

一、选择题(20 分)

1. B

2. C

3. A

4. C

5. D

6. B

7. B

8. B

9. D

10. B

二、填空题(20 分)

1. 0

2. 1.9

3. <, <, <

4. 向右, 不

5. (1)  $\text{Pt} | \text{O}_2(\text{g}, p_2) | \text{H}^+(\text{aq}) | \text{O}_2(\text{g}, p_1) | \text{Pt}$

(2)  $\text{Pb} | \text{Pb}^{2+}(\text{a}_1) || \text{SO}_4^{2-}(\text{a}_2) | \text{PbSO}_4(\text{s}) | \text{Pb}$

6. 25.36

三、计算题(110 分)

1. (15 分, 只限统考生做)

$\text{S}(\text{正交}) \rightarrow \text{S}(\text{单斜})$

$$\Delta_r S_m^\theta = 32.55 - 31.88 = 0.67 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$\Delta_r H_m^\theta = -296.90 - (-297.19) = 0.29 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_r G_m^\theta = \Delta_r H_m^\theta - T \Delta_r S_m^\theta = 290 - 298.2 \times 0.67 = 90.206 \text{ J} \cdot \text{mol}^{-1}$$

因正交硫的密度  $\rho >$  单斜硫的密度  $\rho$ , 故正交硫的  $V_m <$  单斜硫的  $V_m$ , 加压会使平衡向  $V_m$  小的方向移动, 故加压也不可能变为单斜硫

2. (15 分, 只限单考生做)

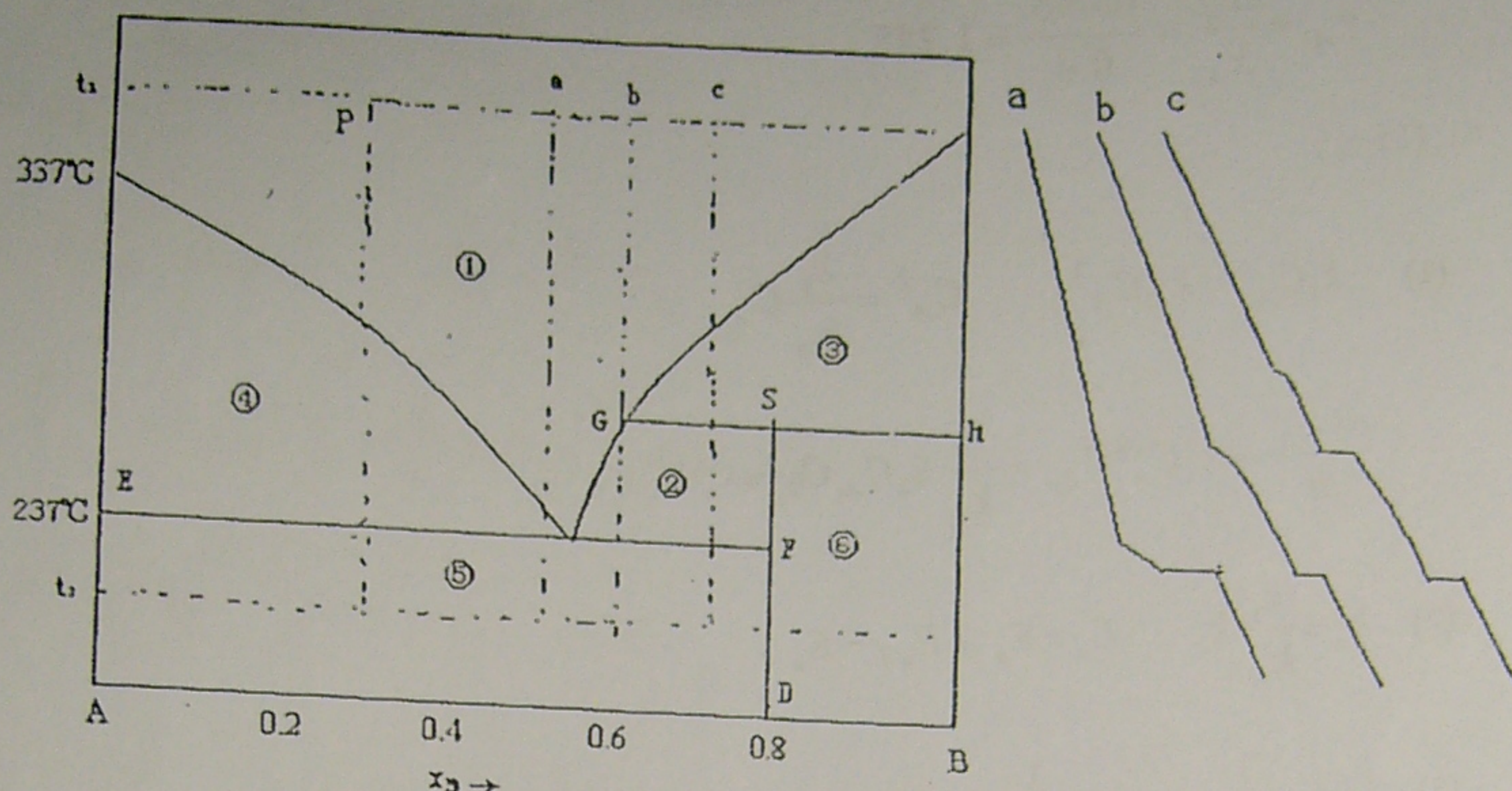
10g He 为 2.5mol



$$p = 11424 \text{ Pa}$$

5. (20 分, 单考生只做 (1)、(2)、(3))

