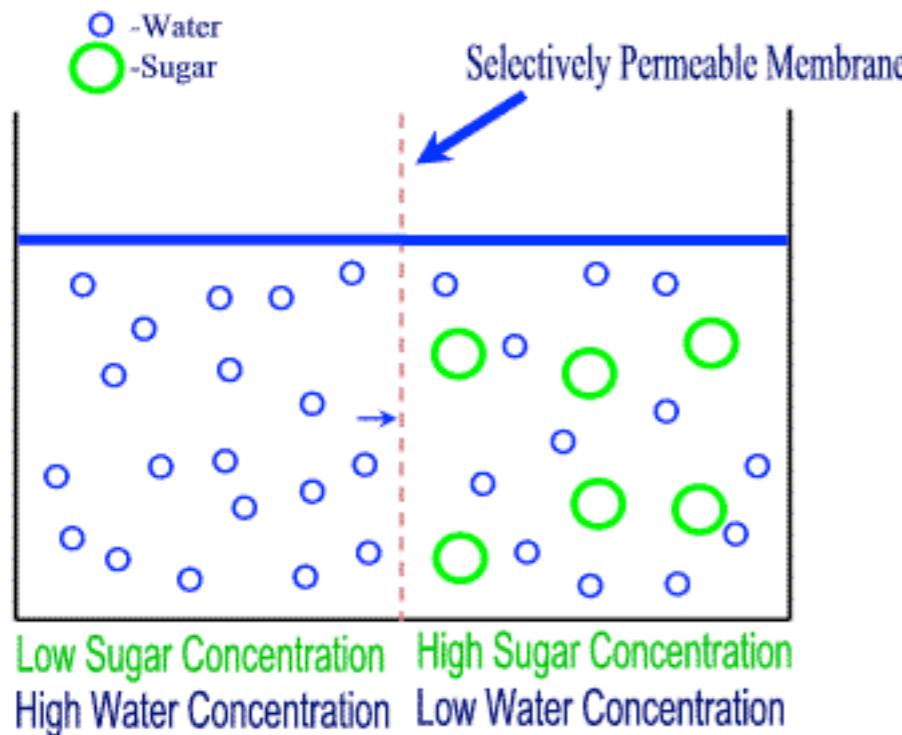
半透膜を固定したU字管に、水(溶媒)とスクロース水溶液(溶液)の水面を並べ入れ放置すると、溶媒が溶液中に浸透して溶液側の水面が高くなる。

