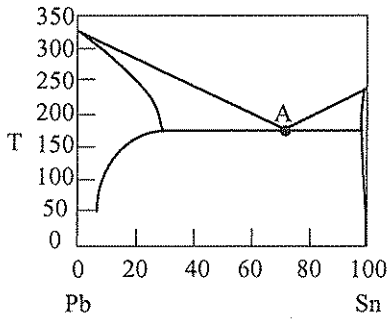
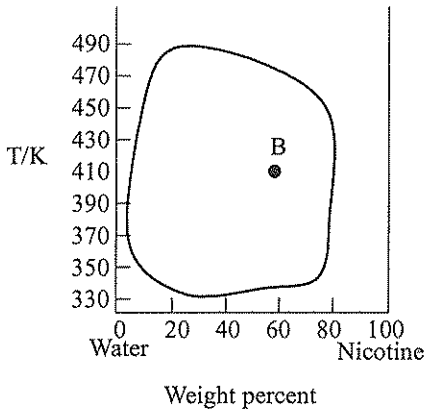
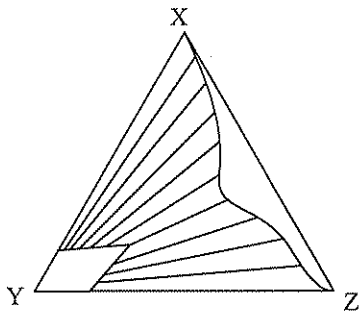
範例 6

(1)說明以下相圖中A、B兩點達成平衡各相之狀態及組成。 （12%）

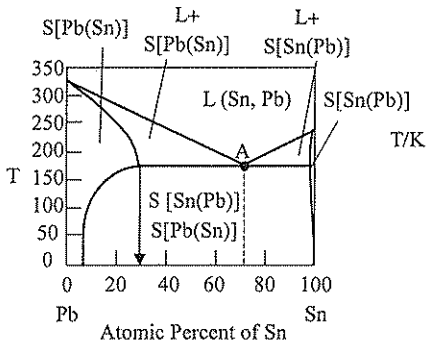


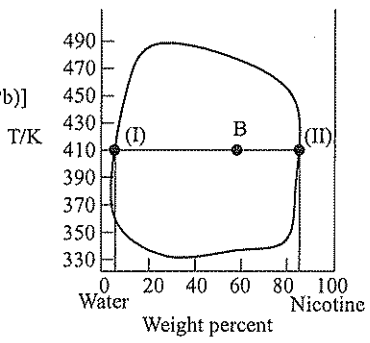


(2)根據以下相圖，說明當系統總組成比例為X：Y：Z＝1：1：1時，達成平衡各相之組成及其相對量比例。 （6%）（97台大化工）



Ans: (1)





Point A: eutectic point為三相共存點

Solid[Sn(Pb)]: 99%Sn +1%Pb.

Solid[Pb(Sn)]: 28%Sn +72%Pb.

Liquid[Pb, Sn]: 75%Sn +25%Pb.

Point B: Two partial miscible liquid, 分成兩相液相共存

(I) Liquid phase: 8%Nicotine +92%Water.

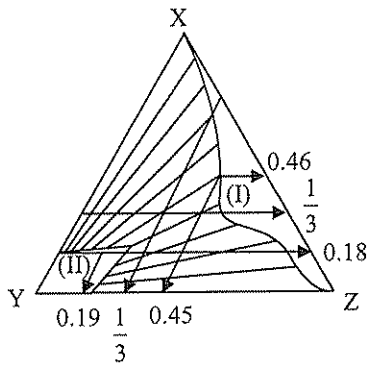
(II) Liquid phase: 83%Nicotine +17%Water.

(2) $X:Y:Z=1:1:1 \Rightarrow X\%=Y\%=Z\%=1/3$,

Two partial miscible liquid

(I) Liquid phase: $X\%=46\%, Y\%=9\%$ and $Z\%=45\%$.

(II) Liquid phase: $X\%=18\%, Y\%=63\%$ and $Z\%=19\%$.



