CHEMISTRY 311 PHYSICAL CHEMISTRY
Homework Assignment # 2

1. Kinetic molecular theory establishes that the temperature of a gas is proportional to the speed with which the atoms/molecules move. Since perfectly elastic collisions in which no energy is gained or lost are rare, it would seem that molecules of a gas in a container would eventually lose energy due to collisions with the walls and cool down. However, our experience is that a gas in a container remains at a constant temperature unless it is heated or cooled by external factors. How would you reconcile these apparently conflicting statements?

   Answer

   The principle of conservation of energy holds universally. Therefore, a molecule that hits the wall and loses energy imparts some energy to the wall, which is then transfered to some other gas molecule through the vibrations of the atoms that make up the walls of the container. Alternately, if the walls of the container are not insulated, the energy may be transfered to gas molecules outside the container but, at the same time, energy from outside is also being transfered into the container by the same mechanism, i.e., vibrations of the atoms. This method of heat transfer (vibrations of atoms that make up a solid substance) is called *conduction*. Because of conduction, the gas remains at the same temperature as its surroundings.

2. Methane is heated from 298 K to 500 K at constant pressure. Find (a) ΔU and (b) ΔH 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

$$\Delta U_m = \int_{T_1}^{T_2} C_{V,m} dT = \int_{T_1}^{T_2} (C_{P,m} - R) dT$$

$$\Delta U_m = \int_{298}^{500} (23.64 - 8.3143 + 47.86 \times 10^{-3}T - 1.92 \times 10^5/T^2) dT$$

$$\Delta U_m = 15.33(500 - 298) + \frac{47.86}{2} \times 10^{-3} \left(500^2 - 298^2\right) + 1.92 \times 10^5 (500^{-1} - 298^{-1})$$

$$= 6693.8 \text{ J mol}^{-1}$$

(b)

$$\Delta H_m = \int_{T_1}^{T_2} \overline{C}_P dT$$

$$\Delta H_m = \int_{298}^{500} (23.64 + 47.86 \times 10^{-3}T - 1.92 \times 10^5/T^2) dT$$

$$\Delta H_m = 23.64(500 - 298) + \frac{47.86}{2} \times 10^{-3} \left(500^2 - 298^2\right) + 1.92 \times 10^5 (500^{-1} - 298^{-1})$$

$$= 8372.4 \text{ J mol}^{-1}$$

3. A gas obeys the equation of state $P(V - nb) = nRT$. (a) Derive the expression for w for an isothermal reversible expansion involving the gas. (b) What is the value of w for one mole of this gas with b =

0.0304 L mol^{-1} for a reversible isothermal expansion from 3.0 L to 6.0 L at 300 K? (c) What will be the value of w for the same expansion against a constant external pressure, where the external pressure is the same as the final pressure of the gas?

Answer

(a) Starting with the definition

$$dw = -PdV,$$

for an expansion from V_1 to V_2, we get

$$w = -\int_{V_1}^{V_2} PdV.$$

Now, substituting for P using the equation of state given, we obtain

$$\begin{aligned} w &= -nRT \int_{V_1}^{V_2} \frac{dV}{V - nb} \\ &= -nRT \ln\left(\frac{V_2 - nb}{V_1 - nb}\right). \end{aligned}$$

(b) For one mole of a gas undergoing reversible expansion with $b = 0.0304\,\text{L}$ mol^{-1}, at 300 K, we get

$$w = -RT \ln\left(\frac{6.0 - 0.0304}{3.0 - 0.0304}\right)$$
$$w = -1741.6 \text{ J}.$$

(c) For one mole of gas undergoing constant pressure expansion, we get

$$P_{\text{ext}} = P_2 = \frac{RT}{V_2 - b} = \frac{0.08314 \times 300}{6.0 - 0.0304}$$
$$= 4.1782\,\text{bar}.$$

Therefore,

$$w = -P_{\text{ext}}(6.0 - 3.0) \times 100 \text{ J (L bar)}^{-1}$$
$$w = -1253.5\,\text{J}.$$

4. 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. (a) Sketch at least four different reversible paths in P-V space (more, if you can think of them) that connect the initial state to the final state. (b) Find (a) ΔU and ΔH for each step and the total process.

Answer

We will consider four possible reversible paths connecting the initial and final states. These paths are sketched on a separate page.

1. Isothermal expansion to the final volume followed by constant volume cooling to the final temperature:

(a) $\Delta U = 0 + C_{V,m}\,(T_f - T_i) = \frac{3}{2}R(283.2 - 300) = -209.5 \text{ J mol}^{-1}$

(b) $\Delta H = 0 + C_{P,m}\,(T_f - T_i) = \frac{5}{2}R(253.2 - 298) = -349.2 \text{ J mol}^{-1}$

2. Isothermal expansion to the final pressure followed by constant pressure cooling to the final temperature:

(a) $\Delta U = 0 + C_{V,m}\,(T_f - T_i) = \frac{3}{2}R(283.2 - 300) = -209.5$ J mol^{-1}

(b) $\Delta H = 0 + C_{P,m}\,(T_f - T_i) = \frac{5}{2}R(283.2 - 300) = -349.2$ J mol^{-1}

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

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

$V_0 T_i^{3/2} = V_f T_f^{3/2}$;

$V_0 = 11.773 \text{ L}\times \left(\frac{283.2}{300.0}\right)^{3/2} = 10.798$ L

(a) $\Delta U = 0 + C_{V,m}\,(T_f - T_i) = \frac{3}{2}R(283.2 - 300) = -209.5$ J mol^{-1}

(b) $\Delta H = 0 + C_{P,m}\,(T_f - T_i) = \frac{5}{2}R(283.2 - 300) = -349.2$ J mol^{-1}