### ●条件による浸透圧の変化



浸透圧は、濃度が濃いほど大きく、温度が高いほど大きい。

# Osmosis

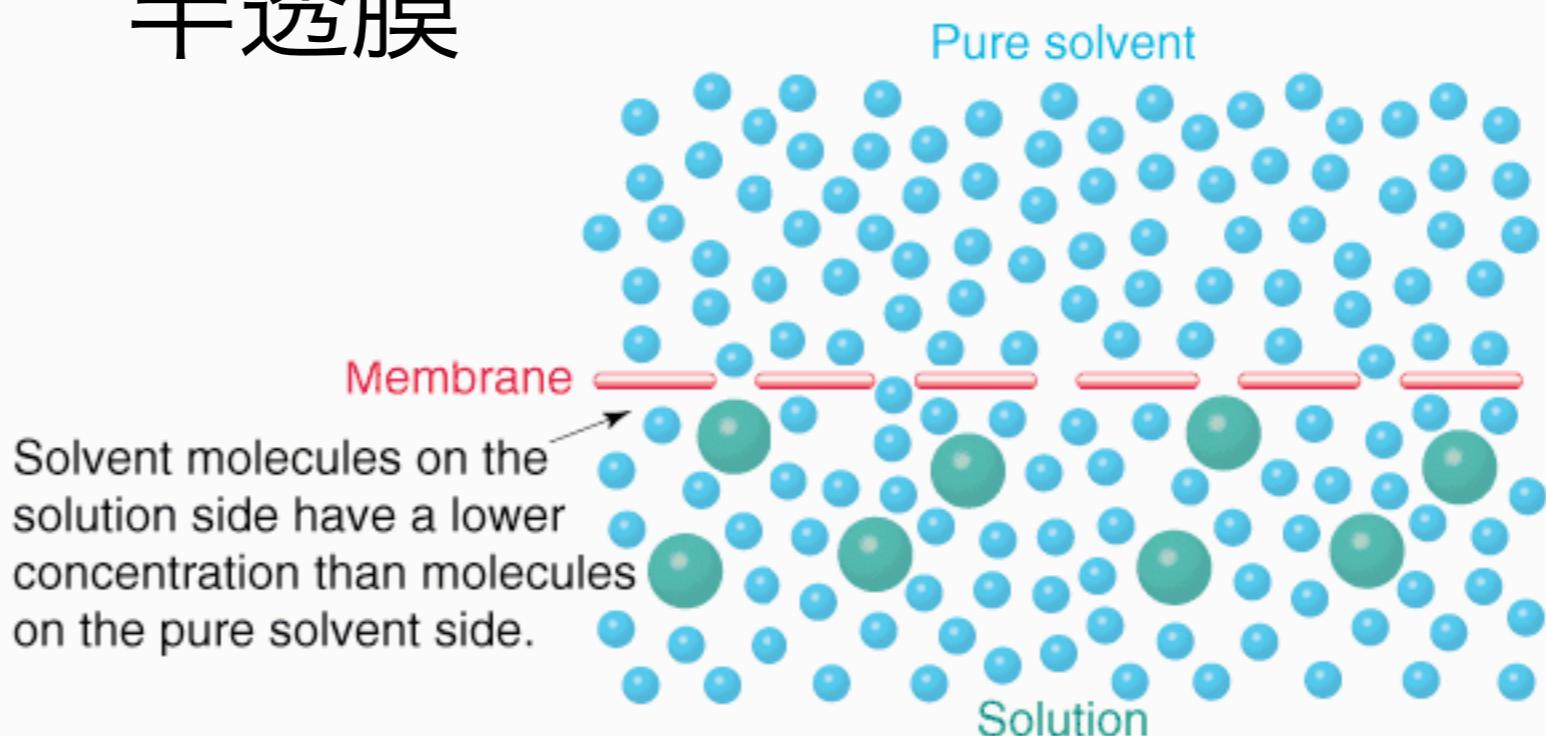


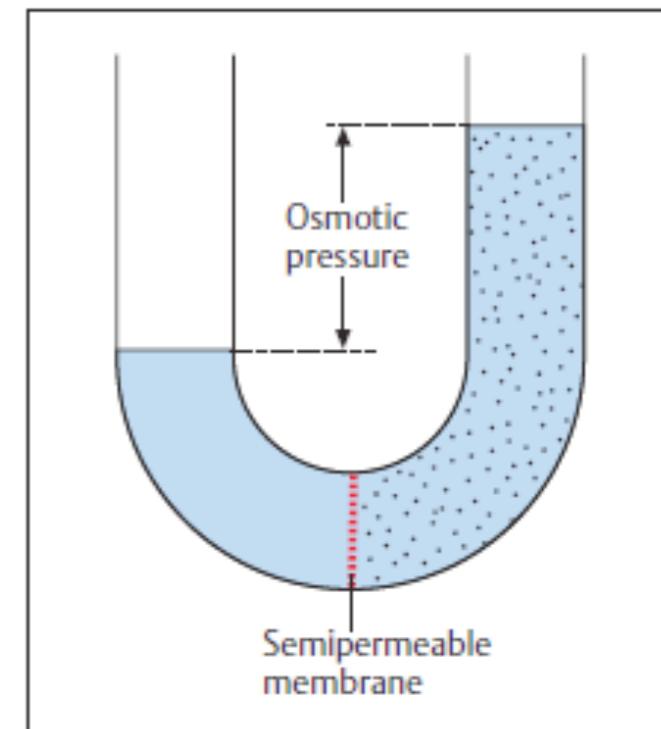
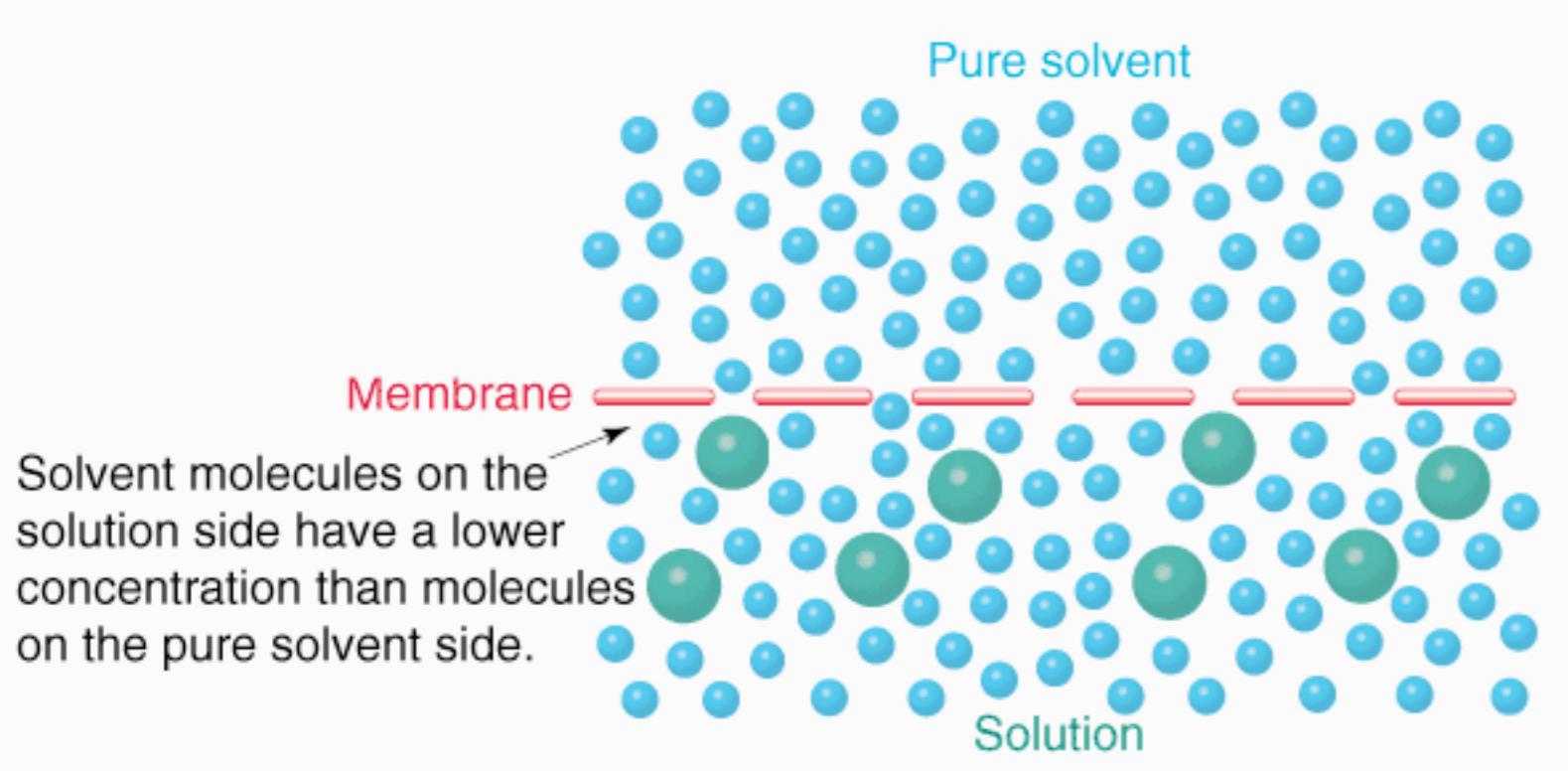
浸透压

