Ch341, Fall 2008 Test 2
Prof. Shattuck Name________________________________

R= 8.314 somethings = 0.08206 L atm mol^{-1} K^{-1} = 0.08314 bar L K^{-1} mol
1 atm = 1.013×10^5 N m^{-2}

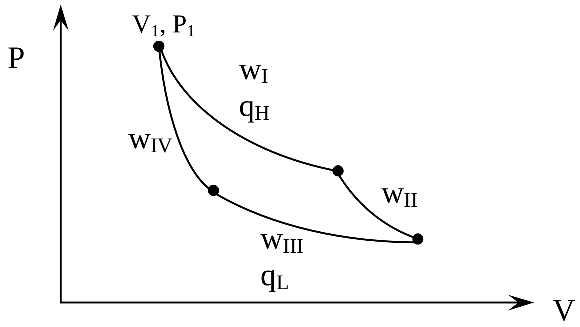
Part 1.

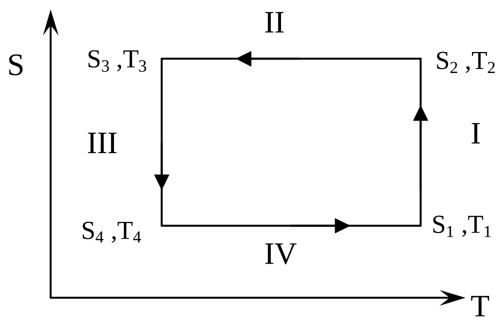
Answer 4 of the following 5 problems. If you answer more than 4, cross out the problem that you don't want graded, otherwise only the first 4 will be graded. (8 points each)

1. What is the molecular interpretation of the "a" constant in the Van der Waals equation of state?

Answer: The Van der Waals a coefficient is a measure of intermolecular attractions.

2. A reversible Carnot cycle is illustrated below. Give a rough sketch of the progress for a reversible Carnot cycle on a plot of entropy versus temperature. Label the steps I-IV so that you can compare with the figure at left. Also indicate the starting point.





3. The activity of 15 ACE inhibitors was fit using the following two alternative QSAR models. The regression coefficient for each QSAR model is given. Which model is the best model and why? Or, rather, are both useful and valid?

Model 1: activity = 4.34 + 0.34 logP – 0.12 ASA – 2.31 dipole + 0.21 E_{sol} $r^2 = 0.897$
Model 2: activity = 2.32 + 0.61 logP – 5.61 MR $r^2 = 0.664$

Answer: With 15 observations you can have at most 3 descriptors; Model 2 is the only valid model. (Model 1 is said to be overdetermined.)

4. One mole of an ideal gas at 298.2 K triples its volume in an isothermal irreversible expansion against $P_{ext} = 0$. Calculate the changes in entropy of the <u>system</u> and the <u>surroundings</u>.

Answer: From Eq. 13.2.10°, $\Delta S = C_v \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$ for any process in an ideal gas. For this isothermal process:

$$\Delta S = nR \ln \frac{V_2}{V_1} = (1 \text{ mol})(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \ln 3 = 9.13 \text{ J K}^{-1}$$

For an isothermal expansion in an ideal gas q = – w = 0, since $P_{ext} = 0$. For the surroundings, q_{surr} = – q giving $\Delta S_{surr} = -q/T_{surr} = 0$.

5. For the work $dw = -P_{ext}\, dV$. Under what circumstances can you substitute P for P_{ext}?

Answer: For any reversible process $P = P_{ext}$. (The pressure need not be constant.)

Part 2

Answer 4 of the following 6 problems. If you answer more than 4, cross out the problems that you don't want graded, otherwise only the first 4 will be graded. (16 points each)

6. A sample consisting of 1.00 mol of an ideal gas with $C_v = {}^3/_2\, nR$ is initially at 3.25 atm and 310. K. The initial volume is 7.83 L. The gas undergoes a reversible adiabatic expansion until its pressure reaches 2.50 atm. Calculate the final volume, temperature, and ΔU for the process.

Answer: For an adiabatic expansion in an ideal gas: q = 0, $\Delta U = C_v\Delta T$, $\Delta H = C_p\Delta T$, and from Eq. 9.8.19°, $(T_2/T_1)^{C_p/nR} = P_2/P_1$. For an ideal gas, $C_p - C_v = nR$, giving ${}^{C_p}/_{nR} = {}^5/_2$:

$$T_2 = T_1\,(P_2/P_1)^{2/5} = 310.\text{ K } (2.50/3.25)^{2/5} = 310.\text{ K } (0.9003) = 279.1 \text{ K}$$

$$\Delta U = C_v\Delta T = {}^5/_2\,(1.00 \text{ mol})\,(279.1 - 310.\text{ K}) = {}^5/_2\,(1.00 \text{ mol})\,(-30.9 \text{ K}) = -642.3 \text{ J}$$

$$\Delta U = -0.64 \text{ kJ}$$

The final volume is given by the equation of state at the final conditions:

$$V = nRT/P = (1.00 \text{ mol})(0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1})(279.1 \text{ K})/2.50 \text{ atm} = 9.16 \text{ L}$$

