

**Problem 1 – Kinetic Theory of Gases in an Ultra-High Vacuum Chamber (20 pts)**

a) Starting with the class notes for kinetic theory, we know that the # of particles that will impact a surface is:

$$\#molecules = \frac{1}{2} \eta v_x A \Delta t \quad (1 \text{ point: with or without coefficient of } 1/2)$$

where  $\eta$  is the number density (molecules per unit volume),  $v_x$  is the average molecular speed in the x-direction,  $A$  is the area of the surface for impact and  $\Delta t$  is the time period for impacts.

When we use scaling, we neglect the numerical coefficient and replace = with  $\sim$ . Note that  $\sim$  represents “is proportional to” or “scales like” when reading from left to right.

$$\#molecules \sim \eta v_x A \Delta t. \quad [1]$$

We want to find the molecular impingement flux,  $\Phi$ , defined in the problem statement as the rate at which molecules impact a surface per unit area:

$$\Phi = \frac{\#molecules}{A \Delta t}. \quad [2]$$

(2 points: equation for impingement rate, whether stated explicitly or used implicitly as part of another equation)

Combining Equations [1] and [2],

$$\Phi \sim \eta v_x. \quad [3]$$

From lecture, you should remember that each translational degree of freedom contributes  $\frac{1}{2}k_B T$  of energy to the kinetic energy, where  $k_B$  is the Boltzmann constant and  $T$  is temperature. Neglecting constants,  $mv_x^2 \sim k_B T$ , where  $m$  is the mass of the molecule.

Combining this result with Equation [3],

$$\Phi \sim \eta \sqrt{\frac{k_B T}{m}}. \quad [4]$$

(2 points: any way that students arrive at the proper functional relationship between speed and temperature/mass/constant. Full credit for looking up the mean speed for a Boltzmann distribution.)

Use the ideal gas law to convert between density ( $\eta$ ) and pressure ( $p$ )

$$\eta = \frac{p}{k_B T}. \quad [5]$$

(1 point: students should use the ideal gas law at some point in the problem – it’s OK if they keep it in symbolic form or substitute values earlier/later. Students: Ideally you’ll use symbols as often as possible and plug in numbers only at the very end.)

Combining Equations [4] and [5],

$$\Phi \sim \frac{p}{\sqrt{mk_B T}} \quad [6]$$

Substitute values in Equation [6] using  $m_{\text{air}} = 0.80 \times m_{\text{N}_2} + 0.20 \times m_{\text{O}_2}$  (the weighted average of O<sub>2</sub> and N<sub>2</sub> based on the composition of air),

$$\Phi \sim \frac{(1 \times 10^{-9} \text{ torr}) \left( \frac{133.3224 \text{ Pa}}{1 \text{ torr}} \right) \left( \frac{1 \text{ m}^2}{10^{18} \text{ nm}^2} \right)}{\left[ (0.80 \times 28.0 \text{ amu} + 0.20 \times 32.0 \text{ amu}) \left( \frac{1.6605 \times 10^{-27} \text{ kg}}{1 \text{ amu}} \right) \left( 1.381 \times 10^{-23} \frac{\text{J}}{\text{mol K}} \right) (295 \text{ K}) \right]^{1/2}}$$

**(2 points)** for Equation 6 and substitution of numbers. -1 if mass of air is calculated incorrectly, because we specifically told you how to do so!

$$\Phi \sim 10^{-2} \text{ molec nm}^{-2} \text{ s}^{-1}$$

**(2 points):** accept  $10^{-3}$ ,  $10^{-2}$ , and  $10^{-1}$  as correct numerical values. No credit for an answer with wrong units or numerical value, since we specifically told you the form for your answer!

**Award full credit for a reasonable derivation, even if steps are out of order or combined**

SIDE NOTE #1: If you include all of the appropriate numerical constants in each of the equations, you'll find  $\Phi = 3.8 \times 10^{-3} \text{ molecules}/(\text{nm}^2 \cdot \text{s})$ .

SIDE NOTE #2: Scaling is a useful skill to learn so that you can write a simple equation, like Equation [6], that captures the relationships between variables and parameters.

b) N<sub>2</sub> has the Lennard-Jones parameter  $\sigma$  of  $3.70 \times 10^{-10} \text{ m}$  (p. 392, OGC, Table 9.4). From OGC (p. 392), we know that the molecular diameter  $R_e$  (the position of the potential energy minimum) is at  $2^{1/6}\sigma$ , or  $4.15\text{\AA}$ . **(2 points)**

The mean free path is given by  $\lambda = \frac{1}{2^{1/2} \pi d^2 n_v}$ , where  $d$  is the molecular diameter, and  $n_v$  is the number of molecules per unit volume. **(1 pt)**

Rearranging the ideal gas law, we obtain  $n_v = \frac{N}{V} = \frac{p}{k_B T}$ . Substituting this in the expression for  $\lambda$ , we get

$$\lambda = \frac{k_B T}{2^{1/2} \pi d^2 p} = \frac{k_B T}{2^{1/2} \pi (2^{1/6} \sigma)^2 p} = \frac{k_B T}{2^{5/6} \pi \sigma^2 p} \quad \textbf{(2 points)}$$

Now plug in numbers and solve. If you are still using scaling, then you can drop the  $2^{5/6}$ :

