

北京化工大学 2019-2020 学年第二学期物理化学模拟试题参考答案:

一、选择题

1-2.

选择题: 在一定温度下、压力下, 某实际气体的 V_m 大于同温同压下的理想气体, 该气体的压缩因子 Z A.

- A. $Z > 1$ B. $Z = 1$ C. $Z < 1$ D. 无法确定

$$Z = \frac{pV_m}{RT} \quad V_m > V \Rightarrow pV_m > RT \Rightarrow Z > 1$$

选择题: 若在高压下, 某实际气体的行为所受到的影响用体积因子 b 来表示, 则描述该气体较合适的状态是 (C)

- A. $pV_m = RT + b$ B. $pV_m = RT - b$
C. $pV_m = RT + bp$ D. $pV_m = RT - bp$

$$\text{考虑分子本身体积进行体积校正, } p(V_m - b) = RT \Rightarrow pV_m = RT + bp$$

3. A 选项熵的定义式成立的条件必须是可逆过程, 选项中没有提到, 因此错误

B 选项熵增原理: 对于一个孤立系统, 可逆过程 $\Delta S = 0$, 本题中给的条件为封闭系统, 因此错误, 由于水凝成冰混乱度减小, 因此 ΔS 小于 0

C 选项对于状态函数来说, 只与过程的始末有关, 因此状态函数变等于始末状态函数之差, 此选项的条件为循环过程, 因此 $\Delta S = 0$, 选项正确

D 选项吉布斯判据: 可逆过程、平衡的过程 $\Delta G = 0$, 因此错误

4.

$$\begin{aligned} \textcircled{1} dH &= Tds + vdp \\ H &= f(s, p) \Rightarrow dH = \left(\frac{\partial H}{\partial s}\right)_p ds + \left(\frac{\partial H}{\partial p}\right)_s dp \quad \because T > 0 \quad v > 0 \\ \therefore \left(\frac{\partial H}{\partial s}\right)_p &= T > 0 \quad \left(\frac{\partial H}{\partial p}\right)_s = v > 0 \\ \textcircled{2} dG &= -sdT + vdp \\ G &= f(T, p) \Rightarrow dG = \left(\frac{\partial G}{\partial T}\right)_p dT + \left(\frac{\partial G}{\partial p}\right)_T dp \quad \because v > 0 \\ \therefore \left(\frac{\partial G}{\partial p}\right)_T &= v > 0 \\ \textcircled{3} \left(\frac{\partial G}{\partial p}\right)_T &= -\left(\frac{\partial V}{\partial T}\right)_p = -\frac{\alpha p}{\beta} < 0 \quad \text{因此选 B} \end{aligned}$$

5.D 6.C

7.D

1. D

$\Delta_f G_m^\ominus(\text{Ag}_2\text{O}, s)$ 等于反应 $2\text{Ag}(s) + \frac{1}{2}\text{O}_2(g) = \text{Ag}_2\text{O}(s)$ 的 $\Delta_r G_m^\ominus$

$$\Delta_f G_m^\ominus(\text{Ag}_2\text{O}, s) = \left[\frac{1}{2} \times (-22.40)\right] = -11.20 \text{ kJ/mol}$$

而 Ag 为稳定单质, $\Delta_f G_m^\ominus(\text{Ag}, s) = 0$

8.A

A $\Delta_r G_m^\ominus = -RT \ln K^\ominus$

$$\therefore \ln K^\ominus = -\Delta_r G_m^\ominus / RT = -\Delta_r H_m^\ominus / RT + \Delta_r S_m^\ominus / R$$

$$\because \Delta_r H_m^\ominus < 0, \Delta_r S_m^\ominus > 0$$

$$\therefore \ln K^\ominus > 0 \quad \text{即 } K^\ominus > 1$$

由 $\Delta_r H_m^\ominus < 0$, 放热反应, 因温度升高平衡向吸热方向移动, $\therefore K^\ominus$ 随温度升高减小

