

中国科学院 & 中国科学技术大学

2004 年硕士学位研究生入学考试试题参考答案

二、计算题：（共 8 小题，75 分）

1. (10 分)

$$T_0 = 273 \text{ K}, T_1 = 373 \text{ K}, T_2 = 473 \text{ K}, P_1 = P^\ominus, P_2 = 3 \times P^\ominus,$$

$$\begin{aligned} \Delta H &= C_{p,m}(l)(T_1 - T_0) + \Delta_v H_m^\ominus + \int_{T_1}^{T_2} C_{p,m}(g) dT + \Delta_f H_m(g, T_2) \Big|_{P_1}^{P_2} \\ &= 75.4 \times 100 + 40600 + [36.86T - 3.975 \times 10^{-4} T^2 + 3.067 \times 10^{-7} T^3] \Big|_{373}^{473} + 0 \\ &= 7540 + 40600 + [17378 - 13709] \\ &= 51809 \text{ J} = 51.81 \text{ kJ} \end{aligned}$$

(5 分)

$$\begin{aligned} \Delta S &= \int_{T_0}^{T_1} \frac{C_{p,m}(l)}{T} dT + \frac{\Delta_v H_m^\ominus}{T_1} + \int_{T_1}^{T_2} \frac{C_{p,m}(g)}{T} dT + \int_{P_1}^{P_2} \left(\frac{\partial S}{\partial P} \right)_T dP \\ &= 75.4 \ln \frac{T_1}{T_0} + \frac{40600}{T_1} + [36.86 \ln \frac{T_2}{T_1} - 7.95 \times 10^{-4} (T_2 - T_1) + 4.60 \times 10^{-7} (T_2^2 - T_1^2)] - \int_{P_1}^{P_2} \left(\frac{\partial V}{\partial T} \right)_P dP \\ &= 75.4 \ln \frac{373}{273} + \frac{40600}{373} + [36.86 \ln \frac{473}{373} - 7.95 \times 10^{-4} (473 - 373) + 4.60 \times 10^{-7} (473^2 - 373^2)] - R \ln \frac{P_2}{P_1} \\ &= 23.53 + 108.85 + [8.755 - 0.0795 + 0.0389] - 8.314 \ln 3 \\ &= 131.96 \text{ J} \cdot \text{K}^{-1} \approx 132.0 \text{ J} \cdot \text{K}^{-1} \end{aligned}$$

(5 分)