Osmotic  
Pressure

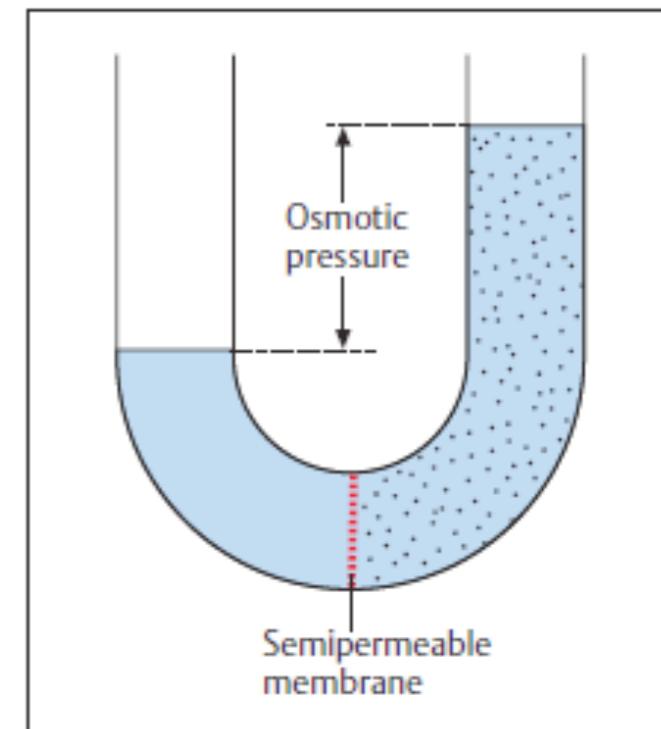
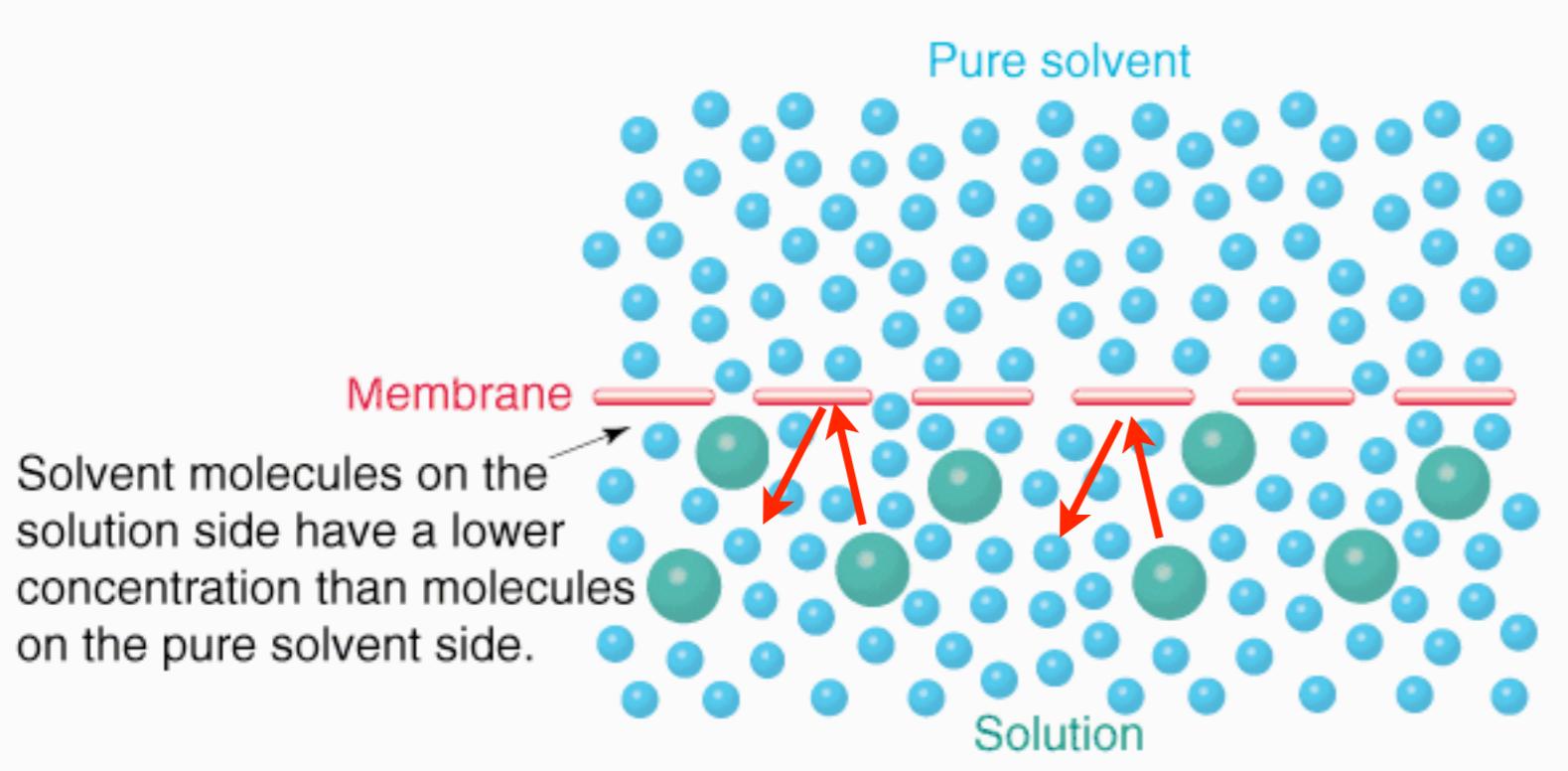


