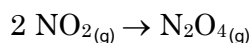


Show all work for credit. State any assumptions made to solve a problem. State all answers with the correct number of significant figures. All answers in scientific notation must be in proper scientific notation (i.e., 6.02×10^{23} not $6.02e23$ or $6.02e23$). Each instance of improper scientific notation will result in the loss of three (3) points. All numbers requiring units must have the units included. Each instance of numbers without units will result in the loss of three (3) points.

1. (28 pts) The dimerization reaction of nitrogen dioxide,



was analyzed at 300.0 K and 400.0 K and the equilibrium constants were determined at each temperature. At 300.0 K the equilibrium constant is 2.25×10^{-11} and at 400.0 K it is 2.53×10^{-12} . From these data, determine the values for $\Delta_r H^\circ$ and $\Delta_r S^\circ$.

$$\ln \frac{K_2}{K_1} = \frac{\Delta H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\Delta H^\circ = \frac{R \ln \frac{K_2}{K_1}}{\left(\frac{1}{T_1} - \frac{1}{T_2} \right)} = \frac{(8.314472 \text{ J mol}^{-1} \text{ K}^{-1}) \ln \frac{2.53 \times 10^{-12}}{2.25 \times 10^{-11}}}{\left(\frac{1}{300.0 \text{ K}} - \frac{1}{400.0 \text{ K}} \right)} = -21803.4989 \text{ J mol}^{-1} = -2.180 \times 10^4 \text{ J mol}^{-1}$$

$$\ln K = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

$$\Delta S^\circ = R \left(\ln K + \frac{\Delta H^\circ}{RT} \right) = (8.314472 \text{ J mol}^{-1} \text{ K}^{-1}) \left(\ln(2.25 \times 10^{-11}) + \frac{-21803.4989 \text{ J mol}^{-1}}{(8.314472 \text{ J mol}^{-1} \text{ K}^{-1})(300.0 \text{ K})} \right)$$

$$= -276.53 \text{ J mol}^{-1} \text{ K}^{-1}$$

2. (24 pts) 100.0 mL each of toluene (C_7H_8) and xylene (C_8H_{10}) are mixed together to make a solution. The density of toluene is 0.87 g cm^{-3} and it has a vapor pressure of 21.0 mmHg at 25°C . The density of xylene is 0.864 g cm^{-3} and it has a vapor pressure of 8.75 mmHg. What is the mole fraction of toluene in the vapor above the solution?

$$n_t = 100.0 \text{ mL} \times \frac{0.87 \text{ g t}}{1 \text{ mL}} \times \frac{1 \text{ mol t}}{92.141 \text{ g t}} = 0.944205 \text{ mol t}$$

$$n_x = 100.0 \text{ mL} \times \frac{0.864 \text{ g x}}{1 \text{ mL}} \times \frac{1 \text{ mol x}}{106.168 \text{ g x}} = 0.813805 \text{ mol x}$$

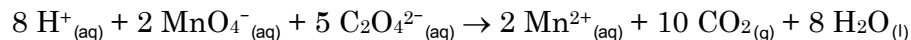
$$x_t = \frac{0.944205 \text{ mol}}{(0.944205 \text{ mol} + 0.813805 \text{ mol})} = 0.54$$

$$x_x = 1 - x_t = 0.46$$

$$P_{sol'n} = P_t^* x_t + P_x^* x_x = (21.0 \text{ mmHg})(0.54) + (8.75 \text{ mmHg})(0.46) = 15.39 \text{ mmHg}$$

$$x_{t,vap} = \frac{P_t^* x_t}{P_{sol'n}} = \frac{(21.0 \text{ mmHg})(0.54)}{15.39 \text{ mmHg}} = 0.74$$

3. (28 pts) An oxidation-reduction reaction occurs between the permanganate ion and the oxalate ion in acidic solution. The balanced net ionic equation is:



- a. Determine if this reaction as written is spontaneous at 15 °C.

Substance (data at 25 °C)	$\Delta_f H^\circ$ (kJ mol ⁻¹)	$\Delta_f G^\circ$ (kJ mol ⁻¹)	S° (J mol ⁻¹ K ⁻¹)
Aqueous permanganate ion	-541.4	-447.2	191.2
Aqueous manganese(II) ion	-220.7	-228.1	-73.6
Aqueous oxalate ion	-825.1	-673.9	45.6
Carbon dioxide gas	-393.509	-394.359	213.74
Liquid water	-285.8	-237.1	69.91
Aqueous hydrogen ion	0	0	0