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Ch 1b, Problem Set Five  
Due Friday, Feb 8, 2013  
at 4 PM PST in the Drop Box

$$\lambda = \frac{(1.381 \times 10^{-23} \text{ J mol}^{-1} \text{ K}^{-1})(295 \text{ K})}{2^{5/6} \pi (3.70 \times 10^{-10} \text{ m})^2 (1 \times 10^{-9} \text{ torr}) \left( \frac{133.3224 \text{ Pa}}{1 \text{ torr}} \right)}$$

$$\lambda = 4 \times 10^4 \text{ m OR } 7 \times 10^4 \text{ m (if factor of } 2^{5/6} \text{ is omitted)}$$

So, the mean free path of the  $\text{N}_2$  molecule is  $4 \times 10^4 \text{ m}$  (or  $7 \times 10^4 \text{ m}$  using scaling). **(2 points, no credit for an answer with wrong units, because we specifically told you what to use!)**

c) From part b), we know that  $\lambda$  scales as  $p^{-1}$ . Increasing  $p$  by a factor of  $10^3$  results in a reduction of  $\lambda$  by  $10^3$ . Thus, we expect the mean free path at  $10^{-6} \text{ torr}$  to be  $4 \times 10^1$  (or  $7 \times 10^1 \text{ m}$  using scaling). **(1 pt for any reasonable mathematics, 2 pts answer, no credit for wrong units)**

In our world, traveling 40 m without a collision may seem like a lot. In the world of UHV experiments, it's not!

**2. van der Waals Parameters (15 points)**

a) Start with van der Waals equation, as given,

$$\left(P + a \frac{n^2}{V^2}\right)(V - nb) = nRT.$$

Substitute specific molar volume in pressure term directly,

$$\left(P + \frac{a}{\hat{V}^2}\right)(\hat{V} - b) = RT.$$

Divide both sides by the number of moles and use definition of specific molar volume,

$$\left(P + \frac{a}{\hat{V}^2}\right)(\hat{V} - b) = RT. \quad (2 \text{ points})$$

b)

**Step 1:**

Solve the equation from part a) for pressure:

$$P = \frac{RT}{\hat{V} - b} - \frac{a}{\hat{V}^2}.$$

Take the first derivative with respect to  $\hat{V}$ , evaluate at critical point, and set equal to zero.

$$\left(\frac{\partial P}{\partial \hat{V}}\right)_{T=T_c; P=P_c} = -\frac{RT_c}{(\hat{V}_c - b)^2} + 2\frac{a}{\hat{V}_c^3},$$

$$0 = -\frac{RT_c}{(\hat{V}_c - b)^2} + 2\frac{a}{\hat{V}_c^3}. \quad (2 \text{ points}) \quad [1]$$

Now the second derivative with respect to  $\hat{V}$ , evaluate at critical point, and set equal to zero,

$$\left(\frac{\partial^2 P}{\partial \hat{V}^2}\right)_{T=T_c; P=P_c} = 2\frac{RT_c}{(\hat{V}_c - b)^3} - 6\frac{a}{\hat{V}_c^4},$$

$$0 = 2\frac{RT_c}{(\hat{V}_c - b)^3} - 6\frac{a}{\hat{V}_c^4}. \quad (2 \text{ points}) \quad [2]$$

**Step 2:**

Solve for  $a$  in Equation [1],

$$a = \frac{1}{2} \frac{\hat{V}_c^3 RT_c}{(\hat{V}_c - b)^2}. \quad (1 \text{ pt}) \quad [3]$$

**Step 3:**

Substitute Equation [3] into Equation [2] and solve for  $b$ ,

$$0 = 2 \frac{RT_c}{(\hat{V}_c - b)^3} - 3 \frac{RT_c}{\hat{V}_c (\hat{V}_c - b)^2},$$

$$(\hat{V}_c - b) = \frac{2}{3} \hat{V}_c,$$

$$b = \frac{1}{3} \hat{V}_c. \quad (1 \text{ point}) \quad [4]$$

**Step 4:**

Substitute this result back into Equation [3],

$$a = \frac{1}{2} \frac{\hat{V}_c^3 RT_c}{\left(\hat{V}_c - \frac{1}{3} \hat{V}_c\right)^2},$$

$$a = \frac{1}{2} \frac{\hat{V}_c^3 RT_c}{\left(\frac{2}{3} \hat{V}_c\right)^2},$$

$$a = \frac{9}{8} \hat{V}_c RT_c. \quad (2 \text{ points}) \quad [5]$$

**Step 5:**

Substitute Equations [4] and [5] into the result for Part (a) evaluated at the critical point,

$$\left(P_c + \frac{a}{\hat{V}_c^2}\right)(\hat{V}_c - b) = RT_c,$$

$$\left(P_c + \frac{\frac{9}{8} \hat{V}_c RT_c}{\hat{V}_c^2}\right)\left(\hat{V}_c - \frac{1}{3} \hat{V}_c\right) = RT_c,$$

$$\left(P_c + \frac{9 RT_c}{8 \hat{V}_c}\right) \frac{2}{3} \hat{V}_c = RT_c,$$

$$\left(\frac{2}{3} \hat{V}_c P_c + \frac{3}{4} RT_c\right) = RT_c,$$

$$\hat{V}_c = \frac{3}{8} \frac{RT_c}{P_c}. \quad (2 \text{ points})$$

**Step 6:**

Substitute these results into Equations [4] and [5],

$$b = \frac{1}{8} \frac{RT_c}{P_c} \text{ and } a = \frac{27}{64} \frac{(RT_c)^2}{P_c}. \quad (3 \text{ points total; 1.5 points each})$$