範例 7

水的正常沸點為373.15K，又知道在溫度為293.15K時，水的蒸氣壓為2.339kPa，應用Clausius-Clapeyron方程式，且假設ΔH^{vap}與溫度無關，估算水的莫耳蒸發熱（heat of vaporization, ΔH^{vap}）為若干kJ/mol？（20%）（90化工技師）

Ans: $\ell n\left(\frac{P_2}{P_1}\right)=-\left(\frac{\Delta H^{vap}}{R}\right)(T_2^{-1}-T_1^{-1})$

$\Rightarrow \ell n\left(\frac{2339}{101325}\right)=-\left(\frac{\Delta H^{vap}}{R}\right)[(293.15)^{-1}-(373.15)^{-1}]$

$\Rightarrow \Delta H^{vap}=42.84\,(kJ/mol)$

範例 8

氯化氫固體和液體在不同的溫度下的飽和蒸氣壓分別為：

$\log P^{Vap} = 9.33902 - (1864.8/T)$ for solid (243~258K),

$\log P^{Vap} = 7.74460 - (1453.06/T)$ for liquid (265~300K),

其中壓力 P^{Vap} 與溫度T的單位分別為mmHg和K。氣體常數為 $R = 8.314 J/mol \cdot K$。試求氯化氫之下列性質：

(1)昇華熱（heat of sublimation）？

(2)汽化熱（heat of vaporization）？

(3)熔解熱（heat of fusion）？

(4)三相點（triple point）時之溫度及壓力？

(5)沸點（normal boiling point）？ （20%）（90化工高考二級）

Ans: (1) $\frac{\Delta H^{Sub}}{(2.303 \times R)} = 1864.8 \Rightarrow \Delta H^{Sub} = 35.0\ (kJ/mol)$

(2) $\frac{\Delta H^{Vap}}{(2.303 \times R)} = 1453.1 \Rightarrow \Delta H^{Vap} = 27.82\ (kJ/mol)$

(3) $\Delta H^{Sub} = \Delta H^{Fusion} + \Delta H^{Vap} \Rightarrow \Delta H^{Fusion} = 411.7\ (J/mol)$

(4) $9.33902 - (1864.8) \cdot T^{-1} = 7.74460 - (1453.06) \cdot T^{-1}$

$\Rightarrow T_{triple} = 258.23\ K$ ； $P_{triple} = 131.08\ mmHg$

(5) $\log(760) = 7.74460 - \left(\frac{1453.06}{T_b}\right) \Rightarrow T_b = 298.75\ K$

範例 9

二氧化碳的三相點（triple point）為−56.2°C，在此溫度以下，固體二氧化碳的蒸氣壓可由下式表示：

$\log P^{Vap} = 9.832 - (1353/T)$

其中壓力 P^{Vap} 的單位為mmHg，溫度T的單位為K。二氧化碳的熔解熱（heat of fusion）為1990 cal/g·mol。估計液體二氧化碳在5°C時的蒸氣壓為若干mmHg。 （20%）（85化工技師）

Ans: $\dfrac{\Delta H^{Sub}}{(2.303\times R)}=1353\Rightarrow \Delta H^{Sub}=6191.41\,(cal/mol)$ ；

$\Delta H^{Sub}=\Delta H^{Fusion}+\Delta H^{Vap}\Rightarrow \Delta H^{Vap}=4201.41\,(cal/mol)$

And $\log P_{triple}=9.832-\left[\dfrac{1353}{(273.15-56.2)}\right]\Rightarrow P_{triple}=3940.4\ mmHg$

$$\ell n\left(\frac{P_2}{P_{triple}}\right)=-\left(\frac{\Delta H^{Vap}}{R}\right)(T_2^{-1}-T_{triple}^{-1})$$

$$\Rightarrow \ell n\left(\frac{P_2}{3940.4}\right)=-\left(\frac{4201.41}{R}\right)[(278.15)^{-1}-(216.95)^{-1}]$$

