

**5.60/20.110: Thermodynamics and Kinetics**  
**Solutions to Problem Set #1**

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**1. Identifying boundary conditions:**

- a. Based on the given information, one could state the system is **closed**: the sealed Petri dish prevents exchange of matter with the surroundings, while heat is able to cross the boundary. However, in reality, the Petri dish is not absolutely sealed: some gas exchange is permitted. (CO<sub>2</sub> present in the incubator dissolves into the culture medium and helps to maintain the pH of the culture medium.) In the latter view, the system is **open**.
- b. The living cell is an **open** system. It is able to exchange matter (for example, nutrients and excrements) with its surroundings and exchanges heat with its surroundings.
- c. The seal prevents the exchange of matter. The problem also specifies that the flask is thermally insulated: the system is **isolated**.
- d. As in the cell of part (b), exchange of matter is possible through the boundary of the egg. As suggested by the description, it can also reach thermal equilibrium with the surroundings. The fertilized egg is an **open system**.
- e. Consider the molecular origin of heat (as random motion of molecules). Molecules that enter or leave the system will carry with them energy in the form of heat; hence, heat transfer is an inevitable by product of matter transfer. **An open system cannot be adiabatic**. On the other hand, an adiabatic system can also be closed, such as the sealed flask of part (c).

**2. Equations of state:**

- a. The ideal gas law states  $PV=nRT$ , hence:

$$P = \frac{nRT}{V} = \frac{(1\text{mol})\left(8.315 \times 10^{-2} \text{L} \cdot \text{bar} / \text{mol} \cdot \text{K}\right)(600\text{K})}{0.5\text{L}}$$
$$P = 99.78\text{bar}$$

- b. The van der Waals equation of state is:

$$\left(P + \frac{a}{\bar{V}^2}\right)(\bar{V} - b) = RT, \text{ hence: } P = \frac{RT}{(\bar{V} - b)} - \frac{a}{\bar{V}^2}$$

However, the problem gives the critical values of  $T_c$  and  $P_c$  rather than the van der Waals coefficients  $a$  and  $b$ . The critical values are related to the van der Waals coefficients by the following (consult SAB 1.7 and 1.8 for a thorough discussion):

$$a = \frac{27R^2T_c^2}{64P_c} = \frac{27 \cdot \left(0.0831 \text{L} \cdot \text{bar} / \text{mol} \cdot \text{K}\right)^2 (507.7\text{K})^2}{64 \cdot (30.3\text{bar})} = 24.7\text{bar} \cdot \text{L}^2 \cdot \text{mol}^{-2}$$

$$b = \frac{RT_c}{8P_c} = \frac{\left(0.0831 \text{L} \cdot \text{bar} / \text{mol} \cdot \text{K}\right) \cdot (507.7\text{K})}{8 \cdot (30.3\text{bar})} = 0.174\text{L} \cdot \text{mol}^{-1}$$

Using these values, we obtain:

$$P = \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2} = 54.1 \text{ bar}$$

- c. The ideal gas law states that gas molecules occupy no volume and that they have no interactions with one another. However, n-hexane does occupy an appreciable volume, and the attractive forces between the molecules (dispersion forces) produce a pressure that is lower than what is predicted by the ideal gas law.

### 3. Chemical equilibrium of gases:

We first compute the number of moles 1.588g of  $N_2O_4$  represents:

$$1.588 \text{ g } N_2O_4 \times \frac{1 \text{ mol}}{92 \text{ g}} = 0.0173 \text{ mol } N_2O_4.$$

Now, we let the quantity  $x$  represent the amount in moles of  $N_2O_4$  that dissociate into nitrogen dioxide according to the equation:  $N_2O_4(g) = 2NO_2$ . Then at equilibrium the amount of  $N_2O_4$  that remains is:

$$(0.0173 - x) \text{ mol } N_2O_4$$

And since each molecule of  $N_2O_4$  dissociates into two molecules of  $NO_2$ , at equilibrium there will be  $2x$  moles of  $NO_2$ . Hence, the total moles of gas present at equilibrium is the sum of both gases:

$$\text{Total moles of gases: } (0.0173 - x) + 2x = 0.0173 + x \text{ moles}$$

The problem specified that the equilibrium mixture exerted a pressure of 1.0133 bar. Recalling that the ideal gas does not “care” for the identity of the gases under consideration, we equate the number of moles of gas the pressure constraint requires with the algebraic result above:

$$n = \frac{PV}{RT} = \frac{1.0133 \text{ bar} \cdot 0.5 \text{ L}}{(0.08314 \text{ L} \cdot \text{bar} / \text{mol} \cdot \text{K}) \cdot 298 \text{ K}} = (0.0173 + x) \text{ moles}$$

