

①  $q_{\text{lost by hot water}} = -q_{\text{gained by cold water}}$

$$m_1 c_{p,m} (T - T_1) = -m_2 c_{p,m} (T - T_2)$$

$$350\text{g} \times 4.814 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1} (T - 278\text{K}) = -500\text{g} \times 4.814 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1} (T - 343\text{K})$$

$$\Rightarrow T = 316.2 \text{ K}$$

$$\Delta S = \Delta S_1 + \Delta S_2 = m_1 c_p \ln \frac{T}{T_1} + m_2 c_p \ln \frac{T}{T_2}$$

$$= (350\text{g})(4.814 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}) \ln \frac{316.2}{278} + (500\text{g})(4.814 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}) \ln \frac{316.2}{343}$$

$$\Delta S = 21.11 \text{ J/K}$$

②  $\Delta S = nR \ln \left( \frac{V_f}{V_i} \right)$   $V_f = 100V_i$

$$\Delta S = 1 \text{ mol} \times 8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \ln \left( \frac{100V_i}{V_i} \right) = 38.29 \text{ J} \cdot \text{K}^{-1}$$

③  $\Delta G = nRT \ln \left( \frac{P_2}{P_1} \right)$   $P_2 = 0.1 \text{ atm}$  ,  $P_1 = 1 \text{ atm}$

$$T = 298 \text{ K} \quad R = 8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$\Delta G = 1 \text{ mol} \times 8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \times 298 \text{ K} \ln \left( \frac{0.1 \text{ atm}}{1 \text{ atm}} \right)$$

$$\Delta G = -5.705 \times 10^3 \text{ J} = -5.705 \text{ kJ}$$

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$$\Delta_{\text{vap}} S = \frac{\Delta_{\text{vap}} H}{T_b} = \frac{(0.50 \text{ mol}) (39.3 \times 10^3 \text{ J mol}^{-1})}{351.5 \text{ K}} = 56 \text{ J K}^{-1}$$

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$$\textcircled{5} q = \Delta_{\text{vap}} H = -40.79 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta S = \frac{\Delta_{\text{vap}} H}{T} = \frac{-40.79 \text{ kJ} \cdot \text{mol}^{-1}}{373 \text{ K}} = -0.109 \text{ kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

$$W = -P_{\text{ext}} \Delta V \quad \xrightarrow{\text{ideal gas}} \quad W = -P_{\text{ext}} (V_{\text{L}} - V_{\text{G}}) \quad \xrightarrow{V_{\text{G}} \gg V_{\text{L}}}$$

$$\rightarrow W = +P_{\text{ext}} V_{\text{G}} = P \times \frac{nRT}{P} = nRT$$

$$W = 1 \times 8.314 \times 373 = 3101.122 \text{ J} \cdot \text{mol}^{-1} = 3.101 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta U = q + W = 3.101 + (-40.79) = -37.69 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta G = \Delta H - T\Delta S = -40.79 \text{ kJ} \cdot \text{mol}^{-1} - (-40.79) = 0$$

$$\textcircled{b} \quad \Delta G = \Delta H - T\Delta S$$

a) isothermally and reversibly

$$\Delta S = \frac{q_{rev}}{T}$$

$$\Delta U = q + w$$

isothermal process  $\Rightarrow \Delta U = 0 \Rightarrow$

$$q = -w$$

$$w = -nRT \ln \frac{V_2}{V_1} = -(0.35 \text{ mol})(8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(288.8 \text{ K}) \ln \frac{7.4 \text{ L}}{1.2 \text{ L}}$$

$$w = -1.53 \times 10^3 \text{ J} = -q \Rightarrow q = 1.53 \times 10^3 \text{ J}$$

$$\Delta S = \frac{q_{rev}}{T} = \frac{1.53 \times 10^3 \text{ J}}{288.8 \text{ K}} = 5.3 \text{ J}\cdot\text{K}^{-1}$$

$$\Delta U = \Delta H = 0$$

$$\Rightarrow \Delta G = \overset{(\Delta H)}{0} - T\Delta S = 0 - (288.8 \text{ K})(5.3 \text{ J}\cdot\text{K}^{-1}) = -1.530 \times 10^3 \text{ J} = \boxed{-1.53 \text{ kJ}}$$

b) isothermally and irreversibly

$$\Delta U = 0 \Rightarrow \text{isothermal process} \rightarrow q = -w$$

$$w = -P_{ex}\Delta V = -(1.0 \text{ atm})(7.4 \text{ L} - 1.2 \text{ L}) \left( \frac{101.3 \text{ J}}{1 \text{ L}\cdot\text{atm}} \right) = -6.28 \times 10^2 \text{ J}$$

$$q = 6.28 \times 10^2 \text{ J}$$

$$\Delta S = -nRT \ln \frac{V_2}{V_1} = -(0.35 \text{ mol})(8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(288.8 \text{ K}) \ln \frac{7.4 \text{ L}}{1.2 \text{ L}}$$