**3. More Equations of State (20 points)**

a) Start with the result in (2a),

$$\left(P + \frac{a}{\hat{V}^2}\right)(\hat{V} - b) = RT.$$

Rearranging,

$$\begin{aligned}\left(P + \frac{a}{\hat{V}^2}\right) &= \frac{RT}{\hat{V} - b}, \\ P &= \frac{RT}{\hat{V} - b} - \frac{a}{\hat{V}^2}, \\ P &= \frac{RT}{\hat{V}} \left( \frac{1}{1 - b/\hat{V}} \right) - \frac{a}{\hat{V}^2}. \quad (2 \text{ points})\end{aligned}$$

Using  $\frac{1}{1-x} \approx 1 + x$  with  $x = b/\hat{V}$ ,

$$\begin{aligned}P &= \frac{RT}{\hat{V}} \left( 1 + \frac{b}{\hat{V}} \right) - \frac{a}{\hat{V}^2}, \\ P &= \frac{RT}{\hat{V}} + \frac{bRT}{\hat{V}^2} - \frac{a}{\hat{V}^2}, \\ P &= RT \left( \frac{1}{\hat{V}} + \frac{b - a/RT}{\hat{V}^2} \right).\end{aligned}$$

Comparing to the virial equation of state,

$$C_2(T) = b - \frac{a}{RT}. \quad (2 \text{ points: answer})$$

b) At high temperatures,  $\frac{a}{RT} \ll b$ , so  $C_2(T) \approx b$ . (1 pt) This means that attractive forces between molecules are minimal ( $a$ ), and the two-body molecular interactions are dominated by excluded volume interactions ( $b$ ). (1 pt)

c) Start with solution for (3a),

$$C_2(T) = b - \frac{a}{RT}.$$

At the Boyle temperature,

$$C_2(T_{\text{Boyle}}) = b - \frac{a}{RT_{\text{Boyle}}} = 0,$$

Rearrange to obtain

$$T_{\text{Boyle}} = \frac{a}{bR}. \quad \text{(1 point)}$$

Substituting values for nitrogen (using values OGC, p. 390),

$$T_{\text{Boyle}} = \frac{(1.390 \text{ atm L}^2 \text{ mol}^{-2})}{(0.03913 \text{ L})(0.0820574 \text{ L atm mol}^{-1} \text{ K}^{-1})} = 433.0 \text{ K}$$

**(2 points, no credit for incorrect units or sigfigs)**

Note: The Boyle temperature for nitrogen is really 332 K. The van der Waals parameters for nitrogen capture general thermodynamic behavior quite well but sometimes miss specific measurements by wide margins. Be careful when using correlations and understand their limitations.

d) The van der Waals parameter,  $b$ , is a measure of excluded *volume* of a single molecule. The Lennard-Jones parameter,  $\sigma$ , is a measure of the intermolecular *distance* at which the potential energy equals zero. From OGC (p. 392),  $R_e = 2^{1/6}\sigma$ , where  $R_e$  is the equilibrium bond length (diameter). ( $\sigma$  is often viewed as the *diameter* of the molecule). Thus, the excluded volume should be equal to a sphere of radius  $R_e/2$ . Using our expression for  $R_e$ , we obtain

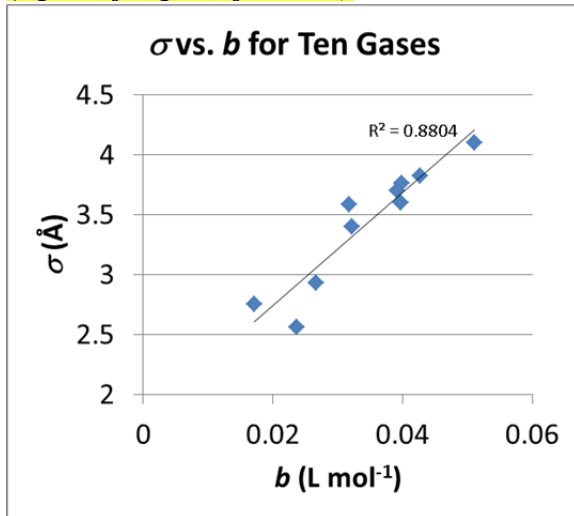
$$b = \frac{4}{3}\pi\left(\frac{R_e}{2}\right)^3 = \frac{1}{6}\pi R_e^3 = \left(\frac{\pi\sqrt{2}}{6}\right)\sigma^3. \quad \text{(1 pt)}$$

Therefore,  $n = 3$ , and a plot of  $\sigma^3$  versus  $b$  should yield a better correlation than  $\sigma$  versus  $b$ . **(1 point)**

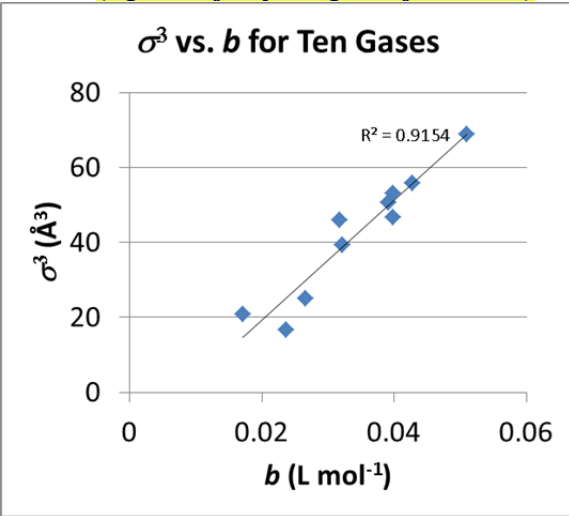
**(Award full credit if the student decided to optimize the expression for the best value of  $n$ )**