Solving for  $x$ , the amount of  $N_2O_4$  that dissociated, we obtain:  $x = 0.0031$  moles. Hence the equilibrium quantities are:

$$N_2O_4 : 0.0142 \text{ moles}$$

$$NO_2 : 0.0062 \text{ moles}$$

- a. The mole fractions are:

$$X_{N_2O_4} = \frac{\text{moles of } N_2O_4}{\text{moles of } NO_2 + \text{moles of } N_2O_4} = 0.70$$

$$X_{NO_2} = 0.30$$

- b. The percentage dissociation is:

$$\frac{\text{Moles of } N_2O_4 \text{ dissociated}}{\text{Initial moles of } N_2O_4} = 0.179$$

#### 4. First law use applied to ideal gases:

- a. For an isothermal process involving ideal gases, Boyle's law applies:

$$P_f \cdot V_f = P_0 \cdot V_0$$

$$P_f = P_0 \cdot \left( \frac{V_0}{V_f} \right) = 6 \text{ atm} \cdot \left( \frac{V_0}{2.5V_0} \right) = 2.4 \text{ atm}$$

Since the gas is taken to be ideal,  $\Delta U = 0$  since the process is isothermal.

- b. Calculating expansion work:

- i. Case 1 – constant  $P_{ext} = 1 \text{ atm}$  :

$$\Delta V = V_f - V_0 = 2.5V_0 - V_0 = 1.5V_0 = 0.00375 \text{ L}$$

$$w = -P_{ext} \cdot \Delta V = -(1 \text{ atm}) \cdot 0.00375 \text{ L} \cdot \left( \frac{8.315 \text{ J/mol} \cdot \text{K}}{0.08206 \text{ L} \cdot \text{atm/mol} \cdot \text{K}} \right) = -0.38 \text{ J}$$

- ii. \*Case 2 – reversible, isothermal expansion:

$$n = \frac{P_0 \cdot V_0}{RT_0} = \frac{(6 \text{ atm})(0.0025 \text{ L})}{(0.08206 \text{ L} \cdot \text{atm/mol} \cdot \text{K})(300 \text{ K})} = 6.09 \times 10^{-4} \text{ mol}$$

$$w = -nRT \ln \left( \frac{V_f}{V_0} \right) = (6.09 \times 10^{-4} \text{ mol})(8.315 \text{ J/mol} \cdot \text{K})(300 \text{ K}) \ln(2.5) = -1.39 \text{ J}$$

Since both processes are isothermal,  $\Delta U = 0$ ; and by the first law we obtain:  $q = -w$ . In the constant  $P_{ext} = 1 \text{ atm}$  and reversible processes, +0.38J and 1.39J of heat enters the gas (system) respectively.

From the point of view of the **system**, the work done is *negative*, as calculated above. From the point of view of the operator (*i.e.* the **surroundings**), the work done is *positive*.

- c. The process described represents an *adiabatic, reversible* expansion.

In such processes, the relationship between T and V of a gas is given by:

$$T_2 = T_1 \cdot \left( \frac{V_1}{V_2} \right)^{\gamma-1}, \text{ where } \gamma \text{ is the ratio of } C_p \text{ to } C_v.$$

$$C_p = 37 \text{ J/mol} \cdot \text{K}$$

$$C_v = C_p - R = 29 \text{ J/mol} \cdot \text{K}$$

$$\gamma = \frac{C_p}{C_v} = 1.3$$

Hence, for our system:

$$T_f = T_0 \cdot \left( \frac{V_0}{V_f} \right)^{\gamma-1} = 300 \text{ K} \cdot \left( \frac{V_0}{2.5V_0} \right)^{0.3} = 230 \text{ K}.$$

A drop of 70K for such an expansion (removing a cork) is very high from common experience. Hence, real systems are not close to the adiabatic limit.

d. Work done by gravity is given by:

$$w_{grav} = mg\Delta h = 0.25 \text{ kg} \cdot 9.8 \text{ m/s}^2 \cdot 0.2 \text{ m} = .5 \text{ J}$$

