2024秋物理化学1第三次测验

1. 偏摩尔量：广度函数 X 固定 p, T.

化学势：对自然变量

$$dU = TdS - pdV + \mu dn$$

$$dA = -SdT - pdV + \mu dn \quad \Rightarrow \quad C.$$

2.

$$\mu = \cancel{\mu^\ominus}\ \mu^* + RT\ln x \quad \Rightarrow D.$$

3. $\Pi \sim cRT$, glucose：几乎全部分子 $c = 0.01$

NaCl：Na^+, Cl^- $c = 0.02$.

$\Rightarrow C.$

4. 混合后，液相作用力比纯态减小 $\Rightarrow p_A > p_A^* x_A$.

液相体积增大 $\Rightarrow A.$

5. 不同相分配定律 $\Rightarrow A.$

都有挥发性，可能沸点降低.

6.

$$\mu^\ominus[c^\ominus] = \mu^\ominus[m^\ominus] + RT\ln \cancel{m[c^\ominus]}/m^\ominus. \quad \Rightarrow B.$$

$$m[c^\ominus] = \frac{1mol}{m[1L]}$$ 其未必是 1kg.

7.

$$\Delta T = 546 - 273 = T.$$

$$\Delta H = C_p \Delta T = \frac{5}{2} nRT.$$

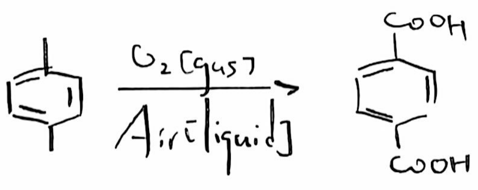
$$dH = TdS + Vdp \Rightarrow dS = \frac{C_p dT}{T} - \frac{V}{T}dp = \frac{C_p}{T}dT - \frac{nR}{p}dp$$

$$\Delta S = C_p \ln T_2/T_1 - nR\ln P_2/P_1$$
$$= \frac{5}{2} nR\ln 2 - nR\ln 1/2$$
$$= \frac{7}{2} nR\ln 2. \quad S_2 = S_1 + \Delta S = \frac{9}{2} nR\ln 2$$

$$\Delta G = \Delta H - \Delta(TS)$$
$$= \frac{5}{2} nRT - (2T \cdot \frac{9}{2} nR\ln 2 - T \cdot nR\ln 2)$$
$$= \frac{5}{2} nRT - 8nRT\ln 2.$$
$$\Delta\mu = \Delta G/n = (5/2 - 8\ln 2)RT.$$

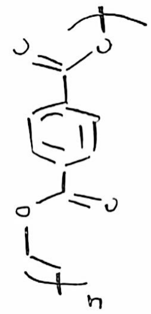
$$\Delta A = \Delta G - \Delta(pV) = \Delta G - nR\Delta T$$
$$= (3/2 - 8\ln 2)nRT. \Rightarrow C.$$

8.



$C_8H_6O_4$

PET:



$M = 166.128.$

理论 $n = m/M = 0.6862$ mol.

实际 $n = \frac{\Delta T}{k_b} \cdot 1\,kg = 0.1977$ mol

平均聚合度 $= 3.47 \approx 3 \Rightarrow D.$

9. $p_B = p(1-0.89) = 5.2503$ kPa $= k_{x,B}\, x \Rightarrow$

$k = 35.002$ kPa $\Rightarrow B.$

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10. 化学势平衡：

$$\mu_- + \mu_+ = 2\mu_\gamma = 0$$

体系热力学势判据：

$$dA = -SdT - pdV + \mu_+ dn_+ + \mu_- dn_-.$$

$$n_+ \longrightarrow \delta n_+.$$

$$\delta A = \mu_+ \delta n_+ + \mu_- \delta n_-$$

$$= \mu_+ \delta n_+ + \mu_- \frac{\partial n_-}{\partial n_+} \delta n_+$$

粒子数守恒：$\left(\frac{\partial n_-}{\partial n_+}\right)_{n_- - n_+} = 1 \Rightarrow$

$$\delta A = (\mu_+ + \mu_-)\delta n_+ = 0, \quad \text{i.e. 化学势平衡.}$$

$$\left(\frac{\partial A}{\partial n_+}\right)_{n_- - n_+} = \left(\frac{\partial A}{\partial n_+}\right)_{n_-}\left(\frac{\partial n_+}{\partial n_+}\right)_{n_- - n_+} + \left(\frac{\partial A}{\partial n_-}\right)_{n_+}\left(\frac{\partial n_-}{\partial n_+}\right)_{n_- - n_+}$$

$$= \mu_+ + \mu_- \Rightarrow A$$

$$dn_- - dn_+ = 0 \Rightarrow B.$$

11.