Your plots do, in fact, indicate better agreement using  $\sigma^3$  vs.  $b$  rather than  $\sigma$  vs.  $b$ . (A crude way to prove this is to note that  $R^2$  is greater for the  $\sigma^3$  vs.  $b$  plot)

(1 point for plot of  $\sigma$  vs.  $b$ )



(2 points for your plot of  $\sigma^3$  vs.  $b$ )



(Award credit for the second plot if  $\sigma^n$  is consistent with a wrong value of  $n$  in the derivation)

e) Take the answer from part (a) and set it equal to the given equation, (1 point)

$$b - \frac{a}{RT} = \frac{2}{3} \pi N_A \sigma^3 \left( \frac{4\epsilon}{k_B T} \right)^{1/4} \left( 4.902 - 0.151 \left( \frac{4\epsilon}{k_B T} \right)^{1/2} \right).$$

From the hint, the second terms on each side are equal:

$$\begin{aligned} \frac{a}{RT} &= \frac{2}{3} \pi N_A \sigma^3 \left( \frac{4\epsilon}{k_B T} \right)^{1/4} 0.151 \left( \frac{4\epsilon}{k_B T} \right)^{1/2}, \\ \frac{a}{RT} &= \frac{2}{3} 0.151 \pi N_A \sigma^3 \left( \frac{4\epsilon}{k_B T} \right)^{3/4}. \end{aligned}$$

Make the substitution  $R = k/N_A$  and isolate a  $1/RT$  on right-hand side. Then solve for  $a$ .

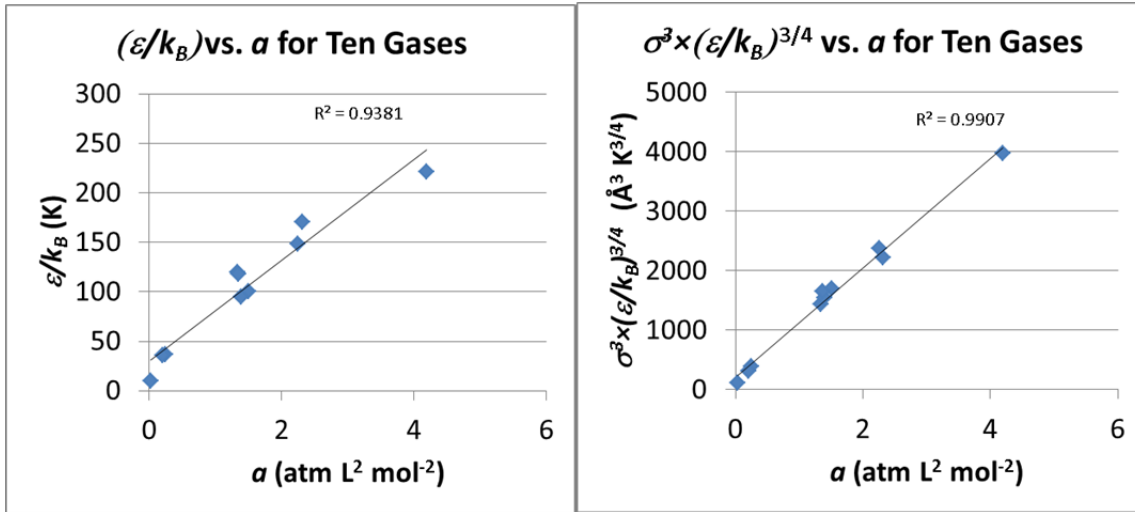
$$\begin{aligned} \frac{a}{RT} &= \frac{2}{3} 0.151 \pi N_A \sigma^3 \left( \frac{k_B T}{4\epsilon} \right)^{1/4} \left( \frac{4\epsilon}{k_B T} \right), \\ \frac{a}{RT} &= \frac{2}{3} 0.151 \pi \sigma^3 4\epsilon \left( \frac{k_B T}{4\epsilon} \right)^{1/4} \left( \frac{N_A}{k_B T} \right), \\ \frac{a}{RT} &= \frac{2}{3} 0.151 \pi \sigma^3 (4\epsilon)^{3/4} (k_B T)^{1/4} \left( \frac{1}{RT} \right), \\ a &= \frac{2}{3} 0.151 \pi \sigma^3 (4\epsilon)^{3/4} (k_B T)^{1/4}. \end{aligned}$$

Since we want to plot  $a$  versus some combination of Lennard-Jones parameters, we can ignore temperature and all constants,

$$a \sim \sigma^3 \epsilon^{3/4}. \quad (2 \text{ points})$$



f) Shown below are the plots of  $\epsilon/k_B$  vs.  $a$  and  $\sigma^3(\epsilon/k_B)^{3/4}$  vs.  $a$ . We observe excellent correlation when we take scaling into account (again, shown crudely by the value of  $R^2$ ).



