# **PHYSICS 140A : STATISTICAL PHYSICS HW ASSIGNMENT #6 SOLUTIONS**

(1)  $\nu = 8$  moles of a diatomic ideal gas are subjected to a cyclic quasistatic process, the thermodynamic path for which is an ellipse in the (V, p) plane. The center of the ellipse lies at  $(V_0, p_0) = (0.25 \text{ m}^3, 1.0 \text{ bar})$ . The semimajor axes of the ellipse are  $\Delta V = 0.10 \text{ m}^3$  and  $\Delta p = 0.20$  bar.

- (a) What is the temperature at  $(V, p) = (V_0 + \Delta V, p_0)$ ?
- (b) Compute the net work per cycle done by the gas.
- (c) Compute the internal energy difference  $E(V_0 \Delta V, p_0) E(V_0, p_0 \Delta p)$ .
- (d) Compute the heat *Q* absorbed by the gas along the upper half of the cycle.

#### Solution :

(a) The temperature is  $T = pV/\nu R$ . With  $V = V_0 + \Delta V = 0.35 \text{ m}^3$  and  $p = p_0 = 1.0 \text{ bar}$ , we  $T = \frac{(10^5 \,\mathrm{Pa})(0.35 \,\mathrm{m}^3)}{(10^5 \,\mathrm{Pa})^2}$ have

$$T = \frac{(10^{5} \text{ Pa})(0.35 \text{ m}^{3})}{(8 \text{ mol})(8.31 \text{ J/mol K})} = 530 \text{ K}$$

(b) The area of an ellipse is  $\pi$  times the product of the semimajor axis lengths.

$$\oint p \, dV = \pi \, (\Delta p)(\Delta V) = \pi \, (0.20 \times 10^6 \, \text{bar}) \, (0.10 \, \text{m}^3) = 6.3 \, \text{kJ} \, .$$

(c) For a diatomic ideal gas,  $E = \frac{5}{2}pV$ . Thus,

$$\Delta E = \frac{5}{2} \left( V_0 \,\Delta p - p_0 \,\Delta V \right) = \frac{5}{2} \left( -0.05 \times 10^5 \,\mathrm{J} \right) = -13 \,\mathrm{kJ}$$

(d) We have  $Q = \Delta E + W$ , with

$$W = 2 p_0 \Delta V + \frac{\pi}{2} (\Delta p) (\Delta V) = 23 \,\mathrm{kJ} \;,$$

which is the total area under the top half of the ellipse. The difference in energy is given by  $\Delta E = \frac{5}{2} p_0 \cdot 2\Delta V = 5 p_0 \Delta V$ , so

$$Q = \Delta E + W = 7 p_0 \Delta V + \frac{\pi}{2} (\Delta p) (\Delta V) = 73 \,\mathrm{kJ} \;.$$

(2) Determine which of the following differentials are exact and which are inexact.

- (a) xy dx + xy dy
- (b)  $(x+y^{-1}) dx xy^{-2} dy$
- (c)  $xy^3 dx + 3x^2y^2 dy$
- (d)  $(\ln y + \ln z) dx + xy^{-1} dy + xz^{-1} dz$

## Solution :

Recall  $dF = \sum_i A_i(x) dx_i$  is exact if  $\frac{\partial A_i}{\partial x_j} = \frac{\partial A_j}{\partial x_i}$  for all *i* and *j*. Thus,

(a) dF = xy dx + xy dy is inexact, since  $\partial A_x / \partial y = x$  but  $\partial A_y / \partial x = y$ . However, dF = xy d(x+y),  $(xy)^{-1} dF = d(x+y)$  is exact.

(b)  $dF = (x + y^{-1}) dx - xy^{-2} dy = d(\frac{1}{2}x^2 + xy^{-1})$  is exact.

(c)  $dF = xy^3 dx + 3x^2y^2 dy$  is inexact, since  $\partial A_x/\partial y = 3xy^2$  but  $\partial A_y/\partial x = 6xy^2$ . However,  $dF = x d(xy^3)$ , so  $x^{-1}dF = d(xy^3)$  is exact.

(d)  $dF = (\ln y + \ln z) dx + xy^{-1} dy + xz^{-1} dz = d(x \ln y + x \ln z)$  is exact.

(3) Liquid mercury at atmospheric pressure and temperature  $T = 0^{\circ}$  C has a molar volume of 14.72 cm<sup>3</sup>/mol and a specific heat a constant pressure of  $c_p = 28.0 \text{ J/mol} \cdot \text{K}$ . Its coefficient of expansion is  $\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_p = 1.81 \times 10^{-4}/\text{K}$  and its isothermal compressibility is  $\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_T = 3.88 \times 10^{-12} \text{ cm}^2/\text{dyn}$ . Find its specific heat at constant volume  $c_V$  and the ratio  $\gamma = c_p/c_V$ . [Reif problem 5.10]

Solution :

According to eqn. (2.307) in the notes,

$$c_p - c_V = \frac{vT\alpha_p^2}{\kappa_T} = \frac{(14.72 \times 10^{-6} \text{m}^3/\text{mol})(273 \text{ K})(1.81 \times 10^{-4}/\text{K})^2}{3.88 \times 10^{-11} \text{ m} \text{ s}^2/\text{kg}} = 3.39 \text{ J/K} \; .$$

Thus,

$$c_V = 24.6 \,\mathrm{J/K}$$
 ,  $\gamma = \frac{c_p}{c_v} = \frac{28.0}{24.6} = 1.14$  .