半透膜





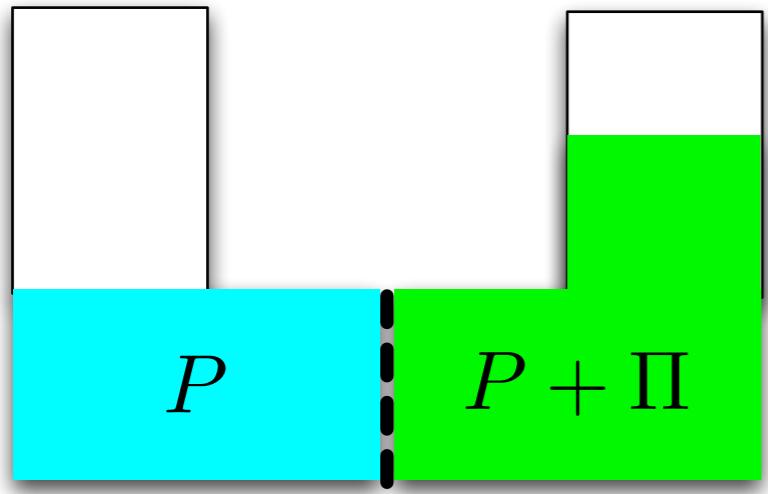
本来は、溶媒分子が半透膜を透過しようとする駆動力と溶液側の(高)圧力がバランスしているというのが正しい理解であるが。。



本来は、溶媒分子が半透膜を透過しようとする駆動力と溶液側の(高)圧力がバランスしているというのが正しい理解であるが。。

溶質が、理想気体のように壁に衝突して、浸透圧を生成していると考えることもできる。(教科書)

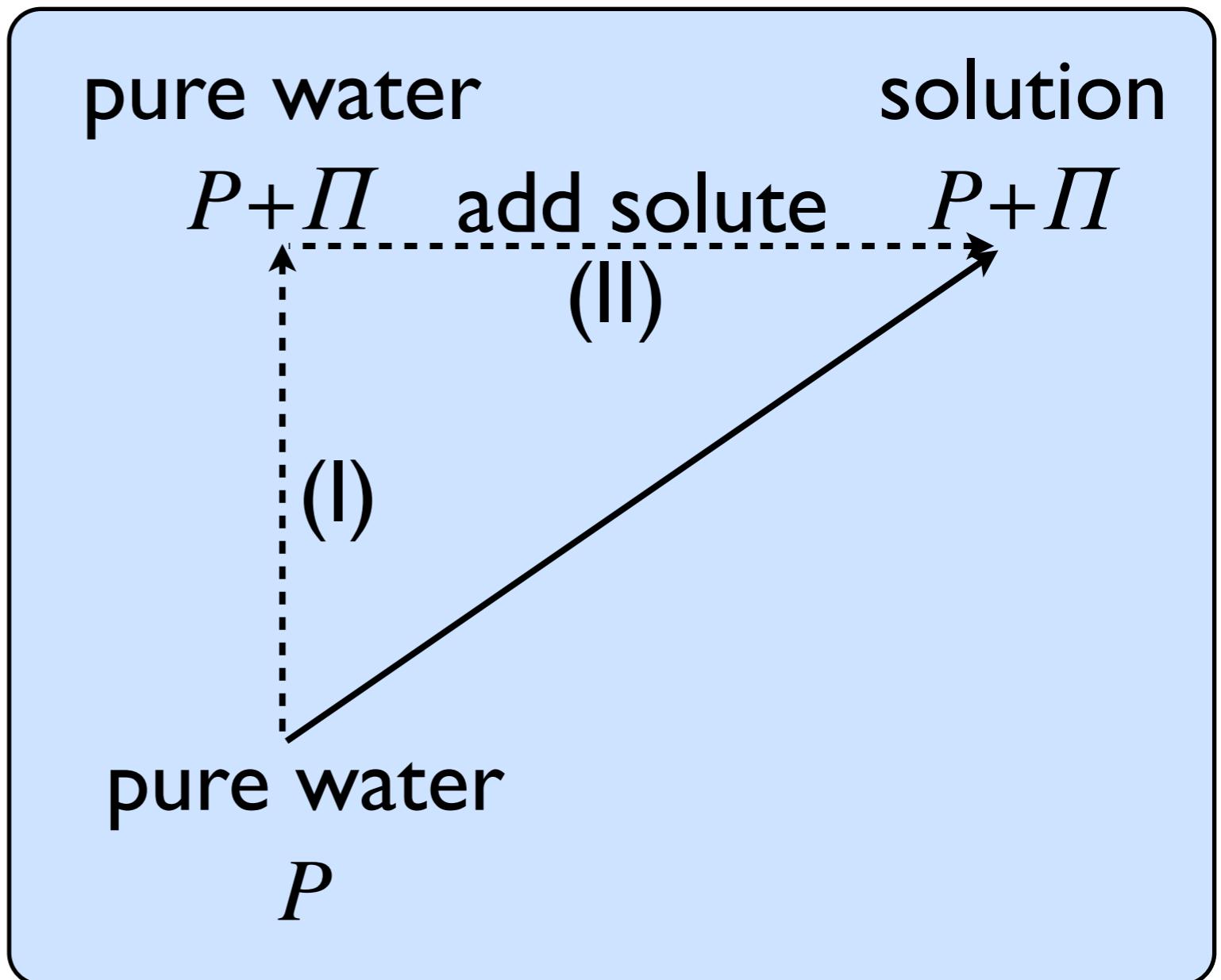
# 化学ポテンシャルによる説明



pure water    solution  
W            (solute A+  
              solvent W)

