

Solutions

Solution 1:

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$$\Delta_{\text{vap}}H_m = T \Delta_{\text{vap}}S_m \approx (334.8 \text{ K})(88 \text{ J K}^{-1} \text{ mol}^{-1}) = 2.95 \times 10^4 \text{ J mol}^{-1}$$

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

$$\ln\left(\frac{P_2}{1.00 \text{ atm}}\right) \approx -\frac{29500 \text{ J mol}^{-1}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}} \left(\frac{1}{323.15 \text{ K}} - \frac{1}{334.8 \text{ K}}\right) \approx -0.382$$

$$P_2 = (1.000 \text{ atm})e^{-0.382} = 0.68 \text{ atm} = 520 \text{ torr} = 69 \text{ kPa}$$

Solution 2:

a. Since the activities of the solids are nearly equal to unity,

$$K = \frac{a_{\text{eq}}(\text{CaO})a_{\text{eq}}(\text{CO}_2)}{a_{\text{eq}}(\text{CaCO}_3)} \approx a_{\text{eq}}(\text{CO}_2) \approx \frac{P_{\text{eq}}(\text{CO}_2)}{p^\circ}$$

b. From the Gibbs energy changes of formation

$$\begin{aligned} \Delta G^\circ &= (1)(-603.501 \text{ kJ mol}^{-1}) - 394.389 \text{ kJ mol}^{-1} \\ &\quad + (-1)(-1128.79 \text{ kJ mol}^{-1}) \\ &= 130.90 \text{ kJ mol}^{-1} \end{aligned}$$

$$\begin{aligned} K &= \exp\left[-\frac{130900 \text{ J mol}^{-1}}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}\right] \\ &= 1.17 \times 10^{-23} \end{aligned}$$

$$\begin{aligned} P_{\text{eq}}(\text{CO}_2) &= (p^\circ)(1.17 \times 10^{-23}) \\ &= 1.17 \times 10^{-23} \text{ bar} = 1.15 \times 10^{-23} \text{ atm} \end{aligned}$$

This equilibrium constant is strongly temperature-dependent and becomes much larger at higher temperatures. At high temperatures this reaction is used to make CaO(s) ("quicklime") commercially from limestone.

Solution 3:

Spontaneous means ΔG should be negative

$$\Delta G = nRT \ln(p_2/p_1)$$

$$= 2.0 \times 8.314 \times 273 \times \ln(1/2)$$

$$= -3.147.06 \text{ J}$$

Solution 4:

We have 50 g copper at 393 K and 100 g copper at 303 K. The temperature of the two bodies when they have come to thermal equilibrium can be calculated as follows.

Heat gain = Heat loss

$$m_1 C_p (\Delta T_1) = m_2 C_p (\Delta T_2)$$

$$\text{i.e. } m_1 \Delta T_1 = m_2 \Delta T_2$$

$$100 \text{ g} \times (T - 303 \text{ K}) = 50 \text{ g} \times (393 \text{ K} - T)$$

$$T = 333 \text{ K}$$

$$\Delta S_h = n C_{p,m} \ln (T/T_h)$$

$$= (50 \text{ g} / 63 \text{ g mol}^{-1}) [(0.4184 \text{ J g}^{-1} \text{ K}^{-1}) (63 \text{ g mol}^{-1})] \times 2.303 \log (333/393)$$

$$= -3.466 \text{ JK}^{-1}$$

$$\Delta S_c = n C_{p,m} \ln (T/T_c)$$

$$= (100 \text{ g} / 63 \text{ g mol}^{-1}) [(0.4184 \text{ J g}^{-1} \text{ K}^{-1}) (63 \text{ g mol}^{-1})] \times 2.303 \log (333/303)$$

$$= 3.951 \text{ JK}^{-1}$$

$$\Delta S_{\text{total}} = \Delta S_c + \Delta S_h = 0.485 \text{ JK}^{-1}$$

Solution 5:

$$\text{a) } \Delta S(\text{gas}) = nR \ln (V_f/V_i) = (21 \text{ g} / 39.95 \text{ g mol}^{-1}) * (8.314 \text{ JK}^{-1} \text{ mol}^{-1}) \ln (4.6/1.2) = +\mathbf{5.867 \text{ JK}^{-1}}$$

$$\Delta S(\text{surrounding}) = -\Delta S(\text{gas}) = \mathbf{-5.867 \text{ JK}^{-1} \text{ (REVERSIBLE)}}$$

$$\Delta S(\text{total}) = \mathbf{0}$$

$$\text{b) } \Delta S(\text{gas}) = +\mathbf{5.867 \text{ JK}^{-1} \text{ (S is a state function)}}$$

$$\Delta S(\text{surrounding}) = \mathbf{0 \text{ (no change in surroundings)}}$$

$$\Delta S(\text{total}) = +\mathbf{5.867 \text{ JK}^{-1}}$$

$$\text{c) } q_{\text{rev}} = 0 \text{ so } \Delta S(\text{gas}) = \mathbf{0}$$

$$\Delta S(\text{surrounding}) = \mathbf{0 \text{ (no heat is transferred to the surroundings)}}$$

$$\Delta S(\text{total}) = \mathbf{0}$$

Solution 6:

$$\text{a) } \varepsilon = 1 - T_c/T_h = 1 - (500 \text{ K} / 1000 \text{ K}) = \mathbf{0.5}$$

$$\text{b) Maximum work} = \varepsilon \{q_h\} = 0.5 * 1 \text{ kJ} = \mathbf{0.5 \text{ kJ}}$$

$$\text{c) } \varepsilon_{\text{max}} = \varepsilon_{\text{rev}} \quad \{w_{\text{max}}\} = \{q_h\} - \{q_{c,\text{min}}\}$$

$$\begin{aligned} \dot{Q}_{c,\min} &= \dot{Q}_h - \dot{W}_{\max} \\ &= 1.0 \text{ kJ} - 0.5 \text{ kJ} = \mathbf{0.5 \text{ kJ}} \end{aligned}$$

Solution 7:

$$\begin{aligned} dP/dT &= \Delta_{\text{vap}}H / T (V_g - V_l) \text{ (Clapeyron Equation)} \\ &= (40,690 \text{ J mol}^{-1}) / (373.15 \text{ K})(30.180 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}) \\ &= 3613 \text{ Pa K}^{-1} \end{aligned}$$

$$\text{Thus } dT/dP = 1/3613 = 2.768 \times 10^{-4} \text{ K Pa}^{-1}$$

Solution 8:

