

EXP3: Vapor Pressure of a Pure Liquid: Boiling Point Method

實驗計算：

1. 校正所有壓力計讀數。 $\Delta h_{corr.} = (h_R - h_L)(1 - 1.8 \times 10^{-5} t)$ ，其中 t 是壓力計的攝氏溫度。

(sol)

$$\Delta h \text{ (cmHg)} \rightarrow \Delta h_{corr.} \text{ (mmHg)} \rightarrow P \text{ (mmHg)} \rightarrow \log P$$

2. 繪製 $\log P$ 與 $1/T$ 並計算 ΔH_{vap} 。

(sol)

$$T(^{\circ}\text{C}) \rightarrow T(\text{K}) \rightarrow 1/\text{K}$$

$$\log P \text{ VS } 1/\text{K} \text{ 作圖 } d(\log P)/d(1/T) = -\Delta H/2.303R \cdots \cdots (1)$$

$$\text{slope} = d(\log P)/d(1/T) \text{ 其中 } R = 8.3145 \text{ J/K} \cdot \text{mol}$$

$$\Delta H_{vap} = ? \text{ kJ/mol}$$

1. 繪製 $\log P - 1/T$ 曲線，找出 $P = 760 \text{ mmHg}$ 時的溫度。將此值與正確的沸點進行比較。

(sol)

由圖 $\log P - 1/T$ 曲線， $\log P = -a(1/T) + b$ ， $P = 76 \text{ cmHg}$ 代入求 $T_{bp} = ?$

H_2O 理論值 100°C

$$\text{所以 error \%} = |100 - ?/100| \cdot 100\% = ?$$

2. 用 Trouton 的規則檢查結果。

(sol)

$$\text{Trouton rule: } \Delta S_{vap} = \Delta H_{vap} / T_{bp} = 21 \text{ cal/deg} \cdot \text{mol} = 87 \text{ J/deg} \cdot \text{mol}$$

ΔH_{vap} 由 2. T_{bp} 由 3. 得 ΔS_{vap}

$$\text{所以 error \%} = 87 - \Delta S_{vap} / 87 = ? (\text{取正值})$$

Exp.3

T _{room}	21.7	°C
P _{room}	750.0	mmHg

water									
	h _R (cmHg)	h _L (cmHg)	Δh(cmHg)	Δh _{corr} (mmHg)	P (mmHg)	logP	T(°C)	T(K)	1/K
60	80.40	19.18	61.22	609.8	140.2	2.1467	56.0	329.2	3.038E-03
50	74.51	24.99	49.52	493.3	256.7	2.4095	68.9	342.1	2.924E-03
40	69.88	29.69	40.19	400.3	349.7	2.5437	75.8	349.0	2.866E-03
30	64.72	34.85	29.87	297.5	452.5	2.6556	82.0	355.2	2.816E-03
20	59.80	39.80	20.00	199.2	550.8	2.7410	86.8	360.0	2.778E-03
10	54.85	44.78	10.07	100.3	649.7	2.8127	91.0	364.2	2.746E-03
0	49.90	49.70	0.20	2.0	748.0	2.8739	94.2	367.4	2.722E-03
n-heptane									
	h _R (cmHg)	h _L (cmHg)	Δh(cmHg)	Δh _{corr} (mmHg)	P (mmHg)	logP	T(°C)	T(K)	1/K
60	80.00	19.45	60.55	603.1	146.9	2.1669	43.5	316.7	3.158E-03
50	74.50	24.90	49.60	494.1	255.9	2.4081	56.5	329.7	3.034E-03
40	69.40	29.50	39.90	397.4	352.6	2.5472	64.4	337.6	2.963E-03
30	64.80	34.70	30.10	299.8	450.2	2.6534	71.0	344.2	2.906E-03
20	59.99	39.60	20.39	203.1	546.9	2.7379	75.8	349.0	2.866E-03
10	54.99	44.65	10.34	103.0	647.0	2.8109	80.0	353.2	2.832E-03
0	49.70	49.80	-0.10	-1.0	751.0	2.8756	84.0	357.2	2.800E-03

Calculation

(1) 以 water 為例

(a) 以 Δh=61.22(cmHg) 為例 T=21.7 °C

$$\begin{aligned}\Delta h_{corr} &= \Delta h \times (1 - (1.8 \times 10^{-4} \times T)) \\ &= 61.22 \text{ cmHg} \times (1 - (1.8 \times 10^{-4} \times 21.7^\circ\text{C})) \\ &= 609.8 (\text{mmHg})\end{aligned}$$

$$P = P_{room} - \Delta h_{corr} = 750.0 - 609.8 = 140.2 (\text{mmHg})$$

(b) log(P) vs. 1/T (for water)

$$\log(P) = a \times \frac{1}{T} + b$$

$$y = -2290.3x + 9.1051$$

$$\text{slope} = -2290.3 = \frac{d(\log P)}{d\left(\frac{1}{T}\right)} = -\frac{\Delta \bar{H}_{vap}}{2.303R}$$

$$\Delta \bar{H}_{vap} = 2290.3 (\text{K}) \times 2.303 \times 8.3145 \frac{\text{J}}{\text{K} \times \text{mol}} = 43.85 \left(\frac{\text{kJ}}{\text{mol}}\right)$$