水（溶媒）の化学ポ  
テンシャルが半透膜  
の左右で等しい

$$\mu_W(\text{pure water}, P, x_W = 1) = \mu_W(\text{solution}, P + \Pi, x_W)$$



$$(I) \quad \mu_W(\text{pure water}, P + \Pi, x_W = 1) = \mu_W(\text{pure water}, P, x_W = 1) + \int_P^{P+\Pi} \frac{\partial \mu_W}{\partial P} dP$$

$$\frac{\partial \mu_W}{\partial P} = \frac{\partial V}{\partial N_W} = v_W$$

$$dG = VdP - SdT + \sum_i \mu_i dN_i \quad \checkmark \quad (I)$$

$$\mu_W(\text{pure water}, P + \Pi, x_W = 1) = \mu_W(\text{pure water}, P, x_W = 1) + \Pi v_W, \\ (v_W \text{ indep. } P)$$

$$\mu_W(\text{pure water}, P, x_W = 1) = \mu_W(\text{pure water}, P + \Pi, x_W = 1) - \Pi v_W$$

(II)

$$\begin{aligned} \mu_W(\text{solution}, P + \Pi, x_W) &= \mu_W(\text{pure water}, P + \Pi, x_W = 1) + RT \ln a_W \\ &= \mu_W(\text{pure water}, P + \Pi, x_W = 1) + RT \ln \gamma_W x_W \\ &= \mu_W(\text{pure water}, P + \Pi, x_W = 1) + RT \ln \gamma_W + RT \ln(1 - x_A) \\ &\simeq \mu_W(\text{pure water}, P + \Pi, x_W = 1) - RT x_A, \quad (\gamma_W = 1, \quad x_A \ll 1) \end{aligned}$$

$$\begin{aligned} \ln(1 - x) &\simeq \ln(1 - 0) + \left. \frac{-1}{1 - x} \right|_{x=0} x + \left. \frac{-1}{2!} \frac{(-1)(-1)}{(1-x)^2} \right|_{x=0} x^2 + \dots \\ &= -x - \frac{1}{2} x^2 \dots \end{aligned}$$

$$\mu_W(\text{pure water}, P, x_W = 1) = \mu_W(\text{solution}, P + \Pi, x_W)$$

$$\mu_W(\text{pure water}, P + \Pi, x_W = 1) - \Pi v_W = \mu_W(\text{pure water}, P + \Pi, x_W = 1) - RTx_A$$
$$\Pi v_W = RTx_A$$

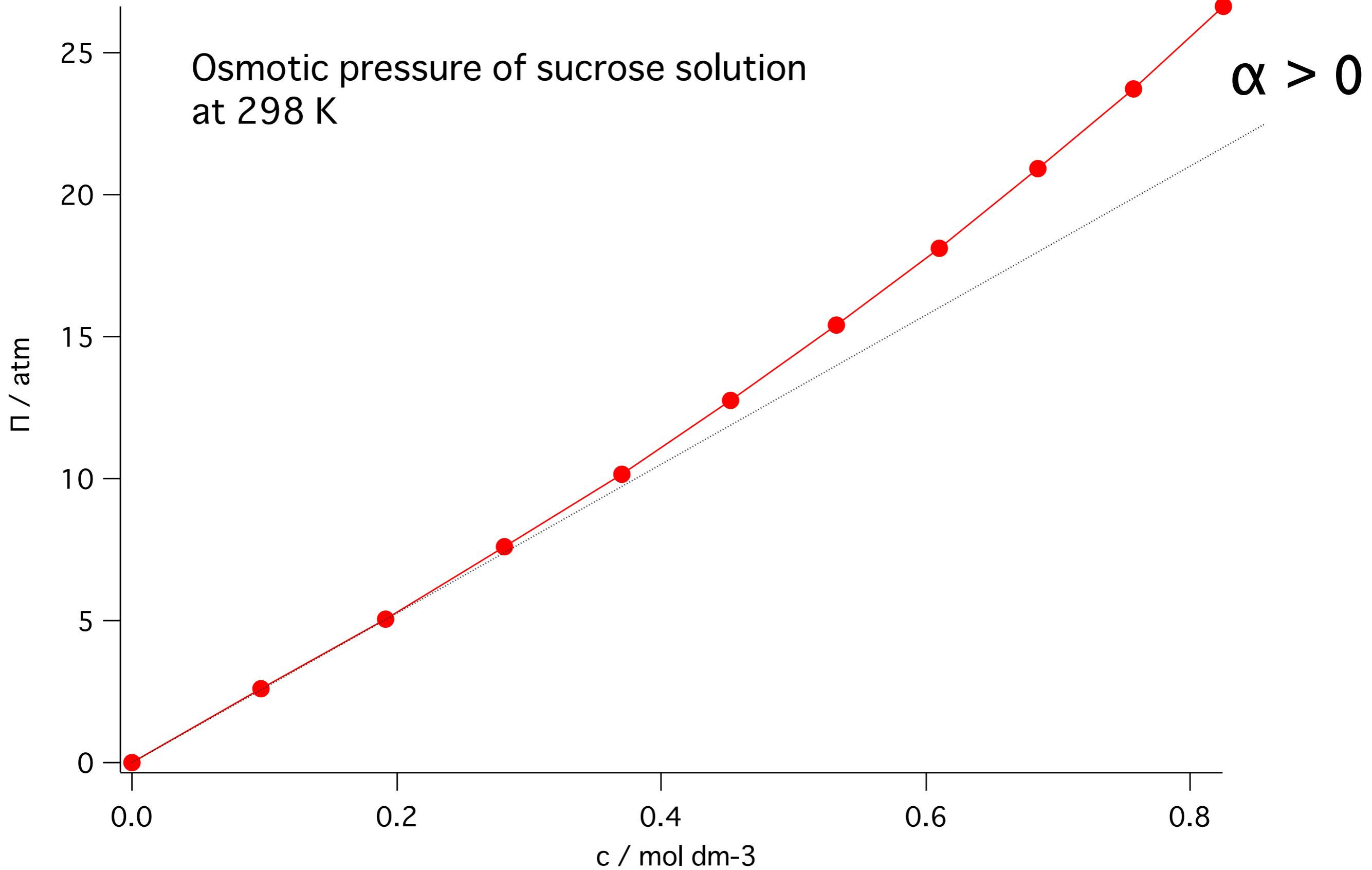
$$\Pi \frac{V}{N_W} = RT \frac{N_A}{N_W + N_A}$$