(1) 步冷曲线;



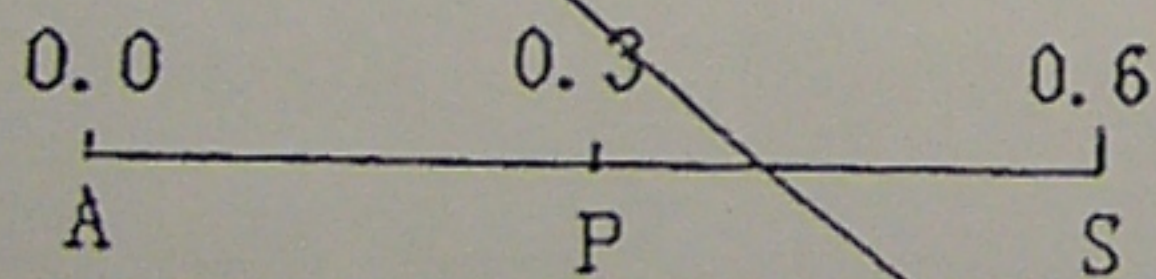
(2)

相区	①	②	③	④	⑤	⑥
相态	L	L+C <sub>s</sub>	L+B <sub>s</sub>	L+A <sub>s</sub>	A <sub>s</sub> +C <sub>s</sub>	C <sub>s</sub> +B <sub>s</sub>

水平线 EF, GH 的自由度为 0, 垂直线 DS 上体系的自由度为 1

(3) 此小题有两问题: ①共晶体是指什么? 应是低共熔点组成的固体。②未给出 A 与 B 的摩尔质量, 横坐标是摩尔分数, 无法进行计算。

如果给定的不是 1kg 而是 1000 mol 的话, 可计算如下:



$$\frac{n_c}{n} = \frac{\overline{AP}}{\overline{AS}} \quad n_c = \frac{\overline{AP}}{\overline{AS}} n = \frac{0.3}{0.6} \times 1000 = 500 \text{ mol}$$

(4) 在 337°C 时 (610 K):  $A(L) \rightarrow A(s)$

$$\Delta H = -18027 \text{ J} \cdot \text{mol}^{-1} \quad \Delta G = \Delta H - T\Delta S = 0$$

$$\Delta S = \Delta H/T = -18027/610 = -29.55 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

在 237°C 时 (510 K) 时:  $\Delta S$  和  $\Delta H$  仍同上。这时 A(s) 与共熔点液体  $x_B = 0.6$  ( $x_A = 0.4$ )

中 A 达平衡,  $\mu_A^*(s) = \mu_A(L) = \mu_A^*(L) + RT \ln a_A$



$$\Delta G = \mu_A^*(s) - \mu_A^*(L) = RT \ln a_A = \Delta H - T\Delta S = -18027 + 510 \times 29.55 = -2955 \text{ J}$$

$$a_A = \exp\left(\frac{\Delta G}{RT}\right) = \exp\left(\frac{-2955}{8.314 \times 510}\right) = 0.498$$

$$\gamma_A = \frac{a_A}{x_A} = \frac{0.498}{0.4} = 1.245$$

6. (15 分)

$$(1) \quad k_1 C_{A_2} = k_{-1} C_A^2 \quad C_A^2 = \frac{k_1}{k_{-1}} C_{A_2}$$

$$\frac{dC_{AB}}{dt} = k_2 C_A^2 C_{B_2} = \frac{k_1}{k_{-1}} k_2 C_{A_2} C_{B_2} = k_a C_{A_2} C_{B_2}$$

$$(2) \quad k_a = \frac{k_1}{k_{-1}} k_2 \quad E_a = E_{a1} + E_{a2} - E_{a-1}$$

$$(3) \quad t_{\frac{1}{2}} = \frac{1}{k_a C_{A,0}} = \frac{1}{1.60 \times 0.01} = 62.5 \text{ min}$$

7. (15 分)

$$(1) \quad \Gamma = -\frac{C}{RT} \frac{d\sigma}{dC} = -\frac{C}{RT} \left( -a \frac{b/C^\theta}{1+bC/C^\theta} \right) = \frac{abC/C^\theta}{RT(1+bC/C^\theta)}$$

$$(2) \quad \ln \frac{p_r}{p} = \frac{2M\sigma}{RT\rho r} = \frac{2 \times 18 \times 10^{-3} \times 0.072}{8.314 \times 298 \times 1.0 \times 10^3 \times 2 \times 10^{-9}} = 0.523$$

$$p_r = 1.687 \times 3.167 = 5.343 \text{ kPa}$$

$P = 4.5 \text{ kPa} < p_r$ , 故不能聚成水珠降落下来

8. (15 分, 只限统考生做)

