

**EXP7: Partial molar volume**

1. Although to a great extent the weights themselves enter into the calculations, it is necessary also to have the density  $d$  of every solution to within an accuracy of at least one part per thousand:

$$d = W_{\text{sol}}/V = W - W_g / V_p$$

The volume of the pycnometer  $V_p$  is obtained by use of the density of pure water at  $30.0^\circ\text{C}$ ,  $d_0$  (with the value  $0.9957 \text{ g} \cdot \text{cm}^{-3}$ ), and  $W_0 - W_e$ .

**(sol)** 先計算  $M$

- (1). 由  $\text{H}_2\text{O}$  計算  $V_p = W - W_e / d = ?$  其中:  $W = W_{\text{sol}} + W_e$   $W_e$ : 比重瓶重  $d$ : 查表  
 (2). 分別計算 4 瓶  $d = W - W_g / V_p$

dilution	1/8	1/4	1/2	1
$M_{\text{NaCl}}(\text{M})$				
$d(\text{g}/\text{cm}^3)$				

2. The molalities  $m$  (concentration in mole per Kg of solvent) which are needed for the calculations can be obtained from the molarities  $M$  (concentration in mole per liter of solution) obtained from the volumetric procedures by using the equation

$$m = 1 / (1 - (M/d \cdot M_2/1000)) \cdot M/d = 1 / (d/M - M_2/1000)$$

Where  $M_2$  is the solute molecular weight ( $58.45 \text{ g}/\text{cm}^3$ ) and  $d$  is the experimental density in  $\text{g} \cdot \text{cm}^{-3}$  units.

**(sol)**  $M_2 = 58.45 \text{ g}/\text{mol}$

由  $m = 1 / (d/M - M_2/1000)$  計算出 4 個  $m(\text{mol}/\text{Kg})$

3. Calculate  $\Phi$  for each solution using Eq. (7) and plot  $\Phi$  vs.  $m^{1/2}$ . Determine the slope  $d\Phi/dm^{1/2}$  and the intercept  $\Phi^0$  at  $m$  equal zero from the best straight line through these data points.

**(sol)**

(1) 計算出 4 個  $\Phi(\text{ml}/\text{mol})$

$$\Phi = 1/d (M_2 - (1000/m)(W - W_0)/(W_0 - W_e)) \text{ -----(7)}$$

$$\text{或} = 1/d (M_2 - (1000/m)(d - d_0)/(d_0))$$

(2)  $\Phi$  對  $m^{1/2}$  作圖

$\Phi(\text{ml}/\text{mol})$				
$m(\text{mol}/\text{kg})$				
$m^{1/2}(\text{mol}/\text{kg})^{1/2}$				

4. Calculate  $V_2$  and  $V_1$  for  $m = 0, 0.5, 1.0, 1.5, 2.0,$  and  $2.5$ . Plot them against  $m$  and draw a smooth curve for each of the two quantities

(sol)

(1)

$$V_1 = V_1^0 - m/55.51(m^{1/2}/2 \cdot d\Phi/dm^{1/2}) \dots\dots\dots(12)$$

$$V_2 = \Phi^0 + 3/2m^{1/2} \cdot d\Phi/dm^{1/2} \dots\dots\dots(11)$$

再由上式  $\Phi$  對  $m^{1/2}$  作圖得  $\Phi = a m^{1/2} + b$

可得  $m = 0$  時  $\Phi_0 =$

$$d\Phi/dm^{1/2} =$$

(2) 由  $\Phi_0$ 、 $d\Phi/dm^{1/2}$ 、及  $m = 0, 0.5, 1.0, 1.5, 2.0,$  and  $2.5$ . 分別代入(12)、(11) 求得 6 組  $V_1, V_2$

5. In your report, present the curves ( $\Phi$  vs.  $m, V^{1/2}$  and  $V_1$  vs.  $m$ ) mentioned above. Present also in tabular form the quantities  $d, M, m,$  and  $\Phi$  for each solution studied. Give the values obtained for the pycnometer volume  $V_p$  and for  $\Phi^0$  and  $d\Phi/dm^{1/2}$

dilution	H2O	1/8	1/4	1/2	1
$M_{NaCl}(M)$					
$d(g/ml)$					
$m(mol/kg)$					
$\Phi(ml/mol)$					