$$\Pi = RT \frac{N_A}{V} \frac{N_W}{N_W + N_A} \simeq c_A RT$$

## 非理想性

$$\ln a_W = -x_A \underbrace{(1 + \alpha x_A + \beta x_A^2 - \dots)}_{= \phi(\text{osmotic coefficient})}$$

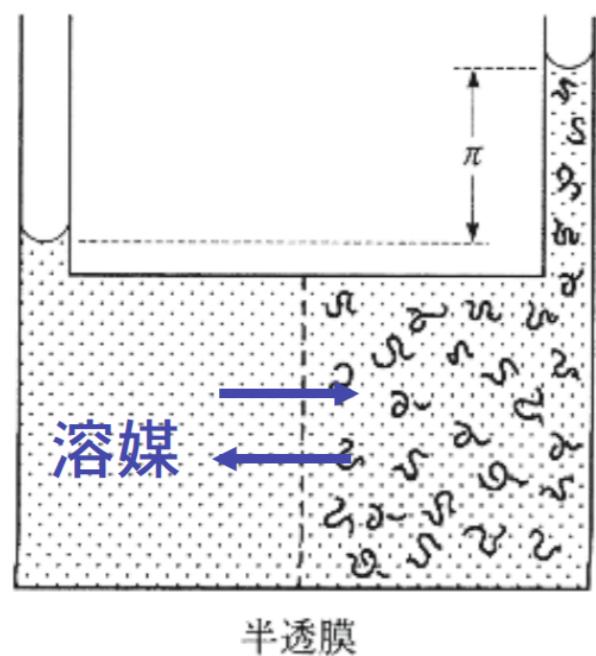
$$\Pi v_W = RTx_A(1 + \alpha x_A)$$



# 浸透圧

$$\mu_0^\circ(p, T) = \mu_0(p + \pi, T, c)$$

$$= \mu_0(p, T) + \left( \frac{\partial \mu_0}{\partial p} \right)_{T, c} \pi + \dots$$



