Chemistry 2740 Spring 2008 Practice Test 1 Solutions

1. The number of gas-phase molecules decreases, which decreases the number of microscopic states available to the system (fewer ways to arrange one than two types of molecules in the gas phase). The entropy therefore decreases.

2. ΔG gives the maximum **non-$\boldsymbol{PV}$** work at constant temperature and pressure.

3. See figure 1. In a reversible expansion, we follow the isotherm (the solid curve in the figure). During an expansion from V_1 to V_2, the work done is the area under this curve between the two dashed lines. On the other hand, in an irreversible expansion, we would have to drop the pressure below the equilibrium pressure represented by the isotherm. The simplest case is to drop the pressure in one step to the final pressure, as illustrated by the dotted line in the figure. The work done in this case is just the area of the little rectangle. In general, even if we took many steps, we would have to fall away from the isotherm, which would cut into the area, i.e. into the work done.

4. The second law requires the entropy change of the universe to be positive. The argument is wrong because it says nothing about the entropy change of the surroundings. We simply can't conclude anything from the information given in the question.

5. The entropy would be the same in both cases. In the first case, we would need to figure out how many ways we can put $N/10$ molecules on N sites. In the second case, we could tell ourselves that we are choosing the $N/10$ unoccupied sites. Either way, the number of configurations is exactly the same.

6. (a) We need to construct a thermodynamic cycle to answer this question:

$$\begin{tikzcd}
C_6H_{12}O_{6(s)} + 6O_{2(g)}(10°C) \arrow[r] \arrow[d, "1"'] & 6CO_{2(g)} + 6H_2O_{(l)}(10°C) \\
C_6H_{12}O_{6(s)} + 6O_{2(g)}(25°C) \arrow[r, "2"] & 6CO_{2(g)} + 6H_2O_{(l)}(25°C) \arrow[u, "3"']
\end{tikzcd} \tag{1}$$

$$\begin{aligned}
\Delta\bar{H}_1 &= \left[\bar{C}_{p(C_6H_{12}O_6)} + 6\bar{C}_{p(O_2)}\right]\Delta T_1 \\
&= \left[218.16 + 6(29.35)\,\mathrm{J\,K^{-1}mol^{-1}}\right](15\,\mathrm{K}) \\
&= 5.9\,\mathrm{kJ/mol} \\
\Delta\bar{H}_2 &= 6\Delta_f H^\circ_{(CO_2)} + 6\Delta_f H^\circ_{(H_2O)} - \left(\Delta_f H^\circ_{(C_6H_{12}O_6)} + 6\Delta_f H^\circ_{(O_2)}\right) \\
&= 6(-393.51) + 6(-285.830) - [-1274.4 + 6(0)]\ \mathrm{kJ/mol} \\
&= -2801.6\,\mathrm{kJ/mol} \\
\Delta\bar{H}_3 &= \left[6\bar{C}_{p(CO_2)} + 6\bar{C}_{p(H_2O)}\right]\Delta T_3 \\
&= \left[6(37.1) + 6(75.40)\mathrm{J\,K^{-1}mol^{-1}}\right](-15\,\mathrm{K}) \\
&= -10\,\mathrm{kJ/mol} \\
\therefore \Delta_r\bar{H}_{10} &= \Delta\bar{H}_1 + \Delta\bar{H}_2 + \Delta\bar{H}_3 \\
&= -2806\,\mathrm{kJ/mol.}
\end{aligned}$$

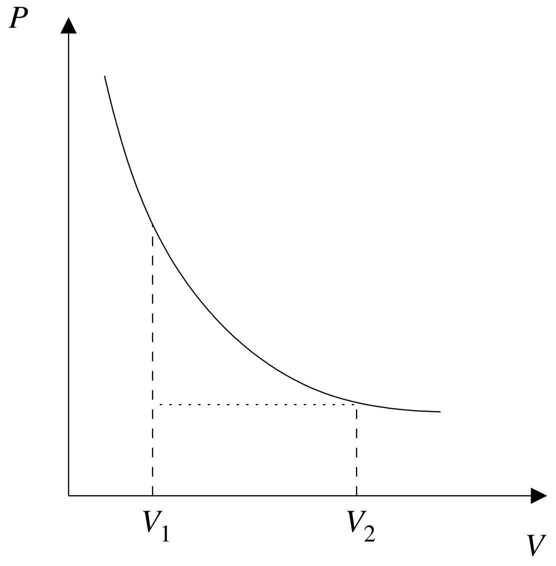

Figure 1: Pressure-volume diagram for an isothermal expansion from volume V_1 to V_2.