9.C B(l)沸点高, 为难挥发组分。一定温度下加入 B 之后系统的总压增大, 按照科诺瓦洛夫-吉布斯定律, 其气相组成 y_B 应大于其液相组成 x_B , 这是在 $p_A^* > p_B^*$ 的一般正偏差和一般负偏差系统的 p - x 图中不可能出现的, 只能存在与 p - x 图有极值点, 即最大正偏差或最大负偏差的系统中。

10.B

根据 $p_g = p_A^* x_A + p_B^* x_B = p_A^* + (p_B^* - p_A^*) x_B$

$$\text{有 } y_B = \frac{p_B}{p} = \frac{p_B^* x_B}{p_A^* + (p_B^* - p_A^*) x_B} = \frac{5 p_A^* x_B}{p_A^* + 4 p_A^* x_B} = \frac{5 x_B}{1 + 4 x_A} = \frac{1}{2}$$

解得 $x_B = 0.167$

二、填空题

1.

根据定义, 等压膨胀系数 $\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p$, 等压压力系数 $\beta = \frac{1}{p} \left(\frac{\partial p}{\partial T} \right)_V$, 等温压缩系数 $k = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T$,
 α, β, k 间的关系为 $\alpha = \beta \beta k$

$$\text{对一定量纯物质有 } \left(\frac{\partial p}{\partial T} \right)_V \left(\frac{\partial T}{\partial V} \right)_p \left(\frac{\partial V}{\partial p} \right)_T = -1$$

$$\text{则 } \alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p = -\frac{1}{V} \left(\frac{\partial p}{\partial T} \right)_V \left(\frac{\partial V}{\partial p} \right)_T = \beta \beta k$$

2. $W = -P_{\text{amb}} (V_2 - V_1) = -nR (T_2 - T_1) = -nR \Delta T = -8.314J$

3. 广延量 X 广延量 X

4.

$$\because \text{由反应 (3)} = \text{反应 (1)} - \text{反应 (2)} \times 2$$

$$\therefore \text{有 } \Delta_r G_{m,3}^\ominus = \Delta_r G_{m,1}^\ominus - 2 \Delta_r G_{m,2}^\ominus, \text{ 由 } \Delta_r G_m^\ominus = -RT \ln K^\ominus$$

$$\text{得 } K_3^\ominus = K_1^\ominus / (K_2^\ominus)^2$$

5. 达到平衡后 $C = 4 - 1 - 2 = 1$, $F = 1 - 2 + 1 = 0$, 再向其中加入 $\text{NH}_3(\text{g})$, 系统达到平衡后 $C = 4 - 1 - 1 = 2$, $F = 2 - 2 + 1 = 0$ 。

三、简答题

1. 适用于均相单组分(或组分一定的多组分)体系, 非体积功为 0 的任何过程; 或组成可变的多相多组分封闭体系, 非体积功为 0 的可逆过程。

2. 均相系统中各组分的偏摩尔量 X_i 并非完全独立, 有 $X = \sum_{i=1}^k n_i X_i$

对此式进行全微分得到 $dX = \sum_{i=1}^k (n_i dX_i + X_i dn_i)$ (1)

又因为 $X = X(T, p, n_1, n_2, \dots, n_k)$, 其全微分为

$$dX = \left(\frac{\partial X}{\partial T} \right)_{p, n_j} dT + \left(\frac{\partial X}{\partial p} \right)_{T, n_j} dp + \sum_{i=1}^k X_i dn_i$$
 (2)

联立式 (1)、式 (2) 即得吉布斯-杜亥姆方程

$$\sum_{i=1}^k n_i dX_i = \left(\frac{\partial X}{\partial T} \right)_{p, n_j} dT + \left(\frac{\partial X}{\partial p} \right)_{T, n_j} dp$$

在同温同压下简化为下式

$$\sum_{i=1}^k n_i dX_i = 0 \quad \text{或者} \quad \sum_{i=1}^k x_i dX_i = 0$$

它表达了无限小过程中各组分的偏摩尔量之间的变化值关系, 即 k 个偏摩尔量 x_i 中, 只有 $k-1$ 个是独立的。

3.