$V_1$  VS.  $m$  作圖一張及  $V_2$  VS.  $m$  作圖一張

$m(mol/kg)$	0	0.5	1	1.5	2	2.5
$V_1(cm^3/mol)$						

$m(mol/kg)$	0	0.5	1	1.5	2	2.5
$V_2(cm^3/mol)$						

## Exp.7

Wt. of NaCl	34.998 g
Molar conc. of NaCl	2.9944mole/L
$W_e$	27.197g
$T_{\text{exp't}}$	23.8°C
$d_{\text{water,exp't}}$	0.9974g/ml

room temperature	23.9°C
room pressure	747.1 mmHg

Run	H <sub>2</sub> O	1/8	1/4	1/2	1
$M_{\text{NaCl}}$	0	0.3743	0.7486	1.4972	2.9944
$W_{\text{sol'n}} + W_e$	77.123	77.915	78.674	80.137	82.888

Calculation (以 3 M 為例)

1.  $\text{NaCl}_{(\text{aq})}$  取 34.998 g

$$M_{\text{NaCl}} = \frac{n_{\text{NaCl}}}{V(L)} = \frac{\frac{34.998 (g)}{58.44 \left(\frac{g}{\text{mol}}\right)}}{0.200 (L)} = 2.994 (M)$$

2. 比重瓶體積

$$V_p = \frac{W_{\text{water}}}{d_{\text{water}}} = \frac{(W_{\text{sol'n}} + W_e) - W_e}{d_{\text{water}}} = \frac{77.145 - 27.197}{0.9974} = 50.078 (ml)$$

3. 密度(density) (以 3M 為例)

$$d_1 = \frac{w_1}{V_p} = \frac{(82.888 - 27.197)g}{50.078 ml} = 1.1121 \left(\frac{g}{ml}\right)$$

4. Molalities (m) (以 3M 為例)

$$m_1 = \frac{1}{\frac{d}{M} - \frac{M_{\text{NaCl}}}{1000}} = \frac{1}{\left(\frac{1.1121 \left(\frac{g}{ml}\right)}{2.9944 \left(\frac{mol}{L}\right)}\right) - \left(\frac{58.44 \left(\frac{g}{mol}\right)}{1000 \left(\frac{g}{kg}\right)}\right)} = 3.195 \left(\frac{mol}{kg}\right)$$

5.  $\phi$ (以 3M 為例)

$$\phi_1 = \frac{1}{d_1} \times \left( M_{\text{NaCl}} - \frac{1000}{m} \times \frac{d_1 - d_0}{d_0} \right)$$

$$\begin{aligned}
&= \frac{1}{1.1121 \left(\frac{g}{ml}\right)} \times (58.44 \left(\frac{g}{mol}\right) - \frac{1000}{3.195 \left(\frac{mol}{kg}\right)}) \\
&\quad \times \left( \frac{1.1121 \left(\frac{g}{ml}\right) - 0.9974 \left(\frac{g}{ml}\right)}{0.9974 \left(\frac{g}{ml}\right)} \right) \\
&= 20.194 \left(\frac{ml}{mol}\right)
\end{aligned}$$

6.  $\phi$  vs.  $\sqrt{m}$  (y 為  $\phi$  x 為  $\sqrt{m}$ )  $y=3.2448x+14.237$

$$\frac{d\phi}{d\sqrt{m}} = slope = 3.2448 \quad m=0 \text{ 時 } \phi^0 = 14.237 \left(\frac{ml}{mol}\right)$$