(c) $\log(P)$ vs. $1/T$ (for n-heptane)

$$\log(P) = a \times \frac{1}{T} + b$$

$$y = -1974.1x + 8.3975$$

$$\text{slope} = -1974.1 = \frac{d(\log P)}{d\left(\frac{1}{T}\right)} = -\frac{\Delta \bar{H}_{vap}}{2.303R}$$

$$\Delta \bar{H}_{vap} = 1974.1(K) \times 2.303 \times 8.3145 \frac{J}{K \times mol} = 37.80 \left(\frac{kJ}{mol}\right)$$

(d) $T_{n,bp}$

For water

$$\log(P) = -2290.3 \frac{1}{T} + 9.1051$$

$$P=760 \text{ 時, } T=367.96 \text{ (K)}$$

For n-heptane

$$\log(P) = -1974.1 \frac{1}{T} + 8.3975$$

$$P=760 \text{ 時, } T=357.84 \text{ (K)}$$

(e) $\Delta S_{vap,n,bp}$

For water

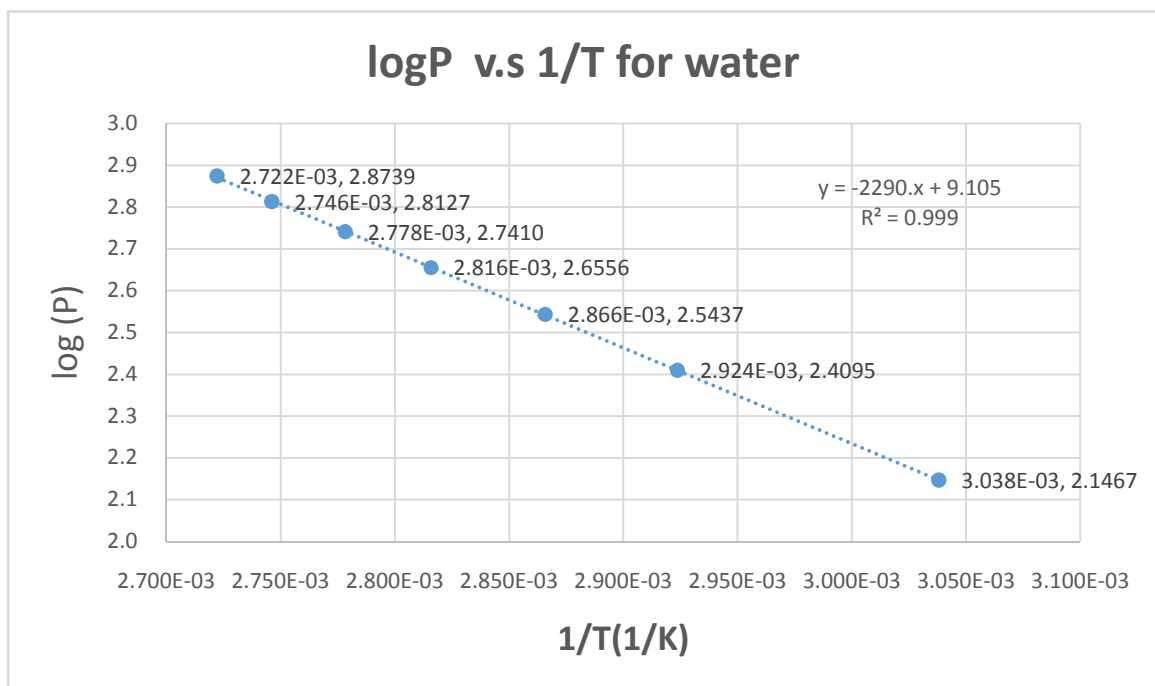
$$\Delta S_{vap,nbp} = \frac{\Delta \bar{H}_{vap,nbp}}{T_{nbp}} = \frac{43855 \left(\frac{J}{mol}\right)}{367.96 \text{ (K)}} = 119.19 \left(\frac{J}{K \times mol}\right)$$

For n-Heptane

$$\Delta S_{vap,nbp} = \frac{\Delta \bar{H}_{vap,nbp}}{T_{nbp}} = \frac{37800 \left(\frac{J}{mol}\right)}{357.84 \text{ (K)}} = 105.63 \left(\frac{J}{K \times mol}\right)$$

	Water	n-Heptane
A	-2290.3	-1974.1
B	9.1051	8.3975
ΔH_{vap}	43852	37799
$\log(760)$	2.881	2.881
T(K)	367.96	357.85
誤差(%)	1.392	3.696
Trouton's rule(J/K*mol)	119.178	105.630

$$y = Ax + B$$



logP v.s 1/T for n-heptane