(1) 通过什么反应的 $\Delta_r H_m^\circ$ 和 $\Delta_r S_m^\circ$ 计算 $\Delta_r G_m^\circ$

$$\Delta_r G_m^\circ = \Delta_r H_m^\circ - T \Delta_r S_m^\circ \quad (1)$$

式中 $\Delta_r H_m^\circ = \sum_B \nu_B \Delta_f H_{m,B}^\circ = - \sum_B \nu_B \Delta_c H_{m,B}^\circ$

$$\Delta_r S_m^\circ = \sum_B \nu_B S_{m,B}^\circ \quad [\text{注: 用此式即算对}]$$

(2) 通过 $\Delta_f G_m^\circ$ 计算 $\Delta_r G_m^\circ$

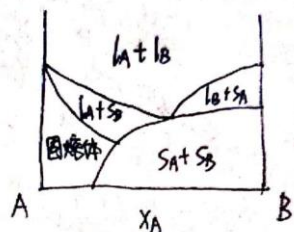
$$\Delta_r G_m^\circ = \sum_B \nu_B \Delta_f G_{m,B}^\circ$$

(3) 通过相关反应计算. 如果一个反应可由其他反应线性组合得到
则 $\Delta_r G_m^\circ$ 也可由相关反应的 $\Delta_r G_m^\circ$ 线性组合得到

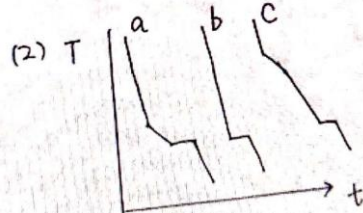
意思对即可得分.

4.

(1)



(2)



四、计算题

1

(1) 理想气体恒温可逆膨胀

$$\Delta U=0, \Delta H=0, Q=-W=nRT \ln \frac{V_2}{V_1}=1728.85 \text{ J}$$

$$\Delta S = \frac{Q_r}{T} = 5.76 \text{ J} \cdot \text{K}^{-1} \quad \therefore W = -1728.85 \text{ J}$$

$$(2) Q = -W = 50\% \quad W_r = 864.44 \text{ J} \quad W = -864.44 \text{ J}$$

$$\Delta S = 5.76 \text{ J} \cdot \text{K}^{-1}, \Delta U=0, \Delta H=0$$

$$(3) Q=0, W=0, \Delta U=0, \Delta H=0$$

$$\Delta S = 5.76 \text{ J/K}$$

2. 据题意

$$\gamma_A = \frac{P_A}{P_A^* x_A} = \frac{P y_A}{P_A^* x_A} = 0.254$$

$$\text{则活度 } \sigma_A = \gamma_A x_A = 0.181$$

3.

① 因系统恒容, 300°C 下 A 不分解, 则那一瞬时系统初始压力 $P_{A,0}$ 为

$$P_{A,0} = P_2 = \frac{T_2}{T_1} P_1 = \frac{573.15}{298.15} \times 53.33 \text{ kPa} = 102.5 \text{ kPa}$$

物料衡算: $A(g) = Y(g) + Z(g)$

$$\text{初始: } P_{A,0} \quad 0 \quad 0$$

$$\text{平衡: } P_A \quad P_{A,0}-P_A \quad P_{A,0}-P_A \quad \text{总压 } P = 2P_{A,0}-P_A$$

$$\text{因此有 } P_A = 2P_{A,0} - P = 18.3 \text{ kPa}$$

$$P_Y = P_Z = P_{A,0} - P_A = 84.2 \text{ kPa}$$

$$K^\theta = \frac{P_Y P_Z}{P_A P^\theta} = 3.874$$

$$\Delta_r G_m^\theta = -RT \ln K^\theta = -6.453 \text{ kJ/mol}$$

② 加入的 $Y(g)$ 考虑其初始压力 $P_{Y,0}$

$$P_{Y,0} = \frac{n_Y RT}{V} = \frac{0.02 \times 8.314 \times 573.15}{2 \times 10^{-3}} = 47.65 \text{ kPa}$$

物料衡算 $A(g) = Y(g) + Z(g)$

$$\text{初始: } P_{A,0} \quad P_{Y,0} \quad 0$$

$$\text{平衡: } P_A \quad (102.5 - P_A) \quad 47.65 + 102.5 - P_A$$

$$K^\theta = \frac{P_Y P_Z}{P_A P^\theta} = 3.874 = \frac{(47.65 + 102.5 - P_A) \times 102.5}{P_A (102.5 - P_A)}$$

$$\text{解得 } \alpha = 0.756$$

4.