(1) 353K时蒸汽压下降：$p = p^* x \Rightarrow x = \frac{89330}{101325} = 0.88162$, 3' 2'

凝固点降低：$d\mu^l = d\mu^s \Leftrightarrow$ 固相 $x=1$

$$\left(\frac{\partial \mu^l}{\partial T}\right)_x dT + \left(\frac{\partial \mu^l}{\partial x}\right)_T dx = \left(\frac{\partial \mu^s}{\partial T}\right)_x dT + \left(\frac{\partial \mu^s}{\partial x}\right)_T dx. \Rightarrow$$

$$-S_m^l dT + RT/_x dx = -S_m^s dT \Rightarrow$$

$$d\ln x = \frac{S_m^l - S_m^s}{RT} dT = \frac{\Delta_{fus} H_m^\ominus}{RT^2} dT,$$

$$\ln x = -\frac{\Delta_{fus}H_m^{\ominus}}{R}\left(\frac{1}{T_f} - \frac{1}{T_f^*}\right) \Rightarrow T_f = 271.08. \quad 4' \quad 3'$$

(2)

$$x_{萘} = 1 - x = 0.11838 \Rightarrow n_{总} = 0.1 / x_{萘} = 0.8447 \text{ mol}$$

$$n_{苯} = 0.7447 \quad 2' \Rightarrow \Delta n = 0.1553 \text{ mol}. \quad 2'$$

12.

寻找状态 p, V 方程.

gas: $p_i = p^* + p_i^{Air}$ 3'

Henry: $p_i^{Air} = k\, c_i^{Air} = k\frac{n_i^{Air,l}}{V} \equiv k' n_i^{Air,l}$ 2' 2'

Air 物料守恒: $n_i^{Air,l} = n_0 - n_i^{Air,g}$ 3'

$$= n_0 - \frac{p_i^{Air} V_i}{RT} \quad 2'$$

故 $p_i - p^* = k'\left(n_0 - \frac{(p_i - p^*) V_i}{RT}\right)$ 4'

$i = 1, 2, 3 \Rightarrow$ 3 equations, denote (1). (2). (3)

$p^*, k', n_0 \Rightarrow$ 3 viriables.

(1)-(2): $p_1 - p_2 = \frac{k'(p_2 - p^*)V_2}{RT} - \frac{k'(p_1 - p^*)V_1}{RT}$ 3' (4)

(1)-(3): $p_1 - p_3 = \frac{k'(p_3 - p^*)V_3}{RT} - \frac{k'(p_1 - p^*)V_1}{RT}$ 3' (5)

(4)/(5): $\frac{p_1 - p_2}{p_1 - p_3} = \frac{(p_2 - p^*)V_2 - (p_1 - p^*)V_1}{(p_3 - p^*)V_3 - (p_1 - p^*)V_1}$ 3' $\Rightarrow$

$$p^* = 16.0998 \sim 16.10 \text{ kPa}. \quad 2'$$

13. 仅 $CaCO_3$ 发生分解.

分解 3.98mmol $\Rightarrow n'_{CaCO_3} = 11.10 - 3.98 = 7.12$ 3'

(1) $x_{CaCO_3} = 0.55887$. 2'

(2) $K^\theta = \frac{p_{CO_2}/p^\theta \cdot a_{CaO}}{a_{CaCO_3}}$ 4' $= \frac{\frac{1.01e+5}{1e+5}\cdot 1}{a_{CaCO_3}} \Rightarrow$ 3'

$a_{CaCO_3} = 0.28857$ 3' $= \gamma x_{CaCO_3} \Rightarrow$

$\gamma = 0.51635$. 2'

14.

(1) $\Phi = -pV \Leftrightarrow -pV = A - \mu_B n_B \Leftrightarrow \mu_B n_B = A + pV = G$. 4'

(2) $dU = +TdS - pdV + \mu_B dn_B$. 4'

(3) $U[S, V, n_B]$

$U \rightarrow \lambda U[S, V, n_B] = U[\lambda S, \lambda V, \lambda n_B] \Rightarrow$ 3'

$U[S, V, n_B] = \frac{\partial U[\lambda S, \lambda V, \lambda n_B]}{\partial(\lambda S)}\frac{\partial(\lambda S)}{\partial\lambda} + \frac{\partial U}{\partial(\lambda V)}\frac{\partial(\lambda V)}{\partial\lambda} + \frac{\partial U}{\partial(\lambda n_B)}\frac{\partial(\lambda n_B)}{\partial\lambda}$ 2' 4'

$= TS - pV + \mu_B n_B \Rightarrow$ 4'

$G = U + pV - TS = \mu_B n_B$. 2'

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