(1 point)

(2 points if consistent with part e)

**Note to future TAs:** These were the values of  $a$ ,  $b$ ,  $\sigma$ , and  $\epsilon$  taken from OGC (p. 390, 392) and Wikipedia:

Molecule	$a$ (atm L <sup>2</sup> mol <sup>-2</sup> )	$b$ (L mol <sup>-1</sup> )	$\sigma$ (m)	$\epsilon$ (J)
Ar	1.345	0.03219	3.40E-10	1.65E-21
CO	1.505	0.03985	3.76E-10	1.38E-21
H <sub>2</sub>	0.2444	0.02661	2.93E-10	5.11E-22
CH <sub>4</sub>	2.253	0.04278	3.82E-10	2.05E-21
N <sub>2</sub>	1.39	0.03913	3.70E-10	1.31E-21
O <sub>2</sub>	1.36	0.03183	3.58E-10	1.62E-21
He	0.034117937	0.0237	2.56E-10	1.41E-22
Ne	0.210708117	0.01709	2.75E-10	4.92E-22
Kr	2.318282754	0.03978	3.60E-10	2.36E-21
Xe	4.194423884	0.05105	4.10E-10	3.06E-21

**4. Isobaric Cooling (10 points)**

a) In its most general form, work is defined as,

$$w = -\int P_{res} dV,$$

where  $w$  is the *work done on the system*,  $P_{res}$  is the resisting pressure, and  $V$  is the system volume. When we are analyzing the system, the resisting pressure is simply the system pressure,  $P_{sys}$ ,

$$w = -\int P_{sys} dV.$$

Since the piston is frictionless, massless, and moving slowly, the system pressure and the external pressure,  $P_{ext}$ , are equal at all times; thus,

$$w = -\int P_{ext} dV.$$

Since the external pressure is constant, we can pull pressure out of the integral,

$$w = -P_{ext} \int dV.$$

Evaluate the integral,

$$w = -P_{ext} (V_{final} - V_{initial}), \quad [1]$$

where  $V_{final}$  and  $V_{initial}$  are the final and initial system volumes, respectively.

**(1 point for either deriving this equation or citing it correctly from OGC, p. 492)**

The problem tells us that argon is an ideal gas. Substitute gas law for volume in Eq [1],

$$w = -P_{ext} \left( \left( \frac{nRT}{P} \right)_{final} - \left( \frac{nRT}{P} \right)_{initial} \right).$$

The system pressure remains constant and is equal to the external pressure; so pressure divides out of the equation. Since the system is closed, no mass escapes and the mass of argon in the container remains constant. Simplify the equation,

$$w = -nR(T_{final} - T_{initial}). \quad \textbf{(1 point)}$$

Substitute known values to solve for work,

$$w = -(2.00 \text{ mol}) \left( 8.3144721 \frac{\text{J}}{\text{mol} \times \text{K}} \right) (298 \text{ K} - 398 \text{ K}),$$

$$w = 1.66 \times 10^3 \text{ J}. \quad \textbf{(1 point, no credit for incorrect units or sigfigs)}$$

b) Since the system is isobaric, we use the heat capacity at constant pressure to find the heat transferred to the system,

$$q = nc_p \Delta T . \quad (1 \text{ point})$$

We know that *any ideal gas* obeys (OGC, p. 502),

$$c_p = c_v + R ,$$

and that a monatomic ideal gas has  $c_v = 3R/2$  (OGC, p. 501); so

$$c_p = \frac{5}{2} R , \quad (1 \text{ point})$$

$$q = \frac{5}{2} n R \Delta T ,$$

$$q = \frac{5}{2} (2.00 \text{ mol}) \left( 8.3144721 \frac{\text{J}}{\text{mol} \times \text{K}} \right) (298 \text{ K} - 398 \text{ K}) ,$$

$$q = -4.16 \times 10^3 \text{ J}$$

**(1 point answer, no credit if incorrect units or sigfigs are used)**

c) From the first law of thermodynamics, the change in the internal energy is defined as (OGC, p. 496):

$$\Delta U = q + w , \quad (1 \text{ point})$$

$$\Delta U = \frac{5}{2} n R \Delta T - n R \Delta T ,$$

$$\Delta U = \frac{3}{2} n R \Delta T ,$$

$$\Delta U = \frac{3}{2} (2.00 \text{ mol}) \left( 8.3144721 \frac{\text{J}}{\text{mol} \times \text{K}} \right) (298 \text{ K} - 398 \text{ K}) ,$$

$$\Delta U = -2.49 \times 10^3 \text{ J} .$$

**(1 point answer; no credit if incorrect units or sigfigs are used)**

You really shouldn't just use values for your final answer from Parts (a) and (b) since you've already rounded them to the proper number of significant figures – you should use the non-rounded answers or develop a new equation, as shown here. (We'll be nice and not deduct for this though)

d) From the definition of enthalpy (OGC, p. 499–500),

$$H = U + PV,$$

**(1 point)**

we find the change in enthalpy,

$$\Delta H = \Delta U + \Delta(PV).$$

Use the ideal gas law for the  $PV$  term and the symbolic result from Part (c) for internal energy,

$$\Delta H = \frac{3}{2}nR\Delta T + \Delta(nRT),$$

$$\Delta H = \frac{3}{2}nR\Delta T + nR\Delta T,$$

$$\Delta H = \frac{5}{2}nR\Delta T,$$

$$\Delta H = \frac{5}{2}(2.00\text{mol})\left(8.3144721\frac{\text{J}}{\text{mol}\times\text{K}}\right)(298\text{K} - 398\text{K}),$$

$$\Delta H = -4.16 \times 10^3 \text{ J}$$

**(1 point answer, no credit if incorrect units or sigfigs are used)**

Notice that  $\Delta H = q$  for this system, just as we should expect for such a system when the work is entirely pressure-volume work and the external pressure is constant.

**(Award full credit for problem if student uses this reasoning, and then takes their answer to part b)**

**5. Expansion-Compression Cycle (35 points)**

**General notes:** It's always a good idea for thermo problems to write down the data you are given for each state and assign symbols to those variables you don't know. (This makes it easier for us to interpret your work too!)