$$\Delta S = 5.3 \text{ J}\cdot\text{K}^{-1}$$

$$\Delta H = 0$$

$$\Delta G = \Delta H - T\Delta S = 0 - (288.8 \text{ K})(5.3 \text{ J}\cdot\text{K}^{-1}) = \boxed{-1.53 \text{ kJ}}$$

$$\textcircled{7} \quad \ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta_{\text{vap}}H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta_{\text{vap}}H}{R} \left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

$$\ln\left(\frac{198 \text{ torr}}{3.82 \text{ torr}}\right) = \frac{\Delta H}{8.314} \left(\frac{200 - 150}{200 \times 150}\right)$$

$$\boxed{\Delta H = 19.69 \text{ kJ} \cdot \text{mol}^{-1}}$$

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$$\Delta_r G = \Delta_r H - T \Delta_r S < 0$$

$$19 \text{ kJ} - (345 \text{ K}) \Delta_r S < 0$$

$$\Delta_r S > \frac{19 \times 10^3 \text{ J}}{345 \text{ K}} = 55 \text{ J K}^{-1}$$

Therefore, the minimum  $\Delta_r S$  must be  $55 \text{ J K}^{-1}$ . At this value of  $\Delta_r S$ , the reaction is at equilibrium. At greater values of  $\Delta_r S$ , the reaction is spontaneous.

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At constant pressure,

$$\Delta S = n \bar{C}_p \ln \frac{T_2}{T_1} = \frac{5}{2} n R \ln \frac{T_2}{T_1} = \frac{5}{2} (3.5 \text{ mol}) (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \ln \frac{350 \text{ K}}{323 \text{ K}} = 5.8 \text{ J K}^{-1}$$

10-

The entropy of the mixture,  $S_f$ , is related to the entropy of mixing,  $\Delta_{\text{mix}}S$ , and the initial entropy of the system,  $S_i$ . Before these quantities can be calculated, the mole fractions of  $\text{O}_2$  and  $\text{N}_2$  need to be determined.

$$x_{\text{O}_2} = \frac{2.4 \text{ mol}}{2.4 \text{ mol} + 9.2 \text{ mol}} = 0.207$$

$$x_{\text{N}_2} = 1 - 0.207 = 0.793$$

The entropy of mixing is

$$\begin{aligned}\Delta_{\text{mix}}S &= -R (n_{\text{O}_2} \ln x_{\text{O}_2} + n_{\text{N}_2} \ln x_{\text{N}_2}) \\ &= - (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) [(2.4 \text{ mol}) \ln 0.207 + (9.2 \text{ mol}) \ln 0.793] \\ &= 49.2 \text{ J K}^{-1}\end{aligned}$$

The initial entropy of system is the sum of the entropies of  $\text{O}_2$  and  $\text{N}_2$ :

$$\begin{aligned}S_i &= n_{\text{O}_2} \bar{S}_{\text{O}_2} + n_{\text{N}_2} \bar{S}_{\text{N}_2} = (2.4 \text{ mol}) (205 \text{ J K}^{-1} \text{ mol}^{-1}) + (9.2 \text{ mol}) (192 \text{ J K}^{-1} \text{ mol}^{-1}) \\ &= 2.26 \times 10^3 \text{ J K}^{-1}\end{aligned}$$

Since  $\Delta_{\text{mix}}S = S_f - S_i$ ,

$$S_f = \Delta_{\text{mix}}S + S_i = 49.2 \text{ J K}^{-1} + 2.26 \times 10^3 \text{ J K}^{-1} = 2.3 \times 10^3 \text{ J K}^{-1}$$

## Bonus

The enthalpy change for the denaturation of the protein is positive. It is an endothermic process, requiring energy to break up the hydrogen bonds and van der Waals interactions present in the native form. Some energy is returned due to additional protein-solvent ( $\text{H}_2\text{O}$ ) intermolecular interactions in the denatured state. Nevertheless, the overall process is endothermic. Typical hydrogen bond enthalpies are  $10 - 15 \text{ kJ mol}^{-1}$ , so the value of  $512 \text{ kJ mol}^{-1}$  for  $\Delta \overline{H}^\circ$  indicates that approximately 40 more hydrogen bonds were broken than were formed. Since the denaturation process takes the specific, ordered native form to a random form,  $\Delta \overline{S}^\circ$  is expected to be positive, although solvent effects may also make a contribution.

The denaturation is spontaneous when  $\Delta G = \Delta H - T\Delta S < 0$ , or  $T > \frac{\Delta H}{\Delta S}$ . Since the values given are standard values, they apply only to a solution that is both  $1 \text{ M}$  in native form and  $1 \text{ M}$  in denatured form. For such a solution, the native form will spontaneously denature to reach a position of equilibrium when

$$\begin{aligned} T &> \frac{\Delta H^\circ}{\Delta S^\circ} \\ &> \frac{512 \text{ kJ mol}^{-1}}{1.60 \text{ kJ mol}^{-1}} \\ &> 320 \text{ K} = 47^\circ \text{ C} \end{aligned}$$