$$\Rightarrow P_2=33691.1\ mmHg$$

範例 10

請由下列不同的溫度測得的硝酸蒸氣壓的實驗數據求出硝酸的汽化熱（ΔH^{Vap}）。

溫度／°C	0	20	40	70	90
壓力／Torr	14.4	47.9	133	467	937

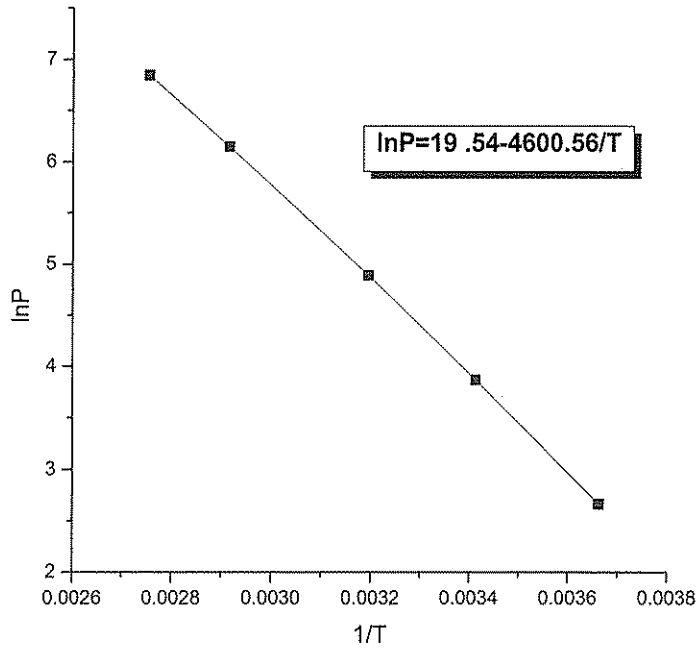
此方程式對解本題應該有幫助：$dP/dT=\Delta S/\Delta V$（20%）

（92公務人員升等考試）

Ans: $\dfrac{dP}{dT}=\dfrac{\Delta S}{\Delta V}=\dfrac{\Delta H}{(\Delta V\cdot T)}=\dfrac{\Delta H}{[(V_2-V_1)\cdot T]}=\dfrac{(P\cdot\Delta H)}{(R\cdot T^2)}$

$$\Rightarrow \ell nP=-\left(\frac{\Delta H}{R}\right)(T)^{-1}+C$$

So, $\Delta H^{Vap}=9141.5\,(cal/mol)$



範例 11

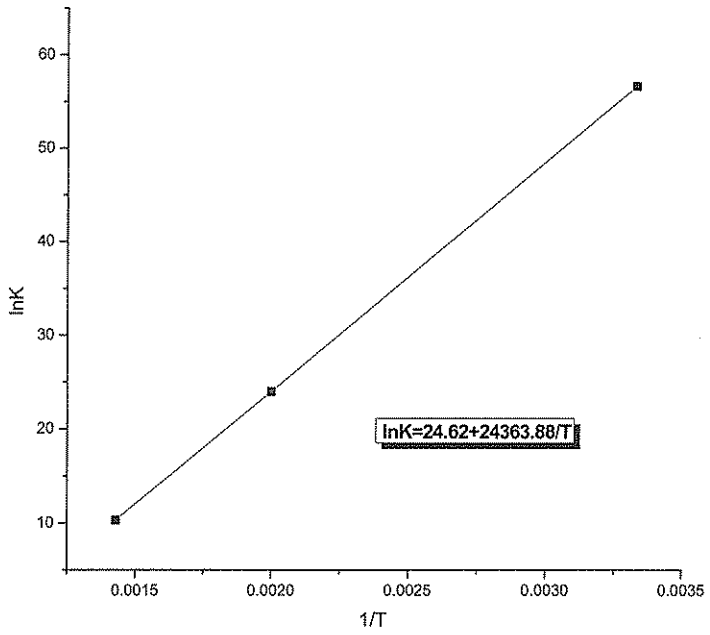
The equilibrium constant of the reaction $2SO_{2(g)} + O_{2(g)} = 2SO_{3(g)}$ is 4.0×10^{24} at 300 K, 2.5×10^{10} at 500 K, and 3.0×10^{4} at 700 K. Estimate the reaction enthalpy and entropy at 500 K. （10%）（90交大應化）

Ans: $\ell nK = -\left(\frac{\Delta H}{R}\right)(T)^{-1} + C$

So, $\Delta H_{reaction} = 48.41\,(kcal/mol)$

And $\Delta G = -RT\ell nK \Rightarrow \Delta G = -23.79\ kcal/mol$

$\Delta G = \Delta H - T\Delta S \Rightarrow \Delta S = 144\,(cal/mol \cdot K)$



範例 12

The following vapor pressure data is available for solid and liquid hydrogen cyanide.

T (K)	245	250	255	T (K)	270	280	290	300
P°, solid (mmHg)	53.4	75.8	106.2	P°, liquid (mmHg)	230.6	359.0	542.1	796.6

With the help of Clausius-Clapeyron equation and assume transition heat is independent of temperature, please calculate

(1)the heat of vaporization (cal/mol)

(2)the heat of fusion (cal/mol)

(3)the triple point (T = ? K, P = ? mmHg)

(4)the normal boiling point and

(5)the entropy of vaporization at the normal boiling point (cal/mol·K)?

（20%）（93淡江化材）