CHEMISTRY 311 PHYSICAL CHEMISTRY
Homework Assignment # 3

1. Methane is heated from 298 K to 500 K at constant pressure. Find (a) ΔU, (b) ΔH, and (c) ΔS for the process. $C_{P,m} = 23.64 + 47.86 \times 10^{-3}T - 1.92 \times 10^5/T^2$.

Answer

(a) Using the relationship $C_{P,m} - C_{V,m} = R$, we get

$$\begin{aligned}\Delta U_m &= \int_{T_1}^{T_2} (C_{P,m} - R)dT \\ \Delta U_m &= \int_{298}^{500} \left[(23.64 - 8.3143) + 47.86 \times 10^{-3}T - 1.92 \times 10^5/T^2\right] dT \\ \Delta U_m &= 15.33(500 - 298) + \frac{47.86}{2} \times 10^{-3}\left(500^2 - 298^2\right) + 1.92 \times 10^5(500^{-1} - 298^{-1}) \\ &= 6693.8 \text{ J mol}^{-1}\end{aligned}$$

(b)

$$\begin{aligned}\Delta H_m &= \int_{T_1}^{T_2} C_{P,m} dT \\ \Delta H_m &= \int_{298}^{500} (23.64 + 47.86 \times 10^{-3}T - 1.92 \times 10^5/T^2)dT \\ \Delta H_m &= 23.64(500 - 298) + \frac{47.86}{2} \times 10^{-3}\left(500^2 - 298^2\right) + 1.92 \times 10^5(500^{-1} - 298^{-1}) \\ &= 8372.4 \text{ J mol}^{-1}\end{aligned}$$

(c) The work done can be calclated from the First Law: $\Delta U = q + w$. Since this is a constant pressure process, $q = q_P = \Delta H$. Therefore,

$$\begin{aligned}w &= \Delta U - q \\ &= \Delta U - \Delta H \\ &= -1678.6 \text{ J mol}^{-1}\end{aligned}$$

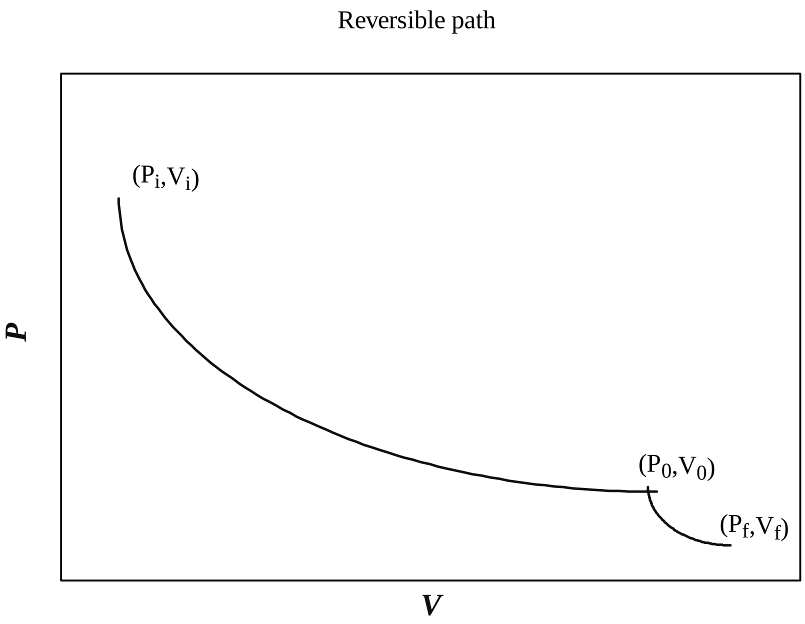
In order for the gas to be heated at constant pressure, the volume must increase with temperature. This work of expansion is done by the system, which is why w is negative.

(d) Since this is a constant pressure process, $dq_{rev} = C_P dT$. Therefore,

$$\begin{aligned}\Delta S_m &= \int_{T_1}^{T_2} \frac{C_{P,m}}{T} dT \\ \Delta S_m &= \int_{298}^{500} \left[\frac{23.64}{T} + 47.86 \times 10^{-3} - 1.92 \times 10^5/T^3\right] dT \\ \Delta S_m &= 23.64 \ln\left(\frac{500}{298}\right) + 47.86 \times 10^{-3}(500 - 298) + \frac{1.92 \times 10^5}{2}\left(\frac{1}{500^2} - \frac{1}{298^2}\right) \\ \Delta S_m &= 21.205 \text{ J K}^{-1} \text{ mol}^{-1}\end{aligned}$$

2. One mole of ideal gas initially at 20 bar and 300 K is allowed to instantaneously (P_{ext} = 0!) expand to 2 bar pressure in an irreversible process that lowers the temperature of the system to 283.2 K. Sketch a reversible path that consists of an isothermal expansion followed by an adiabatic expansion which connects the initial and final states on a P-V diagram. The thermal surroundings remain at 300 K throughout the process. Find (a) w (actual, not w_{rev}!), (b) q (actual, not q_{rev}!), (c) ΔU, (d) ΔH, (e) ΔS, (f) ΔS_{surr} and (g) ΔS_{univ}.

