Chemistry 2850 Spring 2007 Test 1 Solutions

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

2. (a) A state function is a property of a system whose value only depends on the state of the system, and not on the way in which this state was reached.

   (b) P, S and U are state functions while q is not.

3. For an ideal gas, $V \propto T$. The ideal gas law holds for most gases at low pressures, so we could work at a fixed low pressure. We would measure the volume of the gas V_{ref} at a known temperature T_{ref}. Conventionally, we use the triple point of water $(273.16\,\mathrm{K})$. Let the volume at T_{ref} be V_{ref}. Then we have

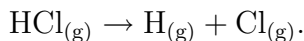$$\frac{T}{T_{\mathrm{ref}}} = \frac{V}{V_{\mathrm{ref}}},$$

or

$$T = \frac{V}{V_{\mathrm{ref}}}T_{\mathrm{ref}}.$$

Thus a measurement of V gives us the corresponding T.

Note that the textbook gives a slightly more complicated prescription involving a limit as $P \to 0$. However, the central ideas are those given above.

4. The reaction is

$$\mathrm{HCl_{(g)}} \to \mathrm{H_{(g)}} + \mathrm{Cl_{(g)}}.$$
$$\Delta H = \Delta U + RT\Delta_{\mathrm{gas}}n.$$

For this reaction $\Delta_{\mathrm{gas}}n = 2 - 1 = 1$. Therefore

$$\begin{aligned}
\Delta H &= 410.0\,\mathrm{kJ/mol} + (8.314\,472 \times 10^{-3}\,\mathrm{kJ\,K^{-1}mol^{-1}})(298.15\,\mathrm{K})(1)\\
&= 412.5\,\mathrm{kJ/mol}.
\end{aligned}$$

5. (a) It's an adiabatic expansion, therefore $\boxed{q = 0}$.

   It's an ideal gas, so U and H only depend on T. Moreover, we know *how* they depend on T:

$$\Delta H = nC_{P,m}\Delta T = (3.4\,\mathrm{mol})(29.12\,\mathrm{J\,K^{-1}mol^{-1}})(250 - 300\,\mathrm{K}),$$

$$\boxed{\therefore \Delta H = -5.0\,\mathrm{kJ}.}$$

$$\begin{aligned}
C_{V,m} &= C_{P,m} - R = 29.12 - 8.314\,472\,\mathrm{J\,K^{-1}mol^{-1}}\\
&= 20.81\,\mathrm{J\,K^{-1}mol^{-1}}.\\
\Delta U &= nC_{V,m}\Delta T = (3.4\,\mathrm{mol})(20.81\,\mathrm{J\,K^{-1}mol^{-1}})(250 - 300\,\mathrm{K}),
\end{aligned}$$

$$\therefore \Delta U = -3.5 \, \text{kJ}.$$

Since $\Delta U = q + w$ and $q = 0$, we have $w = \Delta U = -3.5 \, \text{kJ}$.

Finally, since the expansion is reversible and adiabatic, $dq_{\text{rev}} = 0$. Therefore $\Delta S = \int dq_{\text{rev}}/T = 0$.

(b) During a reversible adiabatic expansion, PV^γ is constant. We can calculate the initial volume from the ideal gas law:

$$
\begin{aligned}
P_1 &= (2.4 \, \text{bar})(100\,000 \, \text{Pa/bar}) = 2.4 \times 10^5 \, \text{Pa}. \\
V_1 &= \frac{nRT_1}{P_1} = \frac{(3.4 \, \text{mol})(8.314\,472 \, \text{J K}^{-1}\text{mol}^{-1})(300 \, \text{K})}{2.4 \times 10^5 \, \text{Pa}} \\
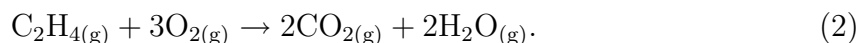&= 0.035 \, \text{m}^3.
\end{aligned}
$$

We want to use $P_1 V_1^\gamma = P_2 V_2^\gamma$ to calculate P_2. Unfortunately, we don't know V_2. We do however know that this volume and the pressure are related by the ideal gas law:

$$
\begin{aligned}
V_2 &= \frac{nRT_2}{P_2}. \\
\therefore P_2 \left(\frac{nRT_2}{P_2} \right)^\gamma &= P_1 V_1^\gamma. \\
\therefore P_2^{1-\gamma} &= P_1 \left(\frac{V_1}{nRT_2} \right)^\gamma. \\
\gamma &= \frac{C_{P,m}}{C_{V,m}} = \frac{29.12 \, \text{J K}^{-1}\text{mol}^{-1}}{20.81 \, \text{J K}^{-1}\text{mol}^{-1}} = 1.400. \\
\therefore P_2^{1-\gamma} &= (2.4 \times 10^5 \, \text{Pa}) \left(\frac{0.035 \, \text{m}^3}{(3.4 \, \text{mol})(8.314\,472 \, \text{J K}^{-1}\text{mol}^{-1})(250 \, \text{K})} \right)^{1.400} \\
&= 0.0091. \\
\therefore P_2 &= (0.0091)^{\frac{1}{1-1.400}} = 1.3 \times 10^5 \, \text{Pa} \equiv 1.3 \, \text{bar}.
\end{aligned}
$$

6. Everything starts with a balanced reaction or, in this case, two balanced reactions. The standard enthalpy of combustion refers to the reaction

$$C_2H_{4(g)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 2H_2O_{(l)}. \tag{1}$$
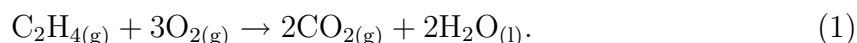
At 400°C on the other hand, the reaction would be

$$C_2H_{4(g)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 2H_2O_{(g)}. \tag{2}$$

To go from reaction 1 to reaction 2, we need to convert two equivalents of liquid water to two equivalents of steam:

$$2H_2O_{(l)} \rightarrow 2H_2O_{(g)}. \tag{3}$$

For this process,

$$\Delta H_3 = 2\Delta_f H_{(g)} - 2\Delta_f H_{(l)} = 2(-241.826) - 2(-285.830) \, \text{kJ/mol} = 88.008 \, \text{kJ/mol}.$$

Using Hess's law, we get

$$\Delta H_2 = \Delta H_1 + \Delta H_3 = -1411.20 + 88.008 \, \text{kJ/mol} = -1323.19 \, \text{kJ/mol}.$$

All we have to deal with now is the temperature change. We can calculate the enthalpy of combustion at 400°C from

$$
\begin{aligned}
\Delta_c H_{400} &= \Delta H_2 + \Delta C_P \Delta T. \\
\Delta C_P &= 2C_{P(\text{CO}_2)} + 2C_{P(\text{H}_2\text{O}_{(\text{g})})} - \left(C_{P(\text{C}_2\text{H}_4)} + 3C_{P(\text{O}_2)} \right) \\
&= 2(37.1) + 2(33.58) - [43.6 + 3(29.35)] \; \text{J K}^{-1}\text{mol}^{-1} \\
&= 9.71 \; \text{J K}^{-1}\text{mol}^{-1}. \\
\therefore \Delta_c H_{400} &= -1323.19 \, \text{kJ/mol} + (9.71 \times 10^{-3} \, \text{kJ K}^{-1}\text{mol}^{-1})(400 - 25 \, \text{K}) \\
&= -1319.55 \, \text{kJ/mol}.
\end{aligned}
$$