解 (1) 101.3 kPa 的压力下, 系统共沸, 所以

$$p(\text{H}_2\text{O}) + p(\text{氯苯}) = 101.3 \text{ kPa}$$

$$y(\text{氯苯}) = \frac{p(\text{氯苯})}{p(\text{H}_2\text{O}) + p(\text{氯苯})} = \frac{29 \text{ kPa}}{101.3 \text{ kPa}} = 0.286$$

$$(2) \quad \frac{p(\text{H}_2\text{O})}{p(\text{氯苯})} = \frac{n(\text{H}_2\text{O})}{n(\text{氯苯})} = \frac{W(\text{H}_2\text{O})/M(\text{H}_2\text{O})}{W(\text{氯苯})/M(\text{氯苯})}$$

$$W(\text{H}_2\text{O}) = \frac{p(\text{H}_2\text{O})}{p(\text{氯苯})} \cdot \frac{W(\text{氯苯})}{M(\text{氯苯})} \cdot M(\text{H}_2\text{O})$$

$$= \left(\frac{101.3 - 29}{29} \times \frac{1000}{112.5 \times 10^{-3}} \times 18.02 \times 10^{-3} \right) \text{ kg} = 398.9 \text{ kg}$$

欲蒸出 1 000 kg 纯氯苯, 需消耗 398.9 kg 水蒸气。

五、证明题

1.

证明题: 某气体服从状态方程 $(p + \frac{a}{V_m^2})V_m = RT$ (设 a 为常数), 证明: 温度恒定时
(等温) 气体的热力学能随体积增大而增加

$$\text{证: } dU = TdS - pdV \quad \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial T}\right)_V - p$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - p = T\left(\frac{\partial p}{\partial T}\right)_V - p$$

$$(p + \frac{a}{V_m^2})V_m = RT \Rightarrow p = \frac{RT}{V_m} - \frac{a}{V_m^2} \Rightarrow \left(\frac{\partial p}{\partial T}\right)_V = \frac{R}{V_m}$$

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{RT}{V_m} - p = \frac{a}{V_m^2} > 0 \quad (a > 0)$$

2.

$$\text{解: } dU = TdS - pdV \quad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - p = T\left(\frac{\partial p}{\partial T}\right)_V - p$$

$$p = \frac{nRT}{V - nb} - \frac{n^2a}{V^2} \quad \left(\frac{\partial p}{\partial T}\right)_V = \frac{nR}{V - nb}$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T \frac{nR}{V - nb} - \frac{nRT}{V - nb} + \frac{n^2a}{V^2} = \frac{n^2a}{V^2}$$

$$\Delta U = \int_{V_1}^{V_2} \left(\frac{\partial U}{\partial V}\right)_T dV = \int_{V_1}^{V_2} \frac{n^2a}{V^2} dV = -n^2a \left(\frac{1}{V_2} - \frac{1}{V_1}\right)$$

$$W_r = \int_{V_1}^{V_2} -pdV = \int_{V_1}^{V_2} \frac{-nRT}{V - nb} dV + \int_{V_1}^{V_2} \frac{n^2a}{V^2} dV = -nRT \ln \frac{V_2 - nb}{V_1 - nb} - n^2a \left(\frac{1}{V_2} - \frac{1}{V_1}\right)$$

$$Q_r = \Delta U - W_r = nRT \ln \frac{V_2 - nb}{V_1 - nb}$$

$$\Delta S = \frac{Q_r}{T} = nR \ln \frac{V_2 - nb}{V_1 - nb}$$

$$\Delta A = \Delta U - T\Delta S = \Delta U - Q_r = W_r = -nRT \ln \frac{V_2 - nb}{V_1 - nb} - na^2 \left(\frac{1}{V_2} - \frac{1}{V_1}\right)$$