Define states (and subscripts for variables):

- 1: initial (1.00 atm; 405K;  $V_1$ )
- 2: intermediate (0.600 atm;  $T_2$ ;  $V_2$ ): after adiabatic reversible expansion from '1'
- 3: final ( $P_3$ ;  $T_3=T_2$ ;  $V_3=V_1$ ): after isothermal reversible compression from '2' to the original volume

a) Find the initial volume,  $V_1$ , using the ideal gas law and recognizing that moles of gas remain constant throughout the entire process since the system is a closed system.

$$P_1 V_1 = nRT_1,$$

$$V_1 = \frac{nRT_1}{P_1}. \quad (2 \text{ points}) \quad [1]$$

For an adiabatic reversible expansion, we know that (OGC, p. 515)

$$P_1 V_1^\gamma = P_2 V_2^\gamma, \quad (2 \text{ points})$$

where  $\gamma$  is the ratio of specific heats,

$$\gamma = \frac{c_p}{c_v}.$$

We know that **any ideal gas** obeys (OGC, p. 502),

$$c_p = c_v + R,$$

and we are given that  $c_p(\text{O}_2) = 29.4 \text{ J K}^{-1} \text{ mol}^{-1}$ ,

$$\gamma = \frac{c_p}{c_p - R},$$

$$\gamma = \frac{29.4 \text{ J / K / mol}}{29.4 \text{ J / K / mol} - 8.31447 \text{ J / K / mol}}$$

$\gamma = 1.3943$  (keeping more sig figs since an intermediate calc, but keep in mind that we still have 3 sigfigs at this point). (2 points for value)

Solve for  $V_2$  using  $P_1 V_1^\gamma = P_2 V_2^\gamma$ ,

$$V_2^\gamma = \frac{P_1}{P_2} V_1^\gamma,$$

$$V_2 = \left( \frac{P_1}{P_2} \right)^{1/\gamma} V_1.$$

Substitute Equation [1],

$$V_2 = \left( \frac{P_1}{P_2} \right)^{1/\gamma} \frac{nRT_1}{P_1},$$

**(2 points)**

We don't actually need the volume, but we do need the temperature for state '2' since the gas next undergoes an isothermal expansion and we need to know the final temperature. Substitute the ideal gas law into the above equation and solve for  $T_2$ , **(1 point)**

$$\frac{nRT_2}{P_2} = \left( \frac{P_1}{P_2} \right)^{1/\gamma} \frac{nRT_1}{P_1},$$

$$T_2 = \left( \frac{P_1}{P_2} \right)^{1/\gamma} \frac{P_2}{P_1} T_1,$$

$$T_2 = \left( \frac{P_2}{P_1} \right)^{-1/\gamma} \frac{P_2}{P_1} T_1,$$

$$T_2 = \left( \frac{P_2}{P_1} \right)^{1-1/\gamma} T_1, \quad [2]$$

$$T_2 = \left( \frac{0.600 \text{ atm}}{1.00 \text{ atm}} \right)^{1-1/1.3943} (405 \text{ K}),$$

$T_2 = 350.524 \text{ K}$  (keeping more sig figs since an intermediate calc. Again, we have three sigfigs at this point)

But we know that  $T_3 = T_2$  (isothermal expansion); so

$$T_3 = 351 \text{ K}$$

**(3 points for answer; no credit for an answer with incorrect units or sigfigs)**

**Solution 5b**

Calculate the final pressure using the ideal gas law,

**(1 point)**

$$P_3 V_3 = nRT_3,$$

$$P_3 = \frac{nRT_3}{V_3},$$

Isothermal compression ( $T_3=T_2$ ) to the original volume ( $V_3=V_1$ ),

**(2 points)**

$$P_3 = \frac{nRT_2}{V_1} = nR \frac{1}{V_1} T_2.$$

Substitute Equations [1] and [2],

$$P_3 = nR \frac{P_1}{nRT_1} \left( \frac{P_2}{P_1} \right)^{1-1/\gamma} T_1,$$

$$P_3 = \left( \frac{P_2}{P_1} \right)^{1-1/\gamma} P_1, \quad [3]$$

$$P_3 = \left( \frac{0.600 \text{ atm}}{1.00 \text{ atm}} \right)^{1-1/1.3943} (1.00 \text{ atm}),$$

$$P_3 = 0.865 \text{ atm}$$

**(2 points answer; no credit for incorrect units or sigfigs)**

Hopefully, in Parts (a) and (b) you can see why you want to perform symbolic mathematics as much as possible before substituting numbers. You'll often end up with quite simple relationships that are very easy to evaluate. Notice that we never used the value of the gas constant (nor the number of moles) to find the final temperature and pressure.

The number of moles is an extensive property and will affect energy ( $U$ ,  $H$ ), work and heat transfer. Temperature and pressure are intensive properties. If you used moles to find your answer, you probably used it twice and its effect canceled out.

c) Find the total thermal energy transferred to the system,

$$q_{total} = q_{1 \rightarrow 2} + q_{2 \rightarrow 3}, \quad (1 \text{ point})$$

where  $q_{1 \rightarrow 2}$  is the thermal energy added to the system during adiabatic expansion and  $q_{2 \rightarrow 3}$  is the thermal energy added to the system during isothermal compression.

Find the total work done on the system,

$$w_{total} = w_{1 \rightarrow 2} + w_{2 \rightarrow 3}, \quad (1 \text{ point})$$

where  $w_{1 \rightarrow 2}$  is the work done on the system during adiabatic expansion and  $w_{2 \rightarrow 3}$  is the work done on the system during isothermal compression.