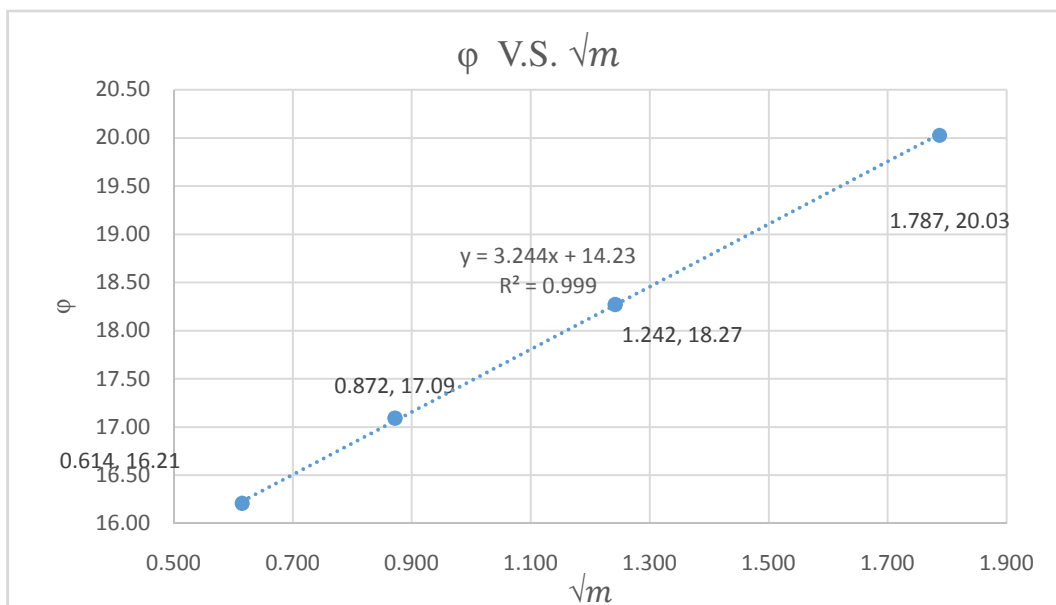
7.  $V_1$  &  $V_2$  以  $m=0.5$  為例

$$\begin{aligned}
\bar{V}_1 &= \bar{V}_1^0 - \frac{m}{55.51(mole)} \times \left( \frac{\sqrt{m}}{2} \times \frac{d\phi}{d\sqrt{m}} \right) \\
&= 18.063(ml) - \frac{0.5 \left(\frac{mole}{kg}\right)}{55.51 \left(\frac{mole}{kg}\right)} \\
&\quad \times \left( \frac{\sqrt{0.5} \left(\frac{mol^{0.5}}{kg^{0.5}}\right)}{2} \times 3.2448 \left(\frac{kg^{0.5}}{mol^{0.5}}\right) \right) \\
&= 18.053 \left(\frac{ml}{mol}\right)
\end{aligned}$$

$$\begin{aligned}
\bar{V}_2 &= \phi^0 + \left( \frac{3\sqrt{m}}{2} \times \frac{d\phi}{d\sqrt{m}} \right) \\
&= 14.237(ml) + \frac{3 \times \sqrt{0.5} \left(\frac{mole^{0.5}}{kg^{0.5}}\right)}{2} \times 3.2448 \left(\frac{kg^{0.5}}{mol^{0.5}}\right) \\
&= 17.679 \left(\frac{ml}{mol}\right)
\end{aligned}$$

$$\left(\bar{V}_1^0 = \frac{18.016}{d_{water}} = \frac{18.016}{0.9974} = 18.063 \left(\frac{cm^3}{mol}\right) \right)$$

Run	H <sub>2</sub> O	1/8	1/4	1/2	1
M <sub>NaCl</sub>	0	0.3743	0.7486	1.4972	2.9944
W <sub>sol'n</sub> + W <sub>e</sub>	77.123	77.915	78.674	80.137	82.888
W <sub>e</sub>	27.197				
W <sub>sol'n</sub>	49.926	50.718	51.477	52.94	55.691
d <sub>water</sub> (g/ml)	0.9974				
V <sub>p</sub> (ml)	50.056				
d <sub>sol'n</sub>	0.9974	1.0132	1.0284	1.0576	1.1126
m(mol/kg)	0	0.378	0.760	1.543	3.194
φ	0	16.21	17.09	18.27	20.03
√m	0.000	0.614	0.872	1.242	1.787



$d\psi/dm=$	3.2448		
$\psi^\circ=$	14.237	ml/mol	
m	V <sub>1</sub>	V <sub>2</sub>	$\sqrt{m}$
0.0	18.063	14.237	0.000
0.5	18.053	17.679	0.707
1.0	18.034	19.104	1.000
1.5	18.009	20.198	1.225
2.0	17.980	21.120	1.414
2.5	17.947	21.933	1.581