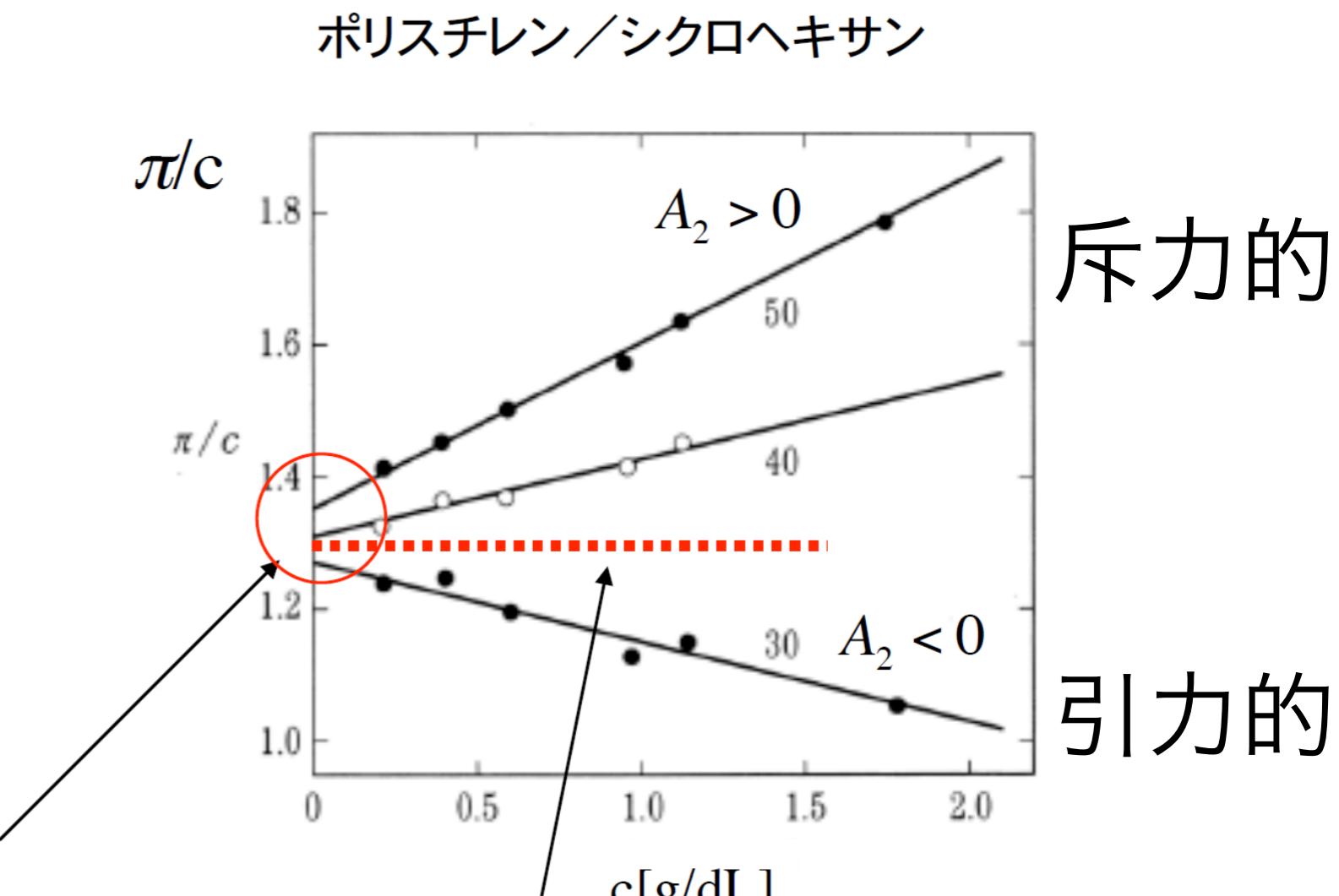
$$\pi = -\Delta \mu_0 / \bar{V}_0$$

van't Hoff則

$$= \frac{RT}{\bar{V}_0} \left( \frac{c}{M} + A_2 c^2 + A_3 c^3 + \dots \right)$$

ビリアル展開

平均分子量:  $M$



斥力的

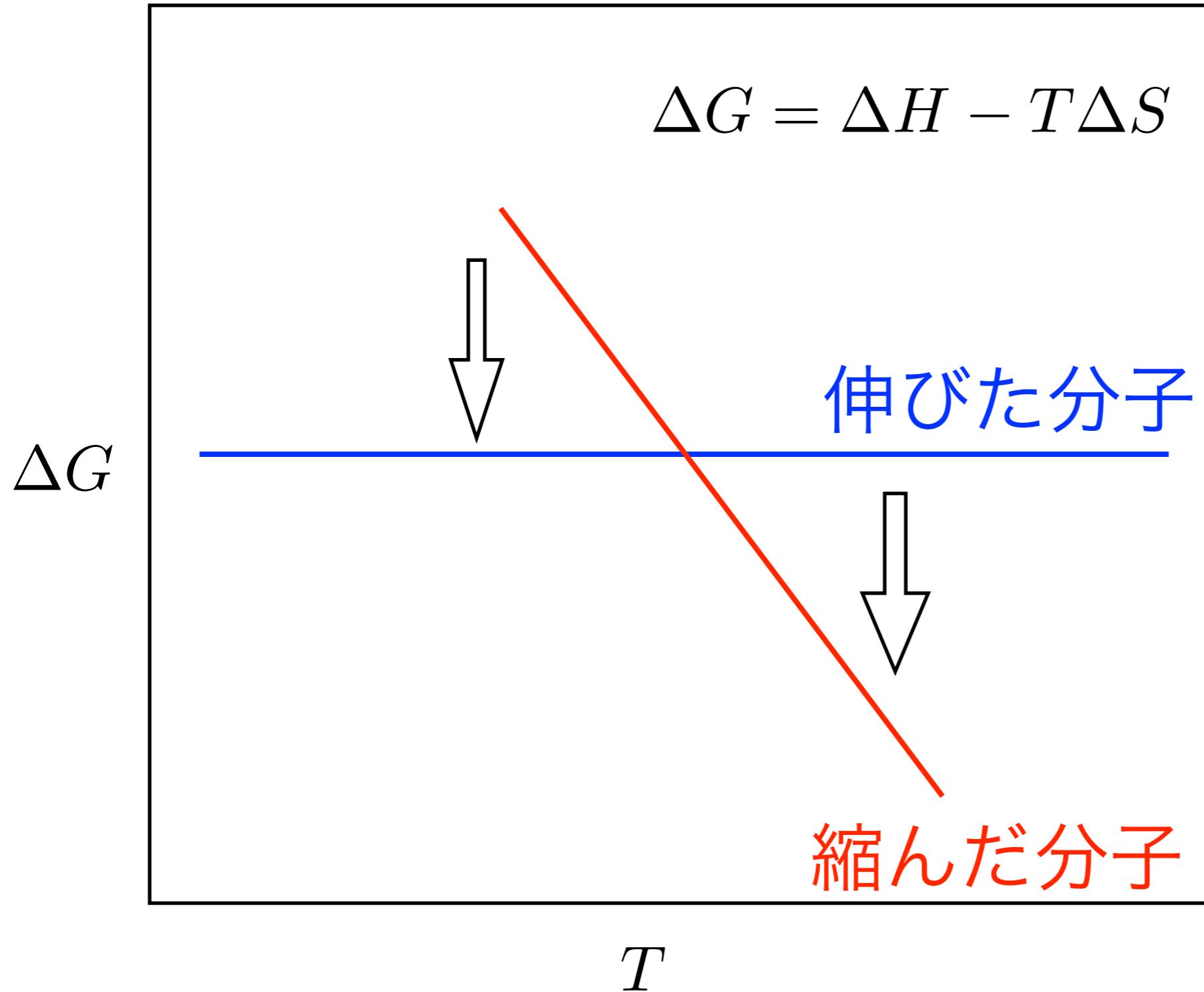
引力的

$A_2(\Theta) = 0$   
データ温度  $\Theta = 34.5$  °C

温度依存性？

(液中の高分子鎖間の相互作用)