**Step 1: Evaluate the adiabatic expansion to find  $q_{1 \rightarrow 2}$  and  $w_{1 \rightarrow 2}$**

Since the first process is adiabatic,  $q_{1 \rightarrow 2} = 0$  by definition. (1 point)

Write the first law of thermo for the first process,

$$\Delta U_{1 \rightarrow 2} = q_{1 \rightarrow 2} + w_{1 \rightarrow 2}, \quad (1 \text{ point})$$

but  $q_{1 \rightarrow 2} = 0$  (adiabatic),

$$\Delta U_{1 \rightarrow 2} = w_{1 \rightarrow 2}.$$

The internal energy,  $U$ , only depends on temperature for an ideal gas (OGC p. 502)

(1 point)

$$\Delta(nc_v T)_{1 \rightarrow 2} = w_{1 \rightarrow 2},$$

$$nc_v(T_2 - T_1) = w_{1 \rightarrow 2}.$$

Substitute Equation [2] and simplify,

$$nc_v T_1 \left( \left( \frac{P_2}{P_1} \right)^{1-1/\gamma} - 1 \right) = w_{1 \rightarrow 2}.$$

Recall that **any ideal gas** obeys (OGC, p. 502),

$$c_p = c_v + R,$$

and substitute,

$$n(c_p - R)T_1 \left( \left( \frac{P_2}{P_1} \right)^{1-1/\gamma} - 1 \right) = w_{1 \rightarrow 2},$$

$$(3.00 \text{ mol}) (29.4 \text{ J/mol/K} - 8.31447 \text{ J/mol/K}) (405 \text{ K}) \left( \left( \frac{0.600 \text{ atm}}{1.00 \text{ atm}} \right)^{1-1/1.3943} - 1 \right) = w_{1 \rightarrow 2}$$

$$w_{1 \rightarrow 2} = -3445.98 \text{ J} \quad (\text{intermediate calc; three sigfigs, but keep more}) \quad (1 \text{ points})$$

Since  $w_{1 \rightarrow 2} < 0$ , the system is doing work on the surroundings. This sign for the answer should not be a surprise since the volume increased.



**Step 2: Evaluate the isothermal compression to find  $q_{2 \rightarrow 3}$  and  $w_{2 \rightarrow 3}$**

Write the first law of thermo for the second process,

$$\Delta U_{2 \rightarrow 3} = q_{2 \rightarrow 3} + w_{2 \rightarrow 3} . \quad (1 \text{ point})$$

Since the internal energy,  $U$ , only depends on temperature for an ideal gas and this process is isothermal, we can say that  $\Delta U_{2 \rightarrow 3} = 0$  and (1 point)

$$w_{2 \rightarrow 3} = -q_{2 \rightarrow 3} .$$

In its most general form, work is defined as,

$$w_{2 \rightarrow 3} = -\int P_{res} dV ,$$

where  $w$  is the *work done on the system*,  $P_{res}$  is the resisting pressure, and  $V$  is the system volume. When we are analyzing the work done on oxygen, the resisting pressure is simply the system pressure,  $P$ ,

$$w_{2 \rightarrow 3} = -\int P dV .$$

The compressed air is an ideal gas that undergoes an isothermal compression. Substitute the ideal gas law into the above equation,

$$w_{2 \rightarrow 3} = -\int \frac{nRT_2}{V} dV .$$

and simplify,

$$w_{2 \rightarrow 3} = -nRT_2 \int \frac{1}{V} dV ,$$

$$w_{2 \rightarrow 3} = -nRT_2 \ln \left[ \frac{V_3}{V_2} \right] . \quad (2 \text{ points})$$

We know that  $V_3 = V_1$  since the gas is compressed back to its original volume. From our earlier work in Part (a), we also know that:

$$V_2 = \left( \frac{P_1}{P_2} \right)^{1/\gamma} \frac{nRT_1}{P_1} .$$

Substitute both of these equations into  $w_{2 \rightarrow 3}$ ,

$$w_{2 \rightarrow 3} = -nRT_2 \ln \left[ \frac{V_1}{\left( \frac{P_1}{P_2} \right)^{1/\gamma} \frac{nRT_1}{P_1}} \right] ,$$

$$w_{2 \rightarrow 3} = -nRT_2 \ln \left[ \left( \frac{P_2}{P_1} \right)^{1/\gamma} \frac{P_1 V_1}{nRT_1} \right] ,$$

$$w_{2 \rightarrow 3} = -nRT_2 \ln \left[ \left( \frac{P_2}{P_1} \right)^{1/\gamma} \right] \text{ using the ideal gas law.}$$

Substitute Equation [2],

$$w_{2 \rightarrow 3} = -nRT_1 \left( \frac{P_2}{P_1} \right)^{1-1/\gamma} \ln \left[ \left( \frac{P_2}{P_1} \right)^{1/\gamma} \right],$$

$$w_{2 \rightarrow 3} = -(3.00 \text{ mol})(8.31447 \text{ J / mol / K})(405 \text{ K}) \left( \frac{0.600 \text{ atm}}{1.00 \text{ atm}} \right)^{1-1/1.3943} \ln \left[ \left( \frac{0.600 \text{ atm}}{1.00 \text{ atm}} \right)^{1/1.3943} \right]$$