4. Constant pressure heating to the final volume followed by constant volume cooling to the final pressure:

The gas will have to be heated to $T_0 = 2832$ K in order for it to reach a volume of 11.773 L at 20 bar pressure. Therefore,

(a) $\Delta U = C_{V,m}\,(T_0 - T_i) + \overline{C}_V\,(T_f - T_0) = \frac{3}{2}R(283.2 - 300) + \frac{3}{2}R(283.2 - 2832) = -209.5$ J mol^{-1}

(b) $\Delta H = C_{P,m}\,(T_0 - T_i) + \overline{C}_P\,(T_f - T_0) = \frac{5}{2}R(283.2 - 300) + \frac{5}{2}R(283.2 - 2832) = -349.2$ J mol^{-1}

Therefore, to summarize, we have

(a) $\Delta U = -209.5$ J mol^{-1}.

(b) $\Delta H = -349.2$ J mol^{-1}.

I am sure many of you figured this out: since ΔU and ΔH are state properties, we really didn't need to construct these reversible paths to find their values. All we needed to know are the initial and final temperatues. Since $C_{V,m}$ and $C_{P,m}$ are constants for ideal gas, we can use the definitions:

$$\Delta U = \int_i^f dU = \int_{T_i}^{T_f} C_{V,m} dT = C_{V,m}(T_f - T_i),$$
$$\Delta H = \int_i^f dH = \int_{T_i}^{T_f} C_{P,m} dT = C_{P,m}(T_f - T_i).$$

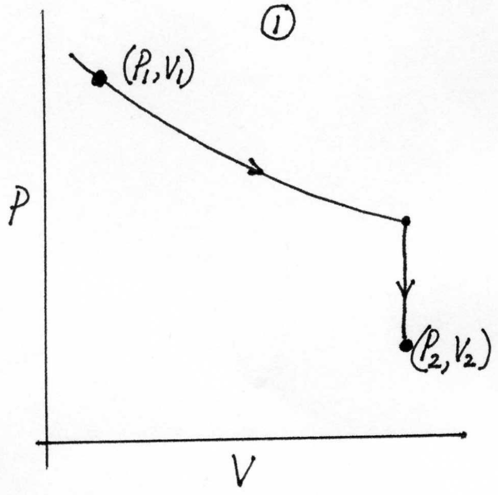
Since the initial and final temperatures are given, we didn't need the information about the inital or final pressures or what the external pressure was during the expansion.

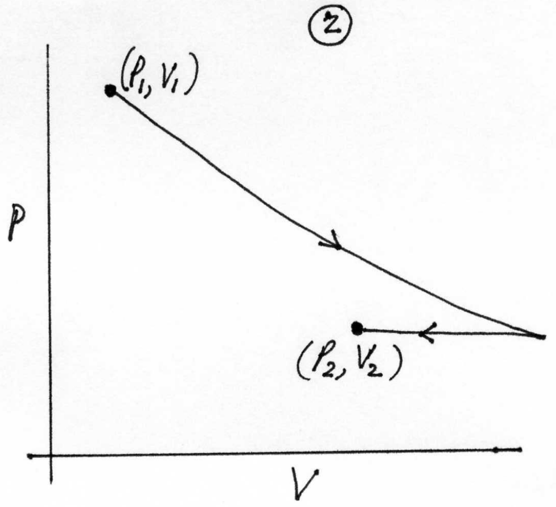
Other possible two-step paths:

5. Adiabatic expansion to the final temperature followed by isothermal expansion to the final volume.

6. Constant volume cooling to the final pressure followed by constant pressure heating to the final temperature.

7. Constant volume cooling to the final temperature followed by isothermal expansion to the final volume.


①
(P_1, V_1)
(P_2, V_2)
P
V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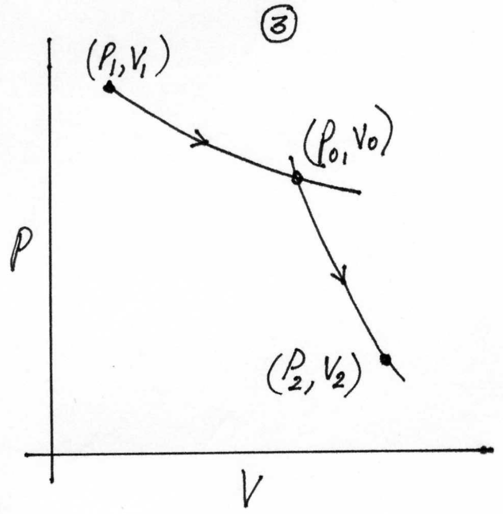
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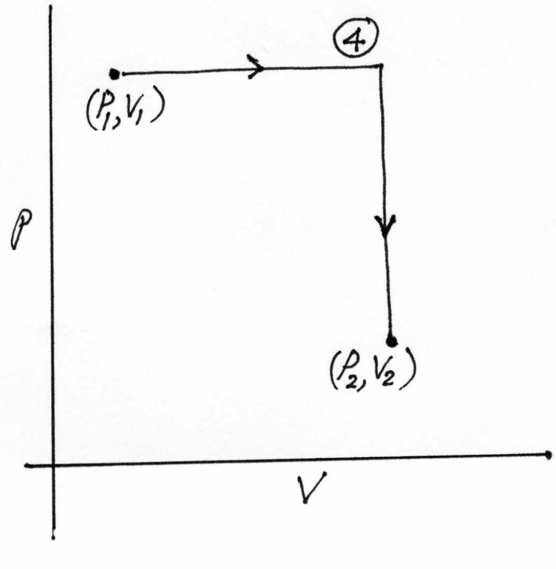
P
V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(P_1, V_1)
(P_2, V_2)
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