$$\begin{aligned} \Delta_r H^\circ &= \sum_{\text{products}} \nu \Delta_f H^\circ - \sum_{\text{reactants}} \nu \Delta_f H^\circ \\ &= \left[\left(\frac{2 \text{ mol Mn}^{2+}}{\text{mol rxn}} \right) \left(\frac{-220.7 \text{ kJ}}{\text{mol Mn}^{2+}} \right) + \left(\frac{10 \text{ mol CO}_2}{\text{mol rxn}} \right) \left(\frac{-393.509 \text{ kJ}}{\text{mol CO}_2} \right) + \left(\frac{8 \text{ mol H}_2\text{O}}{\text{mol rxn}} \right) \left(\frac{-285.8 \text{ kJ}}{\text{mol H}_2\text{O}} \right) \right] \\ &\quad - \left[\left(\frac{16 \text{ mol H}^+}{\text{mol rxn}} \right) \left(\frac{0 \text{ kJ}}{\text{mol H}^+} \right) + \left(\frac{2 \text{ mol MnO}_4^-}{\text{mol rxn}} \right) \left(\frac{-541.4 \text{ kJ}}{\text{mol MnO}_4^-} \right) + \left(\frac{5 \text{ mol C}_2\text{O}_4^{2-}}{\text{mol rxn}} \right) \left(\frac{-825.1 \text{ kJ}}{\text{mol C}_2\text{O}_4^{2-}} \right) \right] \\ &= -1454.6 \text{ kJ mol}^{-1} \\ \Delta_r S^\circ &= \sum_{\text{products}} \nu S^\circ - \sum_{\text{reactants}} \nu S^\circ \\ &= \left[\left(\frac{2 \text{ mol Mn}^{2+}}{\text{mol rxn}} \right) \left(\frac{-73.6 \text{ J}}{\text{mol Mn}^{2+} \text{ K}} \right) + \left(\frac{10 \text{ mol CO}_2}{\text{mol rxn}} \right) \left(\frac{213.74 \text{ J}}{\text{mol CO}_2 \text{ K}} \right) + \left(\frac{8 \text{ mol H}_2\text{O}}{\text{mol rxn}} \right) \left(\frac{69.91 \text{ J}}{\text{mol H}_2\text{O} \text{ K}} \right) \right] \\ &\quad - \left[\left(\frac{16 \text{ mol H}^+}{\text{mol rxn}} \right) \left(\frac{0 \text{ J}}{\text{mol H}^+ \text{ K}} \right) + \left(\frac{2 \text{ mol MnO}_4^-}{\text{mol rxn}} \right) \left(\frac{191.2 \text{ J}}{\text{mol MnO}_4^- \text{ K}} \right) + \left(\frac{5 \text{ mol C}_2\text{O}_4^{2-}}{\text{mol rxn}} \right) \left(\frac{45.6 \text{ J}}{\text{mol C}_2\text{O}_4^{2-} \text{ K}} \right) \right] \\ &= 1939.1 \text{ J mol}^{-1} \text{ K}^{-1} \\ \Delta G^\circ &= \Delta H^\circ - T \Delta S^\circ = -1454.6 \times 10^3 \text{ J mol}^{-1} - (288 \text{ K})(1939.1 \text{ J mol}^{-1} \text{ K}^{-1}) = -2043.0 \times 10^3 \text{ J mol}^{-1} \end{aligned}$$

The reaction is spontaneous.

- b. Determine the equilibrium constant for this reaction at 15 °C.

$$K = e^{-\Delta G^\circ / RT} = e^{\frac{-(-2043.0 \times 10^3 \text{ J mol}^{-1})}{(8.314472 \text{ J mol}^{-1} \text{ K}^{-1})(288 \text{ K})}} = 1.2 \times 10^{365}$$

4. (20 pts) Calculate the freezing point, boiling point and vapor pressure of a solution that is made by dissolving 32.4463 g of sodium phosphate into 148.4699 g of water at 22.7 °C. The density of the solution is 1.233 g mL⁻¹. Assume the van't Hoff factor is the value expected from the chemical formula. The vapor pressure of water at 22.7 °C is 21.5 mmHg.