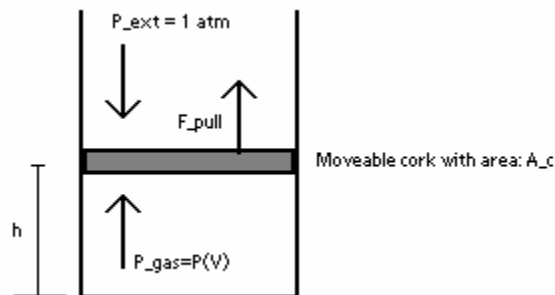
Considering only the magnitudes of the various work:

$$W_{const P} < W_{grav} < W_{reversible}$$

e. The key difference in this problem (from the previous parts) is that, initially, the pressure of the gas is 1 atm. Previously, when we have assumed  $P_0 = 6 \text{ atm}$ , it was plausible that the pressure of the gas alone was sufficient to push the piston outward (against an external pressure of 1 atm) to arrive at the final state. However, in this problem, the initial gas pressure is clearly not sufficient to effect this change of state.

Instead, there must be an *external*, upward force applied in order to achieve the expansion process described. In addition, imagine that you are pulling the cork, thereby increasing the volume available to the gas. As this occurs, as predicted by the ideal gas law, the gas pressure will continuously decrease (at constant T): hence, in order to achieve the expansion, one must apply an upward, *and a steadily increasing* force,  $F_{pull}$ .

Let us describe the system as follows:



Let  $h$  denote the height of the cork with respect to the baseline and  $A_c$  denote the surface area of the cork over which the pressures are applied. In that case, the forces exerted by the gas and the surroundings are

$P_{gas} \cdot A_c$  and  $-P_{ext} \cdot A_c$  respectively, where the signs indicate the direction of force. (As seen in the diagram, “upward” is positive.)

The process has been described to be *reversible*, hence along the path the piston must essentially be in mechanical equilibrium, which requires:

$$\sum \vec{F} = 0 = F_{pull} + P_{gas} \cdot A_c - P_{ext} \cdot A_c$$

This can be rearranged to give:

$$F_{pull} = A_c (P_{ext} - P_{gas})$$

In this problem,  $P_{ext}$  is taken to be a constant but  $P_{gas}$  is not, since the volume available to the gas is changing. Noting that we are under isothermal conditions, we utilize Boyle’s law:

$$P_f \cdot V_f = P_i \cdot V_i$$

$$P_f = P_i \cdot \left( \frac{V_i}{V_f} \right) = P_i \cdot \left( \frac{A_c h_0}{A_c h} \right) = P_i \cdot \left( \frac{h_0}{h} \right)$$

In the above expression,  $h_0$  denotes the initial height of the cork, and  $h$  the current height. We were able to express  $P$  as a function of  $h$ , rather than  $V$  since the volume available to the gas is directly proportional to the height of the cork. (The proportionality constant being the area of the cork.) Also, recall that

$$\text{initially } P_i = P_{ext} = 1 \text{ atm}, \text{ so we may also write: } P_f(h) = P_{ext} \frac{h_0}{h}$$

Since the work is defined as the force integrated over a path, we evaluate it as follows:

$$w = \int F_{pull} \cdot dh = \int A_c (P_{ext} - P_{gas}) \cdot dh = \int A_c \cdot \left( P_{ext} - P_{ext} \cdot \left( \frac{h_0}{h} \right) \right) \cdot dh = A_c P_{ext} \int \left( 1 - \frac{h_0}{h} \right) \cdot dh$$

$$w = A_c P_{ext} \cdot [h - h_0 \ln h]_{h_0}^{h_f} = A_c P_{ext} \cdot (h_f - h_0) - A_c P_{ext} h_0 \ln \frac{h_f}{h_0}$$

$$w = P_{ext} \cdot \Delta V - P_{ext} V_0 \ln \frac{V_f}{V_0}$$

In the last line, we have used the fact that  $A_c h$  represents the volume of the gas and that the volumes are strictly proportional to the heights.

Now we look to the values given for our process. Since  $V_f = 6 \cdot V_0$ ,  $\Delta V = 5V_0 = 0.0125L$ . Hence:

$$w = 1 \text{ atm} \cdot 0.0125L - 1 \text{ atm} \cdot 0.0025L \cdot \ln(6) = .00802 \text{ atm} \cdot L \cdot \left( \frac{8.315 \text{ J/mol} \cdot \text{K}}{0.08206 \text{ L} \cdot \text{atm/mol} \cdot \text{K}} \right) = 0.81J$$

Hence the magnitude of the work involved in moving the cork as described by the problem is 0.81J.

*Additional remarks regarding 4(e); read at leisure:*

To continue the discussion, however, it is now appropriate to ask, is the quantity of work calculated above *positive* or *negative*? This, it turns out, is a very subtle question whose answer depends on the source of the external force, and how we define our system and surroundings. First, let us presume that the source of  $F_{pull}$  is the “operator” who is *external* to the system; in other words, our “system” is restricted strictly to the sample of gas.

If we define our boundaries as above, then the conclusion is that there is actually *no* work being done! In thermodynamics, work is defined as a quantity of energy that crosses the boundary of a system during a change in state\*. If the source of  $F_{pull}$ , the operator, is external to the system, then the process does *not* represent a flow of work across a boundary, but rather a conversion of energy entirely in the surroundings: perhaps the chemical energy of the operator (provided by his breakfast that morning) has now been expended to expand the system against a constant external pressure (which is in principle equivalent to the raising of weight in the surroundings).

If, on the other hand, we consider the operator to be a *part of the system*, then the process may represent the conversion of chemical energy of the operator (who is now contained in the system) to the raising of mass in the surroundings. In this case, the work is nonzero (since it represents a flow from system to surroundings) and is *negative*.

## 5. Mathematical manipulation of state functions:

- a. Since the ideal gas law can be rearranged to give:  $V = V(T, P) = \frac{nRT}{P}$ , the partial derivatives are as

follows:

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{nR}{P} \quad \text{and} \quad \left(\frac{\partial V}{\partial P}\right)_T = \frac{-nRT}{P^2} = \frac{-V}{P}$$

Using the above results in the definition of  $\alpha$  and  $\kappa$ , we obtain:

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P = \frac{nR}{PV} = \frac{1}{T}$$

$$\kappa = \frac{-1}{V} \left(\frac{\partial V}{\partial P}\right)_T = \frac{1}{P}$$

- b. We are now seeking an equation of state  $V = V(T, P)$  such that  $\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P$  and  $\kappa = \frac{-1}{V} \left(\frac{\partial V}{\partial P}\right)_T$

where  $\alpha$  and  $\kappa$  are constants. Clearly, this requires that:

$$\left(\frac{\partial V}{\partial T}\right)_P = V\alpha \quad \text{and} \quad \left(\frac{\partial V}{\partial P}\right)_T = -V\kappa$$

If  $V = V(T, P)$ , then the total derivative of V can be represented as follows:

$$dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP$$

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\* More specifically, work is defined to be the quantity that flows across the boundary of a system during a change in state and is completely convertible into the lifting of a weight in the surroundings.

which becomes:

$dV = V\alpha \cdot dT - V\kappa \cdot dP$  after making suitable substitutions for the partial derivatives.

We can divide the above differential by V and integrate:

$$\int \frac{dV}{V} = \alpha \int dT - \kappa \int dP$$

$$\ln V = \alpha T - \kappa P + C'$$

$$V = Ce^{\alpha T - \kappa P}$$

## 6. Surface tension and the work to create new surfaces:

- a. In order to find the surface energy of 1 mole of water, we need to determine the total surface area of the water when it is dispersed in mist form:

$$\text{Total volume of water: } (1\text{mol}) \cdot \left(\frac{18\text{g}}{1\text{mol}}\right) \cdot \left(\frac{1\text{cm}^3}{1\text{g}}\right) = 18\text{cm}^3$$

Each droplet has volume:  $v_{\text{droplet}} = \frac{4}{3}\pi(10^{-4}\text{cm})^3 = 4.2 \times 10^{-9}\text{cm}^3$ , which means that we have N droplets

$$\text{for 1 mole of water: } N = \frac{18\text{cm}^3}{4.2 \times 10^{-9}\text{cm}^3} = 4.3 \times 10^9 \text{ droplets.}$$

Since each droplet has surface area:  $s_{\text{droplet}} = 4\pi(10^{-4}\text{cm})^2 = 1.26 \times 10^{-5}\text{cm}^2$ , the total surface area is given by:  $s_{\text{total}} = N \cdot s_{\text{droplet}} = 54035\text{cm}^2$

Finally, the surface energy is given by:

$E_s = \gamma \cdot s_{\text{total}}$ , where  $\gamma$  represents the surface tension. Hence:

$$E_s = 71.97 \times 10^{-3} \text{ J/m}^2 \cdot (54035\text{cm}^2) \left(\frac{1\text{m}}{100\text{cm}}\right)^2 = 0.39\text{J}$$

- b. The surface work is given by:

$$w = \int 2\gamma \cdot dA = 2\gamma \int dA = 2\gamma \cdot \Delta A, \text{ assuming } \gamma \text{ to be constant.}$$

If we move the bar through a distance of 1cm, the change in area is  $\Delta A = 5\text{cm}^2$ , since the vertical distance is 5cm.

Using the appropriate values of  $\gamma$ :

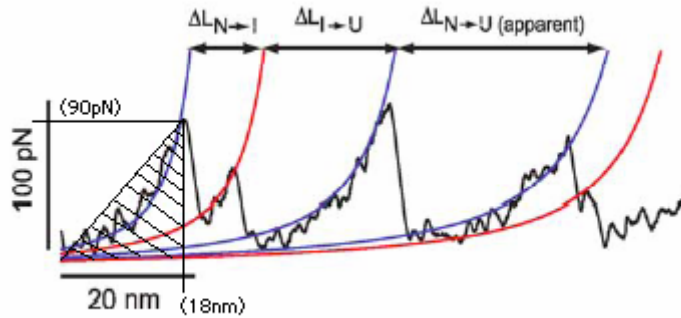
$$w_{\text{water}} = 2 \cdot \left(71.97 \times 10^{-3} \text{ N/m}\right) \cdot (0.05\text{m} \times 0.01\text{m}) = 7.20 \times 10^{-5} \text{ J}$$

$$w_{\text{SDS}} = 2 \cdot \left(60.5 \times 10^{-3} \text{ N/m}\right) \cdot (0.05\text{m} \times 0.01\text{m}) = 6.05 \times 10^{-5} \text{ J}$$

The difference is:  $\Delta w = w_{\text{water}} - w_{\text{SDS}} = 1.15 \times 10^{-5} \text{ J}$

## 7. Work in stretching an extracellular matrix protein:

- a. Recall that for a force-displacement graph, the work done is represented by the area under the curve. If we approximate the (not-quite) triangular area represented by the distension of fibronectin, then:



$$w \approx \frac{1}{2} \cdot (90 \times 10^{-12} \text{ N}) (18 \times 10^{-9} \text{ m}) = 8.1 \times 10^{-19} \text{ J}$$

- b. The work done on fibronectin (as a function of its distension) is given as an integral of the force:

$$w = \int F \cdot dx = \int kx \cdot dx = \frac{1}{2} kx^2$$

If we assume that fibronectin acts as a simple spring with a spring constant of  $5 \text{ mN/m}$ , then the work done in stretching to 20nm beyond the initial state is:

$$w = \frac{1}{2} \cdot (5 \times 10^{-3} \text{ N/m}) \cdot (20 \times 10^{-9} \text{ m})^2 = 1 \times 10^{-18} \text{ J}$$

We can also compute the spring constant using the estimation for work in part (a). Rearranging the work expression above, we find:

$$k = \frac{2w}{x^2} = \frac{2 \cdot 8.1 \times 10^{-19} \text{ J}}{(20 \times 10^{-9} \text{ m})^2} \approx 4 \text{ mN/m} < 5 \text{ mN/m}$$

Our estimation for the spring constant is lower than the reported value of 50 mN/m since the fibronectin does not behave as an ideal (linear) spring. Instead, it has frequent rupture points where the spring constant drops significantly.