(b) A bomb calorimeter is a constant-volume device. Since the heat at constant volume is ΔU, we need the latter quantity. Recall that

$$\Delta\bar{U} = \Delta\bar{H} - \Delta(P\bar{V}) = \Delta\bar{H} - RT\Delta\bar{n}_{\text{gas}}.$$

For this reaction, $\Delta\bar{n}_{\text{gas}} = 6 - 6 = 0$. Thus $\Delta_r\bar{U}^\circ = \Delta_r\bar{H}^\circ = -2801.6\,\text{kJ/mol}$. Also,

$$\begin{aligned} n &= \frac{1.00\,\text{g}}{180.156\,\text{g/mol}} = 0.005\,55\,\text{mol}. \\ \therefore q &= n\Delta_r\bar{U}^\circ = (0.005\,55\,\text{mol})(-2801.6\,\text{kJ/mol}) = -15.6\,\text{kJ}. \end{aligned}$$

7.

$$\begin{aligned} \bar{S}_{\text{ice},0^\circ\text{C}} &= \bar{S}_{\text{water},25^\circ\text{C}} + \Delta_{25\to0^\circ\text{C}}\bar{S} + \Delta_{\text{freezing}}\bar{S}. \\ \Delta_{25\to0^\circ\text{C}}\bar{S} &= \int_{T_1}^{T_2} \frac{\bar{C}_p dT}{T} = \bar{C}_p \int_{298.15}^{273.15\,\text{K}} \frac{dT}{T} \\ &= (75.40\,\text{J}\,\text{K}^{-1}\text{mol}^{-1}) \ln\left(\frac{273.15\,\text{K}}{298.15\,\text{K}}\right) = -6.603\,\text{J}\,\text{K}^{-1}\text{mol}^{-1}. \\ \Delta\bar{S}_{\text{freezing}} &= \frac{\Delta_{\text{freezing}}\bar{H}}{T} = \frac{-6007\,\text{J/mol}}{273.15\,\text{K}} = -21.99\,\text{J}\,\text{K}^{-1}\text{mol}^{-1}. \\ \therefore \bar{S}_{\text{ice},0^\circ\text{C}} &= 69.65 + (-6.603) + (-21.99)\,\text{J}\,\text{K}^{-1}\text{mol}^{-1} = 41.36\,\text{J}\,\text{K}^{-1}\text{mol}^{-1}. \end{aligned}$$

8. (a)

$$\text{CaO}_{(\text{s})} + \text{CO}_{2(\text{g})} \rightarrow \text{CaCO}_{3(\text{s})}$$

$$
\begin{aligned}
\Delta\bar{G}^\circ_{25} &= \Delta_f\bar{G}^\circ_{\mathrm{CaCO_3}} - \left(\Delta_f\bar{G}^\circ_{\mathrm{CaO}} + \Delta_f\bar{G}^\circ_{\mathrm{CO_2}}\right) \\
&= -1128.8 - [-603.30 + (-394.37)]\ \mathrm{kJ/mol} = -131.1\,\mathrm{kJ/mol}. \\
\Delta\bar{H}^\circ &= \Delta_f\bar{H}^\circ_{\mathrm{CaCO_3}} - \left(\Delta_f\bar{H}^\circ_{\mathrm{CaO}} + \Delta_f\bar{H}^\circ_{\mathrm{CO_2}}\right) \\
&= -1206.9 - [-634.92 + (-393.51)]\ \mathrm{kJ/mol} = -178.5\,\mathrm{kJ/mol}. \\
\Delta\bar{S}^\circ &= \frac{\Delta\bar{H}^\circ - \Delta\bar{G}^\circ}{T} \\
&= \frac{-178.5 - (-131.1)\,\mathrm{kJ/mol}}{298.15\,\mathrm{K}} = -0.159\,\mathrm{kJ\,K^{-1}mol^{-1}}. \\
\therefore \Delta\bar{G}^\circ_5 &= \Delta\bar{H}^\circ - T\Delta\bar{S}^\circ \\
&= -178.5\,\mathrm{kJ/mol} - (278.15\,\mathrm{K})(-0.159\,\mathrm{kJ\,K^{-1}mol^{-1}}) = -134.3\,\mathrm{kJ/mol}.
\end{aligned}
$$

(b)

$$
\begin{aligned}
\Delta\bar{G} &= \Delta\bar{G}^\circ + RT\ln Q \\
&= \Delta\bar{G}^\circ + RT\ln\left(\frac{1}{a_{\mathrm{CO_2}}}\right) \\
&= -134.3\,\mathrm{kJ/mol} + (8.314\,472\times10^{-3}\,\mathrm{kJ\,K^{-1}mol^{-1}})(278.15\,\mathrm{K})\ln\left(\frac{1}{4\times10^{-4}}\right) \\
&= -116.2\,\mathrm{kJ/mol}.
\end{aligned}
$$

Since $\Delta\bar{G} < 0$, we conclude that this conversion is spontaneous in air.