(4)  $\nu$  moles of an ideal diatomic gas are driven along the cycle depicted in Fig. 1. Section AB is an adiabatic free expansion; section BC is an isotherm at temperature  $T_A = T_B = T_C$ ; CD is an isobar, and DA is an isochore. The volume at B is given by  $V_B = (1 - x) V_A + x V_C$ , where  $0 \le x \le 1$ .

- (a) Find an expression for the total work  $W_{\text{cycle}}$  in terms of  $\nu$ ,  $T_{\text{A}}$ ,  $V_{\text{A}}$ ,  $V_{\text{C}}$ , and x.
- (b) Suppose  $V_A = 1.0 \text{ L}$ ,  $V_C = 5.0 \text{ L}$ ,  $T_A = 500 \text{ K}$ , and  $\nu = 5$ . What is the volume  $V_B$  such that  $W_{\text{cycle}} = 0$ ?



Figure 1: Thermodynamic cycle for problem 4, consisting of adiabatic free expansion (AB), isotherm (BC), isobar (CD), and isochore (DA).

#### Solution :

(a) We have 
$$W_{AB} = W_{DA} = 0$$
, and  
 $W_{BC} = \int_{B}^{C} p \, dV = \nu R \, T_{A} \int_{B}^{C} \frac{dV}{V} = \nu R \, T_{A} \ln\left(\frac{V_{C}}{V_{B}}\right)$   
 $W_{CD} = \int_{C}^{D} p \, dV = p_{C}(V_{D} - V_{C}) = -\nu R \, T_{A} \left(1 - \frac{V_{A}}{V_{C}}\right)$ 

Thus,

$$W_{\rm CYC} = \nu R T_{\rm A} \left[ \ln \left( \frac{V_{\rm C}}{V_{\rm B}} \right) - 1 + \frac{V_{\rm A}}{V_{\rm C}} \right].$$

(b) Setting  $V_{\rm B} = (1 - x) V_{\rm A} + x V_{\rm C}$ , and defining  $r \equiv V_{\rm A}/V_{\rm C}$ , we have

$$W_{CYC} = \nu R T_{A} \left( -\ln \left( x + (1-x)r \right) + 1 - r \right),$$

and setting  $W_{\mathsf{CYC}} = 0$  we obtain  $x = x^*$ , with

$$x^* = \frac{e^{r-1} - r}{1 - r} \; .$$

For  $V_{\mathsf{A}} = 1.0 \,\mathrm{L}$  and  $V_{\mathsf{C}} = 5.0 \,\mathrm{L}$ , we have  $r = \frac{1}{5}$  and  $x^* = 0.31$ , corresponding to  $V_{\mathsf{B}} = 2.2 \,\mathrm{L}$ .

(5) A strange material found stuck to the bottom of a seat in Warren Lecture Hall 2001 obeys the thermodynamic relation  $E(S, V, N) = a S^6 / V^2 N^3$ , where *a* is a dimensionful constant.

- (a) What are the MKS dimensions of *a*?
- (b) Find the equation of state relating *p*, *V*, *N*, and *T*.
- (c) Find the coefficient of thermal expansion  $\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_p$ . Express your answer in terms of intensive quantities p, T, and n = N/V.
- (d) Find the isothermal compressibility  $\kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_T$ . Express your answer in terms of intensive quantities p, T, and n = N/V.

## Solution :

(a) From [E] = J, [S] = J/K, and  $[V] = m^3$ , we obtain  $[a] = m^6 K^5/J^5$ .

(b) We have

$$T = \left(\frac{\partial E}{\partial S}\right)_{VN} = \frac{6aS^5}{V^2N^3} \qquad , \qquad p = -\left(\frac{\partial E}{\partial V}\right)_{SN} = \frac{2aS^6}{V^3N^3} \ .$$

We can eliminate *S* by finding the ratio  $T^6/p^5$ :

$$\frac{T^6}{p^5} = \frac{6^6}{2^5} \cdot \frac{aV^3}{N^3} = 1458 \, a \, n^{-3} \, .$$

This is an equation of state, which we can recast as

$$p(T,n) = \frac{T^{6/5} n^{3/5}}{(1458 a)^{1/5}} .$$

Contrast this with the ideal gas law,  $p = nk_{\rm B}T$ . For parts (c) and (d) it is useful to take the logarithm, and obtain

$$6 \ln T = 5 \ln p + 3 \ln V - 3 \ln N + \ln(1458 a) .$$

(c) The coefficient of volume expansion is

$$\alpha_p = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_{pN} = \left( \frac{\partial \ln V}{\partial T} \right)_{pN} = \frac{2}{T} \,.$$

(d) The isothermal compressibility is

$$\kappa_T = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_{TN} = - \left( \frac{\partial \ln V}{\partial p} \right)_{TN} = \frac{5}{3p}.$$