Answer



Isothermal expansion to (P_0,V_0) followed by adiabatic expansion to the final state:

Initial Volume:

$$V_i = \frac{0.083143 \text{ L bar K}^{-1} \text{ mol}^{-1} \times 300 \text{ K}}{20 \text{ bar}} \\ = 1.2471 \text{ L mol}^{-1}.$$

Final volume:

$$V_f = \frac{0.083143 \text{ L bar K}^{-1} \text{ mol}^{-1} \times 283.2 \text{ K}}{2 \text{ bar}} \\ = 11.773 \text{ L mol}^{-1}.$$

Note that we need to find the intersection of the isotherm that passes through the initial state and the adiabat that passes through the final state, which occurs at (P_0, V_0) at the temperature of the isotherm, i.e., at T_i. Using the relationships provided above for adiabatic processes, we get

$$\begin{aligned}\frac{T_f}{T_i}&=\left(\frac{V_0}{V_f}\right)^{\gamma-1} = \left(\frac{V_0}{V_f}\right)^{2/3}\\ V_0&=V_f \times \left(\frac{T_f}{T_i}\right)^{3/2} = 10.798\text{ L.}\end{aligned}$$

(a) Since the external pressure is zero, $w = 0$.
(b) Since $w = 0$, the actual heat $q = \Delta U$ (first law).
(c) $\Delta U = 0 + C_{V,m}\,(T_f - T_i) = \frac{3}{2}R(283.2 - 300) = -209.5$ J mol^{-1}
(d) $\Delta H = 0 + C_{P,m}\,(T_f - T_i) = \frac{5}{2}R(283.2 - 300) = -349.2$ J mol^{-1}
(e) $\Delta S = R\ln\left(\frac{V_0}{V_i}\right) + 0 = R\ln\left(\frac{10.798}{1.247}\right) = 17.95$ J K^{-1} mol^{-1}

Entropy change of the surroundings:

The actual process is the expansion of the gas against zero external pressure. For this process, according to the first law,

Since $q_{act} = \Delta U = -209.5$ J mol^{-1}, $q_{surr} = +209.5$ J mol^{-1}.

Now, using the definition of ΔS_{surr}, we get

$$\begin{aligned}\Delta S_{\text{surr}}&=\frac{q_{\text{surr}}}{T_{\text{surr}}}\\ &=\frac{(209.5\,\text{J mol}^{-1})}{300\text{ K}}.\\ \Delta S_{\text{surr}}&=0.698\text{ J K}^{-1}\text{ mol}^{-1}.\end{aligned}$$

Therefore, to summarize, we have

(a) $w = 0$
(b) $q = -209.5$ J mol^{-1}.
(c) $\Delta U = -209.5$ J mol^{-1}.
(d) $\Delta H = -349.2$ J mol^{-1}.
(e) $\Delta S = 17.95$ J K^{-1} mol^{-1}.
(f) $\Delta S_{\text{surr}} = 0.698$ J K^{-1} mol^{-1}.
(g) Therefore, $\Delta S_{\text{univ}} = \Delta S + \Delta S_{\text{surr}} = 18.65$ Joules K^{-1} mol^{-1}.

3. Acetic acid ($C_2H_4O_2$) freezes at 16.6 °C. A flask containing several moles of acetic acid at 16.6 °C is lowered into a large ice-water bath at 0 °C. When it is removed, it is found that exactly 1 mol of acetic acid has frozen. For acetic acid, $\Delta H^\circ_{fus} = 11.45$ kJ mol^{-1}. (a) What is the entropy change for the acetic acid? (b) What is the entropy change for the water bath? (c) Is the freezing of acetic acid under these conditions a spontaneous process?

Answer

(a) Since acetic acid freezes at its normal melting point, the entropy change for the system (i.e., acetic acid) is

$$\begin{aligned}\Delta S = \frac{\Delta H^\circ_{fus}}{T_{fus}} &= \frac{-11,450\text{ J mol}^{-1}}{(273.15 + 16.6)\text{ K}}\\ &= -39.52\text{ J K}^{-1}\text{ mol}^{-1}.\end{aligned}$$

The negative sign on the enthalpy is needed since heat is lost from the system during freezing.

(b) The water bath, which is at 273.15 K, receives $11,450$ J of heat. Therefore,

$$\Delta S_{surr} = \frac{+11,450 \text{ J}}{273.15 \text{ K}}$$
$$= 41.92 \text{ J K}^{-1} \text{ mol}^{-1}.$$

(c) The entropy change of the Universe for this process is

$$\Delta S_{univ} = \Delta S + \Delta S_{surr}$$
$$= 2.4 \text{ J K}^{-1} \text{ mol}^{-1}.$$

Since this is positive, the process is spontaneous.

4. A gas is kept compressed in a perfectly insulated cylinder by a perfectly insulated piston. The piston is released and the gas pressure forces the piston out of the cylinder until the internal and external pressures are the same. (a) Do you think this will be a spontaneous process? (b) Is this an adiabatic process? (c) What is the entropy change of the system? (d) Do you expect the entropy of the Universe to change as a result of this process? Why or Why not?

Answer

(a) Yes, expansion of a compressed gas is is a spontaneous process.

(b) This is not necessarily an adiabatic process, because not all processes with $q = 0$ are adiabatic. In order for a process to be adiabatic, it must be *isentropic*, i.e., $\Delta S = 0$. The answer to part (c) shows that this is not the case for the given process.

(c) The entropy change of the surroundings must be negligible (no heat is transfered to the surroundings). Therefore, the entropy change of the Universe, which must be positive for a spontaneous process, is almost entirely due to the entropy change in the system. So,

$$\Delta S_{Univ} = \Delta S + \Delta S_{surr} = \Delta S + 0 > 0.$$

Therefore, $\Delta S > 0$. If the gas can be assumed to be ideal, the entropy change of the system can be calculated by constructing a two-step reversible path connecting the initial and final states, and using

$$\Delta S_m = C_{V,m} \ln\left(\frac{T_2}{T_1}\right) + R \ln\left(\frac{V_2}{V_1}\right)$$
$$= C_{P,m} \ln\left(\frac{T_2}{T_1}\right) + R \ln\left(\frac{P_1}{P_2}\right),$$

if the required information about initial and final states are given.

(d) The entropy change of the Universe will be positive, since the process is spontaneous.