$$m = \frac{32.4463 \text{ g Na}_3\text{PO}_4 \times \frac{1 \text{ mol Na}_3\text{PO}_4}{163.9407 \text{ g Na}_3\text{PO}_4}}{148.4699 \text{ g H}_2\text{O} \times \frac{1 \text{ kg}}{10^3 \text{ g}}} = 1.33302967 \text{ m}$$

$$M = \frac{32.4463 \text{ g Na}_3\text{PO}_4 \times \frac{1 \text{ mol Na}_3\text{PO}_4}{163.9407 \text{ g Na}_3\text{PO}_4}}{(148.4699 \text{ g} + 32.4463 \text{ g}) \times \frac{1 \text{ mL}}{1.233 \text{ g}} \times \frac{10^{-3} \text{ L}}{1 \text{ mL}}} = 1.34885 \text{ M}$$

$$x_{\text{H}_2\text{O}} = \frac{148.4669 \text{ g H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18.0153 \text{ g H}_2\text{O}}}{\left(148.4669 \text{ g H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18.0153 \text{ g H}_2\text{O}} + (4)32.4463 \text{ g Na}_3\text{PO}_4 \times \frac{1 \text{ mol Na}_3\text{PO}_4}{163.9407 \text{ g Na}_3\text{PO}_4} \right)} = 0.9123574$$

$$\Delta T_f = -K_f m i = -(1.858 \text{ }^\circ\text{C m}^{-1})(1.33302967 \text{ m})(4) = -9.8867 \text{ }^\circ\text{C}$$

$$T_f' = T_f + \Delta T_f = 0.0000 \text{ }^\circ\text{C} + (-9.8867 \text{ }^\circ\text{C}) = -9.887 \text{ }^\circ\text{C}$$

$$\Delta T_b = K_b m i = (0.512 \text{ }^\circ\text{C m}^{-1})(1.33302967 \text{ m})(4) = 2.73004476 \text{ }^\circ\text{C}$$

$$T_b' = T_b + \Delta T_b = 100.0000 \text{ }^\circ\text{C} + (2.73004476 \text{ }^\circ\text{C}) = 102.73 \text{ }^\circ\text{C}$$

$$P = x_w P_w^* = (0.9123574)(21.5 \text{ mmHg}) = 19.6 \text{ mmHg}$$

5. (25 pts) The normal boiling point of cyclohexane, C_6H_{12} , is $80.7\text{ }^\circ\text{C}$. Estimate the temperature at which the vapor pressure of cyclohexane is 100.0 mmHg . (Hint: Use Trouton's Rule).

$$\Delta_{\text{vap}}S \approx 87\text{ J mol}^{-1}\text{ K}^{-1}$$

$$\Delta_{\text{vap}}H = T\Delta_{\text{vap}}S = (353.9\text{ K})(87\text{ J mol}^{-1}\text{ K}^{-1}) = 30784.95\text{ J mol}^{-1}$$

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

$$\frac{1}{T_1} = \frac{R \ln \frac{P_2}{P_1}}{\Delta_{\text{vap}}H} + \frac{1}{T_2} = \frac{(8.314472\text{ J mol}^{-1}\text{ K}^{-1}) \ln \frac{760.0\text{ mmHg}}{100.0\text{ mmHg}}}{30784.95\text{ J mol}^{-1}} + \frac{1}{353.9\text{ K}} = 3.37342403369 \times 10^{-3}\text{ K}^{-1}$$

$$T_1 = 296.4\text{ K} = 23.3\text{ }^\circ\text{C}$$

6. (25 pts) A saturated solution prepared at 70 °C contains 32.0 g CuSO₄ g per 100.0 g solution. A 335 g sample of this solution is then cooled to 0 °C and CuSO₄ · 5H₂O crystallizes out. If the concentration of a saturated solution at 0 °C is 12.5 g CuSO₄/100 g soln, what mass of CuSO₄ · 5H₂O would be obtained? [Hint: Note that the solution composition is stated in terms of CuSO₄ and that the solid that crystallizes is the hydrate CuSO₄ · 5H₂O]

$$g_{\text{CuSO}_4,70} = 335 \text{ g sol'n} \times \frac{32.0 \text{ g CuSO}_4}{100.0 \text{ g sol'n}} = 107.2 \text{ g CuSO}_4$$

$$g_{\text{CuSO}_4,0} = 335 \text{ g sol'n} \times \frac{12.5 \text{ g CuSO}_4}{100.0 \text{ g sol'n}} = 41.875 \text{ g CuSO}_4$$

$$g_{\text{CuSO}_4,\text{ppt}} = 107.2 \text{ g} - 41.875 \text{ g}$$

$$= 65.325 \text{ g CuSO}_4 \times \frac{1 \text{ mol CuSO}_4}{159.609 \text{ g CuSO}_4} \times \frac{1 \text{ mol CuSO}_4 \cdot 5\text{H}_2\text{O}}{1 \text{ mol CuSO}_4} \times \frac{249.686 \text{ g CuSO}_4 \cdot 5\text{H}_2\text{O}}{1 \text{ mol CuSO}_4 \cdot 5\text{H}_2\text{O}}$$

$$= 102.19 \text{ g CuSO}_4 \cdot 5\text{H}_2\text{O} = 1.0 \times 10^2 \text{ g CuSO}_4 \cdot 5\text{H}_2\text{O}$$