

Chem 531: Problem Set #1

SOLUTIONS

(1)

(a) Calculate q , w , ΔU , and ΔH for the reversible isothermal expansion at 300 K of 5.00 mol of an ideal gas from 500 to 1500 cm^3 .(b) What would ΔU and w be if the expansion connects the same initial and final states as in (a) but is done by having the ideal gas expand into vacuum?

(c) Likewise, if the gas expands against a constant pressure of 10 bar, how much work is done by the gas?

Ⓐ isothermal, so $\Delta U = \Delta H = 0$ for an ideal gas

$$w = -\int P dV \quad \text{since reversible}$$

$$= -\int \frac{nRT}{V} dV = -nRT \int \frac{dV}{V} = -nRT \ln \frac{V_f}{V_i}$$

$$= -(5.00)(8.3145)(300) \ln \frac{1500}{500} = -13702 \text{ J}$$

$$= -13.7 \text{ kJ}$$

$$\Delta U = 0 = q + w, \quad \text{so } q = +13.7 \text{ kJ}$$

Ⓑ free expansion: $w = -\int P_{\text{ext}} dV = 0$ since $P_{\text{ext}} = 0$

still isothermal, so $\Delta U = \Delta H = 0$ but now $q = 0$ too

Ⓒ const pressure expansion: $w = -\int P_{\text{ext}} dV = -P_{\text{ext}} \int dV$

$$w = -P_{\text{ext}} \Delta V$$

↑ this is work done on the gas

work done by the gas is $+P_{\text{ext}} \Delta V$

$$w = (10 \text{ bar}) \times \frac{10^5 \text{ Pa}}{\text{bar}} \times (1500 - 500) \times \left(\frac{1 \text{ m}}{100 \text{ cm}}\right)^3$$

$$= +1000 \text{ J} = +1.0 \text{ kJ}$$

(2) A nearly flat bicycle tire becomes noticeably warmer after it has been pumped up.

Approximate this process as a reversible adiabatic compression. Assume the initial pressure and temperature of the air before it is put into the tire to be $P_i = 1.00$ bar and $T_i = 298$ K.

The final volume of the air in the tire is $V_f = 1.00$ L and the final pressure is $P_f = 5.00$ bar.

Calculate the final temperature of the air in the tire. Assume that $\bar{C}_v = 5R/2$.

go ahead and start w/ $\left(\frac{T_f}{T_i}\right) = \left(\frac{V_f}{V_i}\right)^{-R/\bar{C}_v}$

$$\left(\frac{V_f}{V_i}\right) = \frac{\frac{nRT_f}{P_f}}{\frac{nRT_i}{P_i}} = \left(\frac{T_f}{T_i}\right) \left(\frac{P_i}{P_f}\right)$$

so $\left(\frac{T_f}{T_i}\right) = \left(\frac{T_f}{T_i}\right)^{-R/\bar{C}_v} \left(\frac{P_i}{P_f}\right)^{-R/\bar{C}_v}$

$$\left(\frac{T_f}{T_i}\right)^{1+R/\bar{C}_v} = \left(\frac{P_i}{P_f}\right)^{-R/\bar{C}_v}$$

$$\left(\frac{T_f}{T_i}\right) = \left(\frac{P_i}{P_f}\right)^{\frac{-R/\bar{C}_v}{1+R/\bar{C}_v}} = \left(\frac{P_i}{P_f}\right)^{-R/(R+\bar{C}_v)}$$

$$= \left(\frac{P_i}{P_f}\right)^{-R/(R+5R/2)}$$

$$= \left(\frac{P_i}{P_f}\right)^{-2/7}$$

$$\Rightarrow T_f = (298 \text{ K}) \left(\frac{1.00}{5.00}\right)^{-2/7} = 472 \text{ K}$$

(3) For a certain ideal gas, $\bar{C}_v = 2.5R$ at all temperatures. Calculate q , w , ΔU , and ΔH when 2.00 mol of this gas undergoes each of the following processes:

- (a) a reversible isobaric expansion from (1.00 atm, 20.0 L) to (1.00 atm, 40.0 L)
- (b) a reversible isochoric change of state from (1.00 atm, 40.0 L) to (0.500 atm, 40.0 L)
- (c) a reversible isothermal compression from (0.500 atm, 40.0 L) to (1.00 atm, 20.0 L).

Also calculate q , w , ΔU , and ΔH for the cycle that consists of steps (a), (b), and (c).

note: I'm going to use L-atm units for energy in this problem

$$\textcircled{a} \quad w = -\int P dV = -P \Delta V \quad \text{since isobaric \& reversible}$$

$$= -(1.00 \text{ atm})(20.0 \text{ L}) = -20.0 \text{ L-atm}$$

$$\Delta U = \int C_v dT \quad \text{since it's an ideal gas}$$

$$= (2.00 \text{ mol})(2.5R)(T_f - T_i)$$

$$T_f = \frac{P_f V_f}{nR} = \frac{(1.00)(40.0)}{(2.00)(0.08206)}$$

$$= 243.7 \text{ K}$$

likewise, $T_i = 121.9 \text{ K}$

$$\text{so } \Delta U = 50.0 \text{ L-atm}$$

$$q = \Delta U - w = 50.0 - (-20.0) = 70.0 \text{ L-atm}$$

$$\Delta H = \Delta U + \Delta(PV) = \Delta U + P \Delta V \quad (\text{isobaric})$$

