Chemistry 2720 Fall 2003 Test 1 Solutions

1. (a) The following combinations of coins all add up to 10¢:

$$10¢$$
$$2 \times 5¢$$
$$5¢ + 5 \times 1¢$$
$$10 \times 1¢$$

There are 4 microstates, so
$$S = k_B \ln 4.$$

(b) We see here a very clear illustration of entropy as a measure of our ignorance. The number of microstates is purely a function of our lack of knowledge of anything but the total amount which our friend has in his pocket.

(c) If we knew that one of the coins was a 5¢ piece, then two of the above possibilities would be eliminated and the entropy would decrease (to $k_B \ln 2$) as our knowledge of the system increased.

2. Suppose that this process actually occurred. Then

$$
\begin{aligned}
\Delta S_{\text{glass}} &= C_P \ln\left(\frac{T_2}{T_1}\right) \\
&= (1200\,\text{J/K}) \ln\left(\frac{323.15\,\text{K}}{293.15\,\text{K}}\right) \\
&= 116.92\,\text{J/K}. \\
\Delta S_{\text{room}} &= \frac{q_{\text{room}}}{T} \qquad \text{(isothermal)}.
\end{aligned}
$$

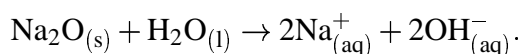The heat extracted from the room comes from the glass warming. Thus $q_{\text{room}} = -q_{\text{glass}}$.

$$
\begin{aligned}
q_{\text{glass}} &= C_P \Delta T \\
&= (1200\,\text{J/K})\,(50 - 20°\text{C}) \\
&= 36000\,\text{J}. \\
\therefore \Delta S_{\text{room}} &= \frac{-36000\,\text{J}}{293.15\,\text{K}} = -122.80\,\text{J/K}. \\
\therefore \Delta S_{\text{universe}} &= \Delta S_{\text{glass}} + \therefore \Delta S_{\text{room}} = -5.88\,\text{J/K}.
\end{aligned}
$$

Since the entropy change of the universe is negative, this is a process which *cannot* occur.

3. It's a heat balance problem where the unknown is the mass of ice (m_{ice}):

$$q = 0 = \left\{\begin{matrix}\text{Heat ice to}\\\text{melting}\end{matrix}\right\} + \left\{\text{ Melt ice }\right\} + \left\{\begin{matrix}\text{Warm } m_{\text{ice}}\\\text{of liquid water}\\\text{to } 4°C\end{matrix}\right\} + \left\{\begin{matrix}\text{Cool } 325\,\text{g}\\\text{of water}\\\text{to } 4°C\end{matrix}\right\}$$

$$\therefore 0 = m_{\text{ice}}\tilde{C}_{P(\text{s})}\Delta T_1 + m_{\text{ice}}\Delta\tilde{H}_{\text{melt}} + m_{\text{ice}}\tilde{C}_{P(\text{l})}\Delta T_2 + m_{\text{drink}}\tilde{C}_{P(\text{l})}\Delta T_3$$

$$= m_{\text{ice}}\left[\left(2.113\,\text{J}\,\text{K}^{-1}\text{g}^{-1}\right)\left(0 - (-5)°C\right) + 333.4\,\text{J/g} + \left(4.184\,\text{J}\,\text{K}^{-1}\text{g}^{-1}\right)(4 - 0°C)\right]$$

$$+ (325\,\text{g})\left(4.184\,\text{J}\,\text{K}^{-1}\text{g}^{-1}\right)(4 - 32°C)$$

$$\therefore m_{\text{ice}} = \frac{38\,074\,\text{J}}{360.7\,\text{J/g}} = 106\,\text{g}.$$

4. (a)

$$Na_2O_{(\text{s})} + H_2O_{(\text{l})} \rightarrow 2Na^+_{(\text{aq})} + 2OH^-_{(\text{aq})}.$$

$$n_{Na_2O} = \frac{1.3241\,\text{g}}{61.98\,\text{g/mol}} = 0.021\,36\,\text{mol}.$$

$$\Delta\tilde{H}^\circ_{\text{rxn}} = 2\Delta\bar{H}^\circ_{f(Na^+)} + 2\Delta\bar{H}^\circ_{f(OH^-)} - \left(\Delta\bar{H}^\circ_{f(Na_2O)} + \Delta\bar{H}^\circ_{f(H_2O)}\right)$$

$$= 2(-240.34) + 2(-230.015) - [-417.98 + (-285.830)]\,\text{kJ/mol}$$

$$= -236.90\,\text{kJ/mol}.$$

Since Na_2O is clearly the limiting reagent, the reaction will liberate

$$\Delta H_{\text{rxn}} = n_{Na_2O}\Delta\bar{H}^\circ_{\text{rxn}} = -5.061\,\text{kJ}.$$