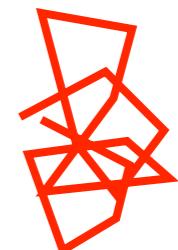
温度上昇により、金属は伸びゴムは縮む



伸びた分子  
乱雑さ↓  $S \approx 0$



縮んだ分子



乱雑さ↑  $S \uparrow$

$$\Delta S > 0$$

# 熱収縮性チューブ

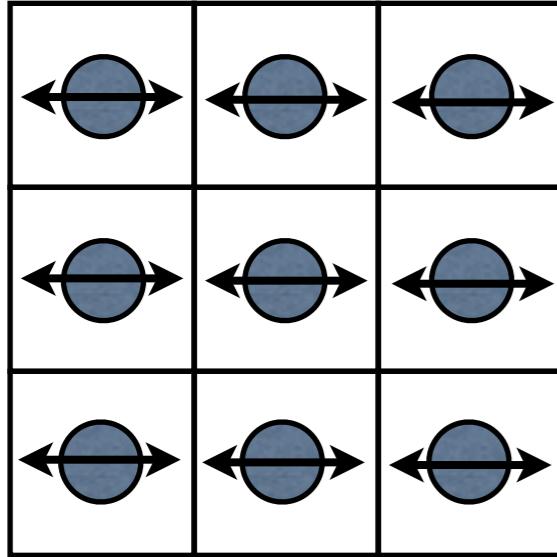
金属は伸びるゴムは縮む



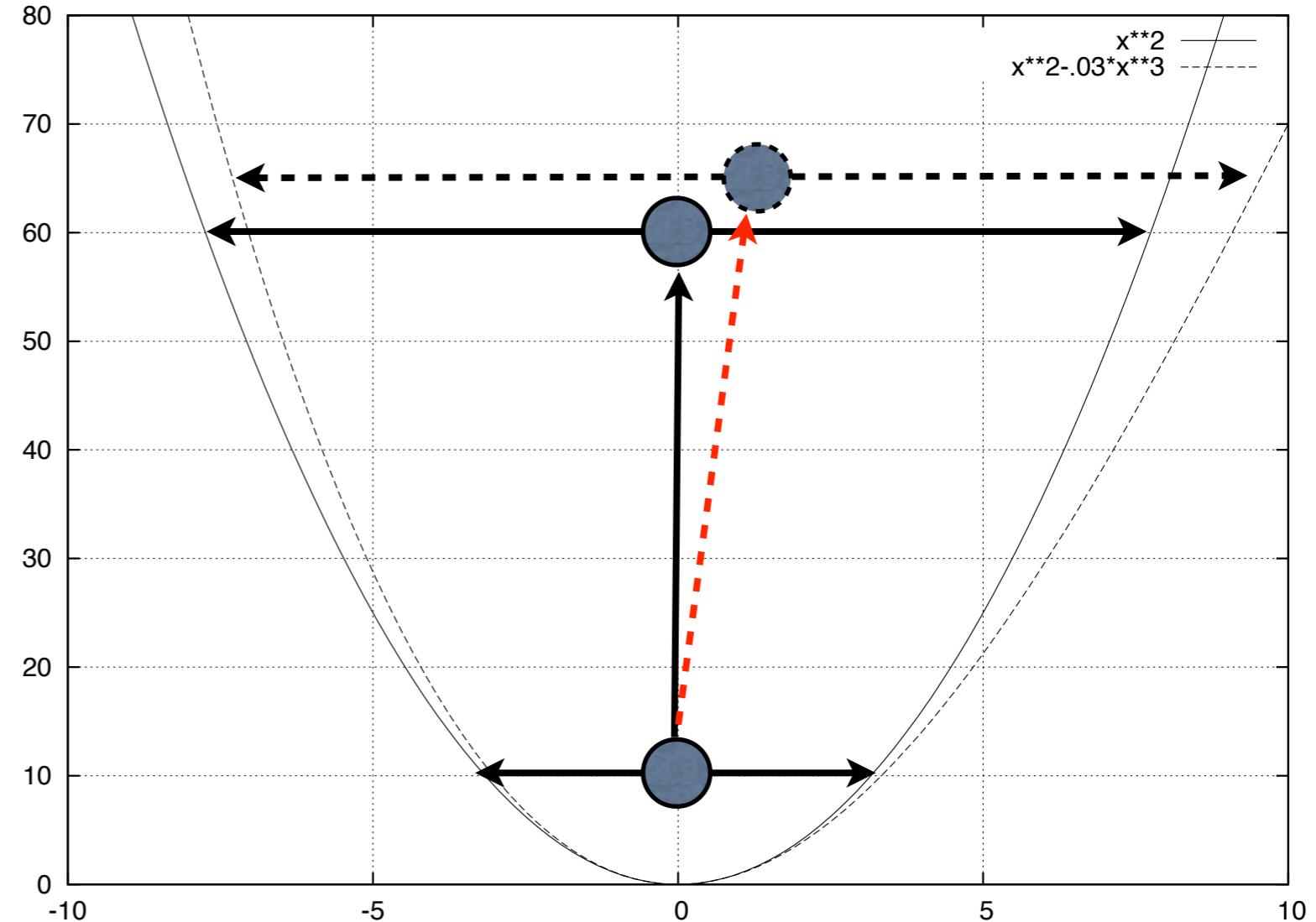
- 伸びた高分子間：ven der Waals引力相互作用
- 球状の高分子間：お互いに排除しあうので,  
斥力相互作用



固体：熱膨張



金属は伸びるゴムは縮む



調和振動( $U=kx^2$ )では温度が上がっても膨張しない

非調和性により ( $U=kx^2-\beta x^3$ ) で膨張