$$= 50.0 + (1.00)(20.0)$$

$$= 70.0 \text{ L-atm} = q_p$$

b) isochoric $1.00 \text{ atm} \rightarrow 0.500 \text{ atm}$ @ 40.0 L

$$T_i = \frac{P_i V_i}{nR} = \frac{(1.00)(40.0)}{(2.00)(0.08206)} = 243.7 \text{ K}$$

$$T_f = 121.9 \text{ K}$$

$w = 0$ since isochoric

$$\Delta U = q_v = \int C_v dT = (2.00)(2.5R)(-121.8) \\ = -50.0 \text{ L-atm}$$

$$\Delta H = \Delta U + \Delta(PV) = \Delta U + V\Delta P \\ = -50.0 + (40.0)(0.500 - 1.00) \\ = -70.0 \text{ L-atm}$$

c) reversible, isothermal $0.500 \text{ atm} \rightarrow 1.00 \text{ atm}$

$$40.0 \text{ L} \rightarrow 20.0 \text{ L}$$

from before $T = 121.9 \text{ K}$

$\Delta U = \Delta H = 0$ since ideal gas + isothermal

$$q = -w \quad \& \quad w = -\int P dV = -nRT \int \frac{dV}{V} = -nRT \ln \frac{V_f}{V_i}$$

$$= -(2.00)(0.08206)(121.9) \ln \frac{20.0}{40.0}$$

$$w = 13.9 \text{ L-atm}$$

$$q = -13.9 \text{ L-atm}$$

d) cycle: $a \rightarrow b \rightarrow c$

$$q = 70.0 + (-50.0) + (-13.9) = 6.10 \text{ L-atm}$$

$$w = -20.0 + 0 + 13.9 = -6.10 \text{ L-atm}$$

$$\Delta U = \Delta H = 0$$

(4)

(a) Starting with the total differential of P as a function of V and T , obtain an expression for ΔP in terms of α (thermal expansion coefficient) and κ (isothermal compressibility) for the situation where both the temperature and volume change in a general process. Show all work.

(b) A rigid container is filled completely with liquid water and sealed at 25.0°C and a pressure of 1.00 bar. What is the final pressure if the temperature of the system is raised to 60.0°C ? Under these conditions $\alpha_{\text{water}} = 2.04 \times 10^{-4} \text{ K}^{-1}$ and $\kappa_{\text{water}} = 4.59 \times 10^{-5} \text{ bar}^{-1}$ are constants. (Note: α is not really a constant - it rises to $5.16 \times 10^{-4} \text{ K}^{-1}$ at 60°C but don't worry about that for this problem)

$$\textcircled{a} \quad P = P(V, T) \quad dP = \left(\frac{\partial P}{\partial V} \right)_T dV + \left(\frac{\partial P}{\partial T} \right)_V dT$$
$$\text{but } \alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \quad \text{and} \quad \kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$$
$$\text{and} \quad \left(\frac{\partial P}{\partial T} \right)_V = \frac{\alpha}{\kappa}$$

$$\text{hence} \quad dP = -\frac{1}{V\kappa} dV + \frac{\alpha}{\kappa} dT$$
$$\Delta P = -\int_{V_i}^{V_f} \frac{1}{\kappa} \frac{dV}{V} + \int_{T_i}^{T_f} \frac{\alpha}{\kappa} dT$$

$$\textcircled{b} \quad \text{for a rigid container, } dV = 0, \text{ so } \Delta P = \int_{T_i}^{T_f} \frac{\alpha}{\kappa} dT$$

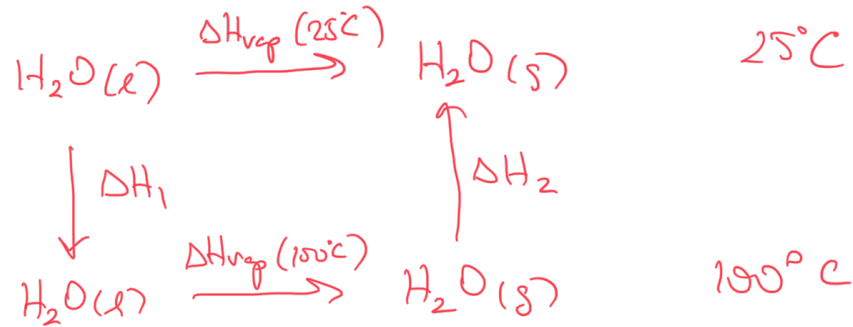
assuming T independence of α and κ ,

$$\Delta P = \frac{\alpha}{\kappa} \Delta T = \frac{2.04 \times 10^{-4}}{4.59 \times 10^{-5}} (60.0 - 25.0) = 156 \text{ bar}$$

$$\text{so } P_f = \Delta P + P_i = \underline{157 \text{ bar}}$$

(5) Calculate the molar heat of vaporization of water at 25°C. The heat of vaporization of water at 100°C is 40.68 kJ/mol.

use the cycle:



$$\Delta H_{\text{vap}}(25^\circ\text{C}) = \Delta H_1 + \Delta H_{\text{vap}}(100^\circ\text{C}) + \Delta H_2$$

$$\Delta H_1 = \int_{25}^{100} C_p(\text{H}_2\text{O}(l)) dT = (75.3)(100-25) = 5647 \text{ J/mol}$$

$$\Delta H_2 = \int_{100}^{25} C_p(\text{H}_2\text{O}(g)) dT = (33.6)(25-100) = -2520 \text{ J/mol}$$

$$\Delta H_{\text{vap}}(25^\circ\text{C}) = 5647 + 40,680 - 2520$$

$$= 43,807 \text{ J} = 43.8 \text{ kJ/mol}$$