The water can only warm to $100°C$ before it boils. Can it absorb as much heat as the reaction liberates before it boils?

$$q_{75 \rightarrow 100} = m_{H_2O}\tilde{C}_P\Delta T = (250\,\text{g})(4.184\,\text{J}\,\text{K}^{-1}\text{g}^{-1})(100 - 75°C) = 26.15\,\text{kJ}.$$

It can. That makes our task relatively easy, since we only really have to calculate the final temperature:

$$q = 0 = \Delta H_{\text{rxn}} + m_{H_2O}\tilde{C}_P\Delta T$$

$$\therefore \Delta T = -\frac{\Delta H_{\text{rxn}}}{m_{H_2O}\tilde{C}_P}$$

$$= \frac{5061\,\text{J}}{(250\,\text{g})(4.184\,\text{J}\,\text{K}^{-1}\text{g}^{-1})} = 4.84\,\text{K}.$$

$$\therefore T_f = T_i + \Delta T = 80°C.$$

(b) We assumed that the reaction would go to completion. We did not take into account the fact that the reaction consumes water in the final step of the calculation. We assumed that the heat capacity of the sodium hydroxide solution which is the result of this reaction is the same as the heat capacity of water. We neglected the fact that the heat capacity of the solution depends on T. We assumed that the container in which the reaction occurs has a negligible heat capacity.

5. It's a reversible compression, so $P_{ext} = P$. From the equation of state, we have

$$P = \frac{1}{b}\left[\left(\frac{\bar{V}_0}{\bar{V}}\right)^a - c\right].$$

$$\therefore \bar{w} = -\int P\,d\bar{V}.$$

$$= -\int_{\bar{V}_0}^{\bar{V}_1} \frac{1}{b}\left[\left(\frac{\bar{V}_0}{\bar{V}}\right)^a - c\right] d\bar{V}$$

$$= -\frac{1}{b}\left[\int_{\bar{V}_0}^{\bar{V}_1} \left(\frac{\bar{V}_0}{\bar{V}}\right)^a d\bar{V} - c\int_{\bar{V}_0}^{\bar{V}_1} d\bar{V}\right]$$

$$= -\frac{1}{b}\left[\bar{V}_0^a \int_{\bar{V}_0}^{\bar{V}_1} \bar{V}^{-a}\,d\bar{V} - c\int_{\bar{V}_0}^{\bar{V}_1} d\bar{V}\right]$$

$$= -\frac{1}{b}\left[\bar{V}_0^a \frac{1}{1-a}\bar{V}^{1-a}\Big|_{\bar{V}_0}^{\bar{V}_1} - c\,\bar{V}\Big|_{\bar{V}_0}^{\bar{V}_1}\right]$$

$$= -\frac{1}{b}\left[\frac{\bar{V}_0^a}{1-a}\left(\bar{V}_1^{1-a} - \bar{V}_0^{1-a}\right) - c\left(\bar{V}_1 - \bar{V}_0\right)\right].$$

Note that we want a 1% compression, so

$$\bar{V}_1 = 0.99\bar{V}_0 = 8.824 \times 10^{-5}\,\mathrm{m}^3/\mathrm{mol}.$$

All we have to do now is plug in the numbers:

$$\bar{w} = -\frac{1}{8.963 \times 10^{-9}\,\mathrm{Pa}^{-1}}$$
$$\times \left[\frac{(8.913 \times 10^{-5}\,\mathrm{m}^3/\mathrm{mol})^{9.269}}{1-9.269}\left((8.824 \times 10^{-5}\,\mathrm{m}^3/\mathrm{mol})^{1-9.269}\right.\right.$$
$$\left.-(8.913 \times 10^{-5}\,\mathrm{m}^3/\mathrm{mol})^{1-9.269}\right)$$
$$\left.-0.9991\left(8.824 \times 10^{-5} - 8.913 \times 10^{-5}\,\mathrm{m}^3/\mathrm{mol}\right)\right]$$
$$= 4.86\,\mathrm{J/mol}.$$

This is a really tiny amount of work given the extraordinary pressure that must be applied (almost 11 MPa).