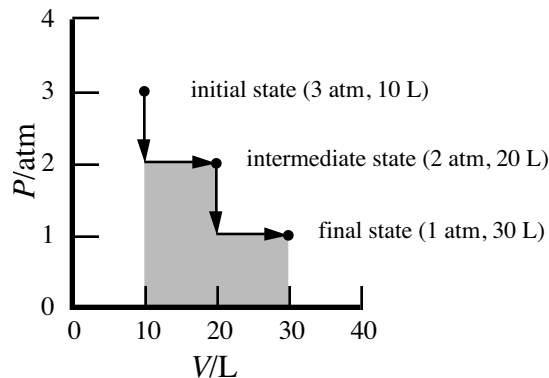


### Problem Set 6 Solutions (For February 17)

1. (a) First, note that the process starts at  $T = 200$  K and *must end* at 200 K because the pressure-volume product  $PV$  is the same at the start and the end, 30 L atm. Along the way, at the intermediate state, the temperature must be  $> 200$  K, because  $PV$  is  $> 30$  L atm. But because  $E$  and  $H$  are both state functions,  $\Delta E$  and  $\Delta H$  depend only on the initial and final states. And here, because the system is an ideal gas that starts and ends at the same temperature,  $\Delta E = \Delta H = 0$ . We calculate the magnitude of  $w$  as the area under the path line in the  $P$ - $V$  diagram, the shaded area below, and note that the process is an expansion, making  $w$  negative: energy was transferred from the system to the surroundings:  $w = -30$  L atm. Because  $\Delta E = 0 = q + w$ ,  $q = -w = +30$  L atm.



(b) In this part of the problem, the volume is fixed (at 30 L), which tells us immediately that there can be no work, because  $w = -P_{\text{ext}}\Delta V$  and “fixed volume” means “ $\Delta V = 0$ .” If the pressure rises from 1.00 atm to 3.00 atm at constant volume, the temperature must have tripled, from 200 K to 600 K, so that  $\Delta T = 400$  K. With  $w = 0$ , and because the system is a sample of ideal gas, we can write  $\Delta E = q = nC_V\Delta T$  with  $C_V = 3R/2$  (we’ll assume a monatomic ideal gas). We could calculate  $n$ , but we don’t need to. Note that  $\Delta T = T_f - T_i = 3T_i - T_i = 2T_i$  because  $T_i = 200$  K and  $T_f = 600$  K =  $3T_i$ . This allows us to write

$$\Delta E = nC_V\Delta T = n\left(\frac{3R}{2}\right)(2T_i) = 3nRT_i = 3P_iV_i = 90 \text{ L atm}$$

For  $\Delta H$ , we can use the *general* expression for an ideal gas,  $\Delta H = nC_P\Delta T$  *even though the pressure isn’t constant*. (Why? Because  $H$  is a state function and doesn’t depend on the details of the path.) For an ideal gas,  $C_P = 5R/2$ , and we find

$$\Delta H = nC_P\Delta T = n\left(\frac{5R}{2}\right)(2T_i) = 5nRT_i = 5P_iV_i = 150 \text{ L atm}$$

We could also find  $\Delta H$  from the definition  $\Delta H = \Delta E + \Delta(PV) = \Delta E + (P_fV_f - P_iV_i) = 90 \text{ L atm} + [(3 \text{ atm})(30 \text{ L}) - (1 \text{ atm})(30 \text{ L})] = 150 \text{ L atm}$ . Note as well that I’ve expressed all energies in L atm rather than joule units. This is fine, but the conversion factor (which will be on the exam in case you feel you need it) is  $101.325 \text{ J} = 1 \text{ L atm}$ . Note that this is the ratio of the two common values we’ve used for  $R$ , the gas constant:

$$\frac{8.314 \text{ J mol}^{-1} \text{ K}^{-1}}{0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}} = 101.3 \text{ J L}^{-1} \text{ atm}^{-1}$$

2. We know that we start at 300 K, 2.00 atm, and 50.0 L, and from this, we could use  $n = PV/RT$  to find the number of moles of gas, but usually this step isn’t necessary. Let’s see how we can manipulate our various  $\Delta E$  and work expressions to avoid doing that. First, the work:  $w = -P_{\text{ext}}\Delta V$ , and we know  $P_{\text{ext}} = 5.00$  atm. This is also the final pressure (because at the final state of the

### Problem Set 6 Solutions (For February 17)

process, the system is at equilibrium, and equilibrium means the external pressure equals the system pressure). Thus, we have

$$w = -P_{\text{ext}}\Delta V = -P_f(V_f - V_i) = P_fV_i - P_fV_f$$

Next, we write the general expression for  $\Delta E$  for an ideal gas:  $\Delta E = nC_V\Delta T$ :

$$\Delta E = nC_V\Delta T = n\left(\frac{3R}{2}\right)(T_f - T_i) = \frac{3}{2}(nRT_f - nRT_i)$$