电池  $\text{Ag}(s), \text{AgCl}(s) | \text{Cl}^-(aq) || \text{Ag}^+(aq) | \text{Ag}(s)$

(1) 阳极:  $\text{Ag} + \text{Cl}^- \rightarrow \text{AgCl}(s) + e$

阴极:  $\text{Ag}^+ + e \rightarrow \text{Ag}$

电池反应:  $\text{Ag}^+ + \text{Cl}^- \rightarrow \text{AgCl}(s)$

(2) 上述电池反应的  $K^\theta = 1/K_{sp}$

$$E^\theta = \frac{RT}{F} \ln K^\theta = -\frac{RT}{F} \ln K_{sp} = \varphi^\theta(\text{Ag}^+/\text{Ag}) - \varphi^\theta(\text{Cl}^-/\text{AgCl}(s), \text{Ag}) =$$



$$\Delta G = \mu_A^*(s) - \mu_A^*(L) = RT \ln a_A = \Delta H - T\Delta S = -18027 + 510 \times 29.55 = -2955 \text{ J}$$

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$$E^\theta = \frac{RT}{F} \ln K^\theta = -\frac{RT}{F} \ln K_{sp} = \varphi^\theta(\text{Ag}^+/\text{Ag}) - \varphi^\theta(\text{Cl}^-/\text{AgCl}(s), \text{Ag}) =$$



$$=0.7994-0.2224=0.577 \text{ V}$$

$$\ln K_{sp} = -\frac{FE^\theta}{RT} = -\frac{96485 \times 0.577}{8.314 \times 298} = -22.47$$

$$K_{sp} = 1.734 \times 10^{-10}$$

$$(3) Q_{r,m} = T\Delta S = ZFT \left( \frac{\partial E}{\partial T} \right)_p = 1 \times 96485 \times 298 \times 3.42 \times 10^{-4} = 9833 \text{ J} \cdot \text{mol}^{-1}$$

(4) AgCl 的溶解度很小, 对 I 影响可先忽略之。

$$I = \frac{1}{2} (b_+ Z_+^2 + b_- Z_-^2) = 0.01$$

$$\ln \gamma_{\pm} = -0.509 Z_+ Z_- \sqrt{I} = -0.509 \sqrt{0.01} = -0.0509 \quad \gamma_{\pm} = 0.889$$

$$K_{sp} = a_{Ag^+} \cdot a_{Cl^-} = b^2 \gamma_{\pm}^2 \quad b = \frac{\sqrt{K_{sp}}}{\gamma_{\pm}} = 1.485 \times 10^{-5} \text{ mol} \cdot \text{kg}^{-1}$$

9. (15 分, 只限单考生做)

电池  $\text{Cu(s)} | \text{Cu}(\text{Ac})_2(b=0.1 \text{ mol} \cdot \text{kg}^{-1}, \gamma_{\pm}=1) | \text{AgAc(s)}, \text{Ag(s)}$

(1) 阳极:  $\text{Cu} \rightarrow \text{Cu}^{2+} + 2e^-$

阴极:  $2\text{AgAc(s)} + 2e^- \rightarrow 2\text{Ag} + 2\text{Ac}^-$

电池反应:  $\text{Cu} + 2\text{AgAc(s)} \rightarrow \text{Cu}(\text{Ac})_2 + 2\text{Ag}$

$$(2) T=298 \text{ K 时}, E=0.327 \text{ V} \quad \left( \frac{\partial E}{\partial T} \right)_p = 2.0 \times 10^{-4} \text{ V} \cdot \text{K}^{-1}$$

$$\Delta_r G_m = -ZFE = -2 \times 96485 \times 0.327 = -63101 \text{ J} \cdot \text{mol}^{-1}$$

$$\Delta_r S_m = ZF \left( \frac{\partial E}{\partial T} \right)_p = 2 \times 96485 \times 2.0 \times 10^{-4} = 38.59 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$\Delta_r H_m = \Delta_r G_m + T\Delta_r S_m = -63101 + 298 \times 38.59 = -51600 \text{ J} \cdot \text{mol}^{-1}$$

$$(3) E = E^\theta - \frac{RT}{2F} \ln(a_+ a_-^2)$$

$$b=0.1 \text{ mol} \cdot \text{kg}^{-1}, \gamma_{\pm}=1 \quad b_+ = 0.1 \quad b_- = 0.2$$

$$E^\theta = E + \frac{RT}{2F} \ln(a_+ a_-^2) = 0.327 + \frac{8.314 \times 298}{2 \times 96485} \ln(b_+ b_-^2) = 0.2561 \text{ V}$$

$$E^\theta = \varphi^\theta(\text{Ac}^-/\text{AgAc(s)}, \text{Ag}) - \varphi^\theta(\text{Cu}^{2+}/\text{Cu})$$

$$\varphi^\theta(\text{Ac}^-/\text{AgAc(s)}, \text{Ag}) = E^\theta + \varphi^\theta(\text{Cu}^{2+}/\text{Cu}) = 0.2561 + 0.337 = 0.593 \text{ V}$$