## 8. First law and closed cycles:

- a. Using the pressure and volume information given in the plot, we can use the ideal gas law to obtain the temperature at 1, 2, 3:

$$T_1 = \frac{P_1 V_1}{nR} = \frac{1.00 \text{ atm} \cdot 22.44 \text{ L}}{1 \text{ mol} \cdot (0.08206 \text{ L} \cdot \text{atm} / \text{mol} \cdot \text{K})} = 273.46 \text{ K} = 273 \text{ K}$$

Similarly,

$$T_2 = 547 \text{ K}$$

$$T_3 = 273 \text{ K}$$

b. We first focus on the 1→2 process, which is a constant pressure process:

The changes in the state functions  $\Delta U$  and  $\Delta H$  are easily calculated due to our sample being an *ideal gas*. (Note that we are using the ideal gas relationship,  $C_p - C_v = R$  as well)

$$\Delta U_{1 \rightarrow 2} = C_v \Delta T = \frac{3}{2} n R \Delta T = \frac{3}{2} \cdot 1 \text{ mol} \cdot 8.315 \text{ J/mol} \cdot \text{K} \cdot (547 \text{ K} - 273 \text{ K}) = 3410 \text{ J}$$

$$\Delta H_{1 \rightarrow 2} = C_p \Delta T = \frac{5}{2} n R \Delta T = \frac{5}{2} \cdot 1 \text{ mol} \cdot 8.315 \text{ J/mol} \cdot \text{K} \cdot (547 \text{ K} - 273 \text{ K}) = 5680 \text{ J}$$

Since the pressure is constant<sup>†</sup>:

$$w_{1 \rightarrow 2} = -P_{\text{ext}} \Delta V = -1.00 \text{ atm} \cdot (44.88 \text{ L} - 22.44 \text{ L}) = -2244 \text{ L} \cdot \text{atm} = -2270 \text{ J}$$

To find  $q$ , we can utilize the first law, or use the fact that for constant pressure processes  $\Delta H_p = q_p$ . In either case,  $q_{1 \rightarrow 2} = 5680 \text{ J}$ .

Now, consider the 2→3 process, which is a constant volume process:

Again, the changes in the state functions are easily calculated:

$$\Delta U_{2 \rightarrow 3} = C_v \Delta T = \frac{3}{2} n R \Delta T = \frac{3}{2} \cdot 1 \text{ mol} \cdot 8.315 \text{ J/mol} \cdot \text{K} \cdot (273 \text{ K} - 547 \text{ K}) = -3410 \text{ J}$$

$$\Delta H_{2 \rightarrow 3} = C_p \Delta T = \frac{5}{2} n R \Delta T = \frac{5}{2} \cdot 1 \text{ mol} \cdot 8.315 \text{ J/mol} \cdot \text{K} \cdot (273 \text{ K} - 547 \text{ K}) = -5680 \text{ J}$$

Assuming PV work only, there can be no work along process 2→3 since the volume is held constant.

Hence:

$$w_{2 \rightarrow 3} = 0$$

$$q_{2 \rightarrow 3} = \Delta U_{2 \rightarrow 3} = -3410 \text{ J}$$

Finally, consider the 3→1 process, which is an isothermal process:

For an ideal gas, isothermal changes in state implies:

$$\Delta U_{3 \rightarrow 1} = 0$$

$$\Delta H_{3 \rightarrow 1} = 0$$

Assuming the process to be a reversible compression:

$$w_{3 \rightarrow 1} = -nRT \ln \left( \frac{V_1}{V_3} \right) = -1 \text{ mol} \cdot 8.315 \text{ J/mol} \cdot \text{K} \cdot 273 \text{ K} \cdot \ln \left( \frac{22.44 \text{ L}}{44.88 \text{ L}} \right) = 1580 \text{ J}$$

And since  $\Delta U_{3 \rightarrow 1} = 0$ ,

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<sup>†</sup> Note that we have assumed  $P_{\text{ext}} = P$  in order to calculate the work. If this assumption were not made, we could not determine  $w$  (and hence  $q$ ) and these two quantities could not be evaluated numerically.

$$q_{3 \rightarrow 1} = -w_{3 \rightarrow 1} = -1580J$$

Overall cycle:

$$w_{total} = -2270J + 0 + 1580J = -690J$$

$$q_{total} = 5680J - 3410J - 1580J = +690J$$

$$\Delta U_{total} = 3410J - 3410J + 0 = 0$$

$$\Delta H_{total} = 5680J - 5680J + 0 = 0$$

## 9. First law and path dependence of work and heat:

- a. If, along path ACB, the heat and work are +80J and -30J respectively, then by the first law  $\Delta U = q + w$ , the change in internal energy from state A to state B is:

$$\Delta U_{A \rightarrow B} = 80J - 30J = 50J$$

Recall that U is a state function, which indicates that the change in internal energy going from A to B is the same *no matter the particular path taken*. Hence,  $\Delta U_{A \rightarrow B}$  through path ADB must also be +50J.

