

# Chemistry 2850 Practice Test 1 Solutions

1. All steps in a Carnot cycle are reversible.

**Step 1:** Isothermal compression, work done *on* the system

**Step 2:** Adiabatic compression, work done *on* the system

**Step 3:** Isothermal expansion, work done *by* the system

**Step 4:** Adiabatic expansion, work done *by* the system

Note: It's a cycle, so you can start in a different place (e.g. start with the isothermal expansion).

2. 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.
3. Figure 2 shows a sketch of the apparatus. The two pistons are both moved from left to right, keeping a constant pressure  $P_1$  on the left and  $P_2$  on the right, with  $P_2 < P_1$ . The motion of the pistons forces the gas being studied through the porous plug, as indicated by the arrows. The temperatures  $T_1$  and  $T_2$  are measured. It is possible to show that this process holds the enthalpy constant. For an ideal gas, we would get  $T_2 = T_1$  because the enthalpy only depends on the temperature. For a real gas however,  $H$  also depends on  $P$  and we would find  $T_2 \neq T_1$ .
4. Since the volume is constant,  $w = 0$ .

Pressure is proportional to temperature for an ideal gas, so we have

$$\begin{aligned}\frac{P_1}{T_1} &= \frac{P_2}{T_2}, \\ \therefore T_2 &= \frac{P_2}{P_1} T_1 = \frac{5 \text{ bar}}{1 \text{ bar}} 300 \text{ K} = 1500 \text{ K}. \\ \therefore q &= C_{V,m} \Delta T = (12.5 \text{ J K}^{-1} \text{ mol}^{-1}) (1500 - 300 \text{ K}) = 15.0 \text{ kJ/mol}. \\ \Delta U &= q + w = 15.0 \text{ kJ/mol}. \\ C_{P,m} &= C_{V,m} + R = 12.5 + 8.314 472 \text{ J K}^{-1} \text{ mol}^{-1} = 20.8 \text{ J K}^{-1} \text{ mol}^{-1}. \\ \therefore \Delta H &= C_{P,m} \Delta T = (20.8 \text{ J K}^{-1} \text{ mol}^{-1}) (1500 - 300 \text{ K}) = 25.0 \text{ kJ/mol}.\end{aligned}$$

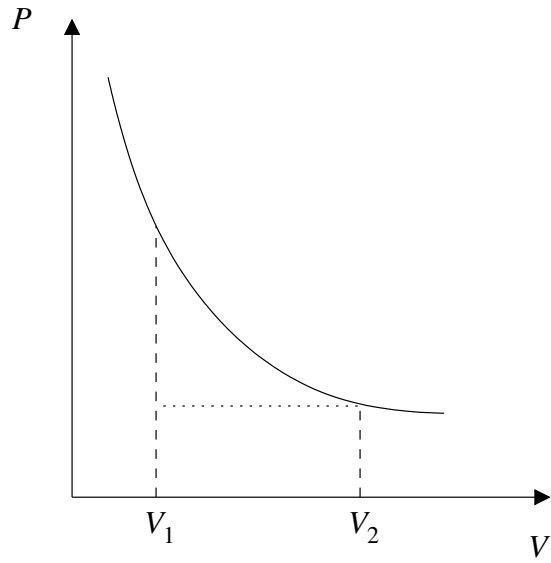


Figure 1: Pressure-volume diagram for an isothermal expansion from volume  $V_1$  to  $V_2$ .

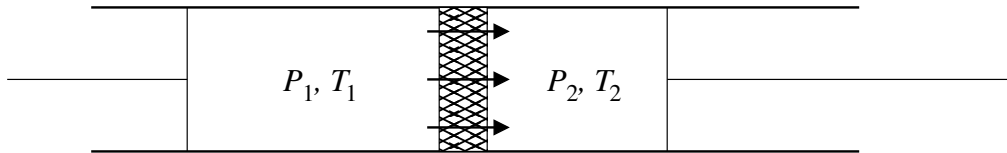
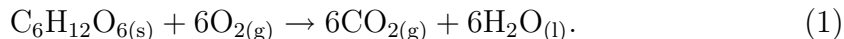


Figure 2: Sketch of the apparatus for the Joule-Thomson experiment.