$$w_{2 \rightarrow 3} = 3203.24 \text{ J} \quad \textbf{(1 points)}$$

Since  $w_{2 \rightarrow 3} = -q_{2 \rightarrow 3}$ ,

$$q_{2 \rightarrow 3} = -3203.24 \text{ J}.$$

**Step 3: Combine results to find  $q_{total}$  and  $w_{total}$**

Calculate  $q_{total} = q_{1 \rightarrow 2} + q_{2 \rightarrow 3}$ :

$$q_{total} = 0 - 3203.24 \text{ J},$$

$$q_{total} = -3.20 \times 10^3 \text{ J}.$$

**(2 points, no credit for incorrect units, sigfigs, or sign)**

Calculate  $w_{total} = w_{1 \rightarrow 2} + w_{2 \rightarrow 3}$ :

$$w_{total} = -3445.98 \text{ J} + 3203.24 \text{ J},$$

$$w_{total} = -242.74 \text{ J},$$

$$w_{total} = -243 \text{ J}. \quad \textbf{(1 point, no credit for incorrect units or sigfigs)}$$

d) There are two ways to think about this question:

**Method 1:**

Write the first law of thermo for the overall process,

$$\Delta U_{total} = q_{total} + w_{total}.$$

Use the results from Part (c),

$$\Delta U_{total} = -3203.24 J - 242.74 J,$$

$$\Delta U_{total} = -3445.98 J,$$

$$\Delta U_{total} = -3.45 \times 10^3 J$$

**(1 point, no credit for incorrect units, sigfigs, or sign)**

From the definition of enthalpy (OGC, p. 499–500),

$$H = U + PV,$$

we find the change in enthalpy,

$$\Delta H_{total} = \Delta U_{total} + \Delta(PV)_{1 \rightarrow 3}.$$

The initial and final volume is the same,

$$\Delta H_{total} = \Delta U_{total} + V_1(P_3 - P_1).$$

**(2 points)**

Substitute the ideal gas law and Equation [3],

$$V_1 = \frac{nRT_1}{P_1} \text{ and } P_3 = \left(\frac{P_2}{P_1}\right)^{1-1/\gamma} P_1,$$

into the equation for  $\Delta H_{total}$ ,

$$\Delta H_{total} = \Delta U_{total} + \frac{nRT_1}{P_1} \left( \left(\frac{P_2}{P_1}\right)^{1-1/\gamma} P_1 - P_1 \right),$$

$$\Delta H_{total} = \Delta U_{total} + nRT_1 \left( \left(\frac{P_2}{P_1}\right)^{1-1/\gamma} - 1 \right),$$

$$\Delta H_{total} = -3445.98 J + (3.00 \text{ mol})(8.31447 J / \text{mol} / K)(405 K) \left( \left(\frac{0.600 \text{ atm}}{1.00 \text{ atm}}\right)^{1-1/1.3943} - 1 \right)$$

$$\Delta H_{total} = -3445.98 J - 1358.82 J,$$

$$\Delta H_{total} = -4804.80 J,$$

$$\Delta H_{total} = -4.80 \times 10^3 J$$

**(1 point, no credit for incorrect units, sigfigs, or sign)**

**Method 2**

Energy is a state function, and we don't need to consider the pathway to get from state '1' to state '3'. The change in the internal energy of an ideal gas can be written,

$$\Delta U_{total} = nc_v \Delta T = nc_v (T_3 - T_1).$$

Substitute Equation [2] and use the fact that  $T_3 = T_2$  during the isothermal compression,

$$T_3 = T_2 = \left( \frac{P_2}{P_1} \right)^{1-1/\gamma} T_1,$$

into the equation for  $\Delta U_{total}$ ,

$$\Delta U_{total} = nc_v T_1 \left( \left( \frac{P_2}{P_1} \right)^{1-1/\gamma} - 1 \right), \text{ (1 pt)}$$

We know that **any ideal gas** obeys (OGC, p. 502),

$$c_p = c_v + R,$$

and we are given that  $c_p(\text{O}_2) = 29.4 \text{ J K}^{-1} \text{ mol}^{-1}$ ,

$$\Delta U_{total} = n(c_p - R)T_1 \left( \left( \frac{P_2}{P_1} \right)^{1-1/\gamma} - 1 \right),$$

$$\Delta U_{total} = (3.00 \text{ mol})(29.4 \text{ J / K / mol} - 8.31447 \text{ J / mol / K})(405 \text{ K}) \left( \left( \frac{0.600 \text{ atm}}{1.00 \text{ atm}} \right)^{1-1/1.3943} - 1 \right)$$

$$\Delta U_{total} = -3.45 \times 10^3 \text{ J} . \text{ (1 pt, no credit for incorrect sigfigs, units, or sign)}$$

The change in the enthalpy of an ideal gas can be written,

$$\Delta H_{total} = nc_p \Delta T = nc_p (T_3 - T_1).$$

Make same substitution for  $T_3$  as for internal energy,

$$\Delta H_{total} = nc_p T_1 \left( \left( \frac{P_2}{P_1} \right)^{1-1/\gamma} - 1 \right), \text{ (1 pt)}$$

$$\Delta H_{total} = (3.00 \text{ mol})(29.4 \text{ J / K / mol})(405 \text{ K}) \left( \left( \frac{0.600 \text{ atm}}{1.00 \text{ atm}} \right)^{1-1/1.3943} - 1 \right),$$

$$\Delta H_{total} = -4.80 \times 10^3 \text{ J} . \text{ (1 pt, no credit for incorrect sigfigs, units, or sign)}$$

What's the important takeaway from this exercise? If you only need to find energy changes for an ideal gas and you aren't asked to calculate work and heat, you should take advantage of the fact that energy is a state function.