The problem indicates that along path ADB the work done (by the system<sup>‡</sup>) is 10J. Hence, by the first law we have:

$$\Delta U_{A \rightarrow B} = q_{ADB} + w_{ADB}$$

$$q_{ADB} = \Delta U_{A \rightarrow B} - w_{ADB} = 50J - (-10J) = 60J$$

- b. The internal energy U is a state function; hence its change measured along a cycle must equal 0. (Mathematically,  $\oint dU = 0$ .)

Note that going from A to B, then returning from B to A constitutes a cycle, hence by the definition of a state function, we must have:

$$\Delta U_{A \rightarrow B} + \Delta U_{B \rightarrow A} = 0$$

$$\Delta U_{B \rightarrow A} = -\Delta U_{A \rightarrow B} = -50J$$

Now we use the first law for the curved path:

$$\Delta U_{B \rightarrow A} = w_{curve} + q_{curve}$$

$$q_{curve} = \Delta U_{B \rightarrow A} - w_{curve} = -50J - 20J = -70J$$

According to the sign of q, heat transfer occurs *from the system to the surroundings*. Hence, the system **liberates** 70J of heat.

- c. The problem specifies that  $\Delta U_{A \rightarrow D} = +40J$ . However we know previously that  $\Delta U_{A \rightarrow B} = 50J$ , hence we know that  $\Delta U_{D \rightarrow B} = 10J$ .

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<sup>‡</sup> According to the wording of the problem, it isn't too clear if the work (10J) is being done by the system or by the surroundings. Credit will be given as long as your answers are consistent.

Let's first focus on the segment DB. According to the PV diagram, the path  $D \rightarrow B$  is an isochoric (constant volume) process. Assuming only PV work, this implies that there *cannot* be any work done along the process DB. Combining this with,  $\Delta U_{D \rightarrow B} = 10J$  we obtain:

$$q_{D \rightarrow B} = 10J$$

$$w_{D \rightarrow B} = 0$$

Now we move onto the segment AD. We know previously (from part b) that along the path ADB

$q_{ADB} = 60J$ . Since  $q_{D \rightarrow B} = 10J$ , hence  $q_{A \rightarrow D} = 50J$ . Using the first law (again) with the fact that

$\Delta U_{A \rightarrow D} = +40J$ , we obtain:  $w_{A \rightarrow D} = 10J$ .

### 10. First law and equivalence of work and heat:

First, we compute the amount of heat that is required to raise the temperature of 1kg of water by  $10^\circ C$ , considering that the specific heat capacity of water is  $4.184 \frac{J}{K \cdot g}$ , we find that the heat required is:

$$q = mc\Delta T = 1000g \cdot \left(4.184 \frac{J}{K \cdot g}\right) \cdot 10K = 41840J$$

- a. The work of a mass falling through a gravitational field is given by:  $E = mg\Delta h$  where  $\Delta h$  is the height the mass descends. Solving for  $\Delta h$ :

$$\Delta h = \frac{E}{mg} = \frac{41840J}{1kg \cdot 9.81 \frac{m}{s^2}} = 4265m = 4000m$$

- b. The power dissipated through a resistor is given by:  $P = I^2 R$ . We can obtain the total work done by integrating the power equation, assuming that R and I are constant:

$E = I^2 R \cdot \Delta t$ , which we can solve for  $\Delta t$ :

$$\Delta t = \frac{E}{RI^2} = \frac{41840J}{(1A)^2 100\Omega} = 418s = 400s$$

- c. If the sun's intensity on the collector is  $4 \frac{J}{cm^2 \cdot min}$  and the area of the collector is  $1m^2 = 10000cm^2$ , then the solar energy provided to the collector is:  $40000 \frac{J}{min}$ . Given this rate, the sun is able to

provide 41840J in:  $\Delta t = \frac{E}{Rate} = \frac{41840J}{40000 \frac{J}{min}} = 1.04 min = 1 min$ .

- d. Let x denote the amount of graphite that needs to be burned to produce 41840J of heat:

$$x \cdot \left(\frac{393 \times 10^3 J}{12g}\right) = 41840J, \text{ hence } x = 1.28g = 1g$$