To calculate the entropy change, we need a reversible path. We can heat a gas reversibly by transferring the heat from a body held at the same temperature as the gas. The entropy change is then simply

$$\begin{aligned}\Delta S &= \int \frac{dq_{\text{rev}}}{T} = \int_{T_1}^{T_2} \frac{C_{V,m} dT}{T} = C_{V,m} \int_{T_1}^{T_2} \frac{dT}{T} = C_{V,m} \ln \left( \frac{T_2}{T_1} \right) \\ &= (12.5 \text{ J K}^{-1} \text{ mol}^{-1}) \ln \left( \frac{1500 \text{ K}}{300 \text{ K}} \right) = 20.1 \text{ J K}^{-1} \text{ mol}^{-1}.\end{aligned}$$

5. (a) The reaction is



At 25°C, we have

$$\begin{aligned}\Delta_r H^\circ &= 6\Delta_f H^\circ_{(\text{CO}_2)} + 6\Delta_f H^\circ_{(\text{H}_2\text{O})} - (\Delta_f H^\circ_{(\text{C}_6\text{H}_{12}\text{O}_6)} + 6\Delta_f H^\circ_{(\text{O}_2)}) \\ &= 6(-393.51) + 6(-285.830) - [-1274.4 + 6(0)] \text{ kJ/mol} \\ &= -2801.6 \text{ kJ/mol.} \\ \Delta C_P &= 6C_{P,m}(\text{CO}_2) + 6C_{P,m}(\text{H}_2\text{O}) - (C_{P,m}(\text{C}_6\text{H}_{12}\text{O}_6) + 6C_{P,m}(\text{O}_2)) \\ &= 6(37.1) + 6(75.40) - [218.16 + 6(29.35)] \text{ J K}^{-1} \text{ mol}^{-1} \\ &= 280.7 \text{ J K}^{-1} \text{ mol}^{-1}. \\ \therefore \Delta_r H_{10} &= \Delta_r H^\circ + \Delta C_P \Delta T \\ &= -2801.6 \text{ kJ/mol} + (0.2807 \text{ kJ K}^{-1} \text{ mol}^{-1})(10 - 25 \text{ K}) \\ &= -2805.9 \text{ kJ/mol.}\end{aligned}$$

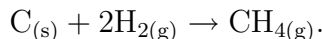
(b) A bomb calorimeter is a constant-volume device. Since the heat at constant volume is  $\Delta U$ , we need the latter quantity. Recall that

$$\Delta U = \Delta H - \Delta(PV) = \Delta H - RT\Delta_{\text{gas}}n.$$

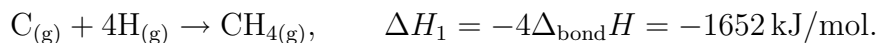
For this reaction,  $\Delta_{\text{gas}}n = 6 - 6 = 0$ . Thus  $\Delta_r U^\circ = \Delta_r H^\circ = -2801.6 \text{ kJ/mol}$ . Also,

$$\begin{aligned}n &= \frac{1 \text{ g}}{180.156 \text{ g/mol}} = 0.00555 \text{ mol.} \\ \therefore q &= n\Delta_r U_m^\circ = (0.00555 \text{ mol})(-2801.6 \text{ kJ/mol}) = -15.6 \text{ kJ.}\end{aligned}$$

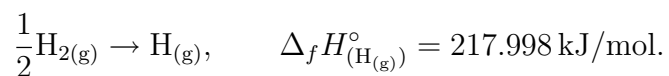
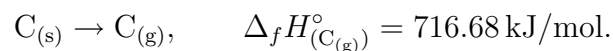
6. The formation reaction is



Using the bond enthalpy, we have the enthalpy change for the following reaction:



We also have the enthalpies of formation of  $C_{(g)}$  and  $H_{(g)}$ :



For the formation reaction, we therefore have

$$\begin{aligned} \Delta_f H_{(CH_4)}^\circ &= \Delta H_1 + \Delta_f H_{(C_{(g)})}^\circ + 4\Delta_f H_{(H_{(g)})}^\circ \\ &= -1652 + 716.68 + 4(217.998) \text{ kJ/mol} = -63 \text{ kJ/mol.} \end{aligned}$$

The accepted value is  $-74.81 \text{ kJ/mol}$ , so this calculation gave a very reasonable result, the error being due to the use of bond enthalpies which are averaged over many different carbon-hydrogen bonds.