Now, as the problem suggested, we write this in terms of the  $PV$  products as shown below:

$$\Delta E = \frac{3}{2}(nRT_f - nRT_i) = \frac{3}{2}(P_fV_f - P_iV_i)$$

and we equate this expression to the one we wrote earlier for  $w$ :

$$\Delta E = w = P_fV_i - P_fV_f = \frac{3}{2}(P_fV_f - P_iV_i)$$

We know everything in this last equality except  $V_f$ , for which we can solve:

$$V_f = V_i \frac{2P_f + 3P_i}{5P_f} = (50.0 \text{ L}) \frac{2(5.00 \text{ atm}) + 3(2.00 \text{ atm})}{5(5.00 \text{ atm})} = 32.0 \text{ L}$$

The final temperature is given by

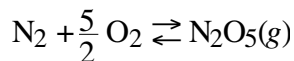
$$\frac{P_iV_i}{T_i} = \frac{P_fV_f}{T_f} \quad \text{or} \quad T_f = T_i \frac{P_fV_f}{P_iV_i} = 300 \text{ K} \frac{(5.00 \text{ atm})(32.0 \text{ L})}{(2.00 \text{ atm})(50.0 \text{ L})} = 480 \text{ K}$$

We find  $\Delta E$  from

$$\Delta E = \frac{3}{2}(P_fV_f - P_iV_i) = 90 \text{ L atm}$$

**3.** We first note that  $\Delta T = (93 - 21)^\circ\text{C} = 72 \text{ K}$ , and the heat needed to raise the water temperature this amount is  $q = nC_p\Delta T = (14 \text{ mol})(75.3 \text{ J K}^{-1} \text{ mol}^{-1})(72 \text{ K}) = 75.9 \text{ kJ}$ . The reaction supplying this heat is  $\text{Na} + (1/2)\text{Cl}_2 \rightleftharpoons \text{NaCl}$ , which is the formation reaction for NaCl. Thus, the enthalpy change of this reaction is just the enthalpy of formation of NaCl,  $-411.15 \text{ kJ mol}^{-1}$ , by definition. We want enough moles of NaCl formed to produce 75.9 kJ. This amount will be  $(75.9 \text{ kJ}/411.15 \text{ kJ mol}^{-1}) = 0.185 \text{ mol}$ . Each mole of NaCl requires 1 mol Na and 0.5 mol  $\text{Cl}_2$ , so that we need 0.185 mol Na and 0.092 mol  $\text{Cl}_2$ .

**4.** For  $\text{N}_2\text{O}_5$ , the formation reaction is

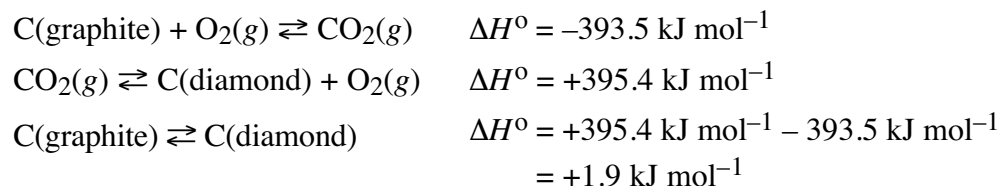


Numbering the three reactions in the problem (1)–(3), top to bottom, we see that this reaction is the combination  $(1) - (2) - (3)/2$ . Reaction enthalpies add in the same way:

$$\begin{aligned} \Delta H^\circ &= \Delta H^\circ(1) - \Delta H^\circ(2) - \frac{\Delta H^\circ(3)}{2} \\ &= 180.6 \text{ kJ mol}^{-1} - 114.4 \text{ kJ mol}^{-1} - \frac{113.4 \text{ kJ mol}^{-1}}{2} \\ &= 9.5 \text{ kJ mol}^{-1} \end{aligned}$$

**Problem Set 6 Solutions** (For February 17)

5. We need the enthalpy change for the reaction  $\text{C}(\text{graphite}) \rightarrow \text{C}(\text{diamond})$ , which we can find if we add the following two reactions and their enthalpies:



The *positive* value for  $\Delta H$  shows that the reaction is *endothermic*. The more stable form of carbon is graphite, and we assign it a standard molar enthalpy of formation value of zero:  $\Delta H_f^\circ = 0$ . That makes the standard molar enthalpy of formation of diamond  $1.9 \text{ kJ mol}^{-1}$ , because the reaction in question,  $\text{graphite} \rightarrow \text{diamond}$ , is the “formation reaction” for diamond.