Alternately, the final volume is given by Eq. 9.8.21°, $P_2 V_2^{\gamma} = P_1 V_1^{\gamma}$ with $\gamma = {}^5/_3$:

$$V_2 = V_1\,(P_1/P_2)^{3/5} = 7.83 \text{ L } (3.25/2.5)^{3/5} = 9.16 \text{ L}$$

7. Show that $\left(\frac{\partial U}{\partial T}\right)_P = C_v + \left(\frac{\partial U}{\partial V}\right)_T V\alpha$

Answer: The total differential of the internal energy with V and T taken as the independent variables:

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \qquad 9.4.3$$

"Dividing" both sides of the equation by dT at constant P gives the partial derivative we are looking for:

$$\left(\frac{\partial U}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_V \frac{dT}{dT} + \left(\frac{\partial U}{\partial V}\right)_T \frac{dV}{dT} \qquad \text{(cst. P)} \qquad 9.4.4$$

where dT/dT is equal to one and the new derivative is at constant pressure:

$$\left(\frac{\partial U}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \qquad 9.4.5$$

The definitions of the constant volume heat capacity and coefficient of thermal expansion are:

$$C_v = \left(\frac{\partial U}{\partial T}\right)_V \qquad \alpha \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \qquad \text{or} \qquad \left(\frac{\partial V}{\partial T}\right)_P = V\alpha \qquad 7.6.8$$

Substitution using the coefficient of thermal expansion and the definition of heat capacity gives:

$$\left(\frac{\partial U}{\partial T}\right)_P = C_v + \left(\frac{\partial U}{\partial V}\right)_T V\alpha$$

8. The standard enthalpy of combustion, at 25.0°C, of the solid amino acid alanine is –1623. kJ/mol. The formula for alanine is $NH_2CH(CH_3)COOH$. The products of the combustion are CO_2(g), H_2O(l), and N_2(g). The enthalpy of formation of CO_2(g) is –393.51 kJ mol^{-1} and for H_2O(l) is –285.83 kJ mol^{-1}. Calculate the enthalpy of formation for alanine.

Answer: The balanced combustion reaction is:

	$NH_2CH(CH_3)COOH$ (s) +	$^{15}/_2\ O_2 \rightarrow$	3 CO_2 (g) +	$^7/_2\ H_2O$ (l) +	½ N_2(g)	units
$\Delta_f H°$	x	0	–393.51	–285.83	0	kJ mol^{-1}

Then $\Delta_r H = \Delta_{comb} H$ = [Σproducts] – [Σreactants] = [3(–393.51) + $^7/_2$(–285.83) + ½(0)] – [x + 0]

–1623. kJ/mol = -2180.935 kJ mol^{-1} – x

$\Delta_f H°$ = x = -558. kJ mol^{-1}

9. The standard enthalpy of combustion, at 25.0°C, of the solid amino acid alanine is –1623. kJ/mol. The formula for alanine is $NH_2CH(CH_3)COOH$. The products are CO_2(g), H_2O(l), and N_2(g) (the same reaction as problem 8). Calculate the internal energy of combustion of alanine.

Answer: From the last problem, for the gases, $\Delta_r n_g = [3 + ½] – [^{15}/_2] = -^8/_2 = -4$. Then from Eq. 8.3.2°, $\Delta_r H = \Delta_r U + \Delta_r n_g RT$:

$$\Delta_r U = \Delta_r H - \Delta_r n_g RT = -1623.\text{ kJ/mol} - (-4)(8.314\text{ J K}^{-1}\text{ mol}^{-1})(1\text{ kJ}/1000\text{ J})(298.15\text{ K})$$
$$= -1623.\text{ kJ/mol} + 9.9\text{ kJ mol}^{-1} = -1613.\text{ kJ mol}^{-1}$$

10. Calculate the molar entropy change for the phase transition of water liquid to water vapor at room temperature, 298.15K, and one atmosphere pressure: $H_2O\ (l) \rightarrow H_2O\ (g)$. The constant pressure heat capacity of liquid water is 75.3 J K^{-1} mol^{-1} and for water vapor is 33.6 J K^{-1} mol^{-1}. The standard enthalpy of vaporization of water <u>at 373.15 K</u> is 40.7 kJ mol^{-1}.

Answer: The phase transition is:

	H_2O (l) →	H_2O (g)	units
$C_{p,m}$	75.3	33.6	J K^{-1} mol^{-1}

giving $\Delta_{tr}C_p$ = -41.7 J K^{-1} mol^{-1}. The change in entropy for vaporization at the normal boiling point, where the process is at equilibrium, is:

$$\Delta_{tr}S = \frac{\Delta_{tr}H}{T_b} = \frac{40.7\text{ kJ mol}^{-1}(1000\text{ J}/1\text{ kJ})}{373.15\text{ K}} = 109._1\text{ J K}^{-1}\text{ mol}^{-1}$$

Then correcting to room temperature using Eq. 12.3.7:

$$\Delta_{tr}S_{T_2} = \Delta_{tr}S_{T_1} + \Delta_{tr}C_p \ln\frac{T_2}{T_1}$$
$$= 109._1\text{ J K}^{-1}\text{ mol}^{-1} + (-41.7\text{ J K}^{-1}\text{ mol}^{-1}) \ln\frac{298.15}{373.15}$$
$$= 109._1 + 9.36\text{ J K}^{-1}\text{ mol}^{-1} = 118._5\text{ J K}^{-1}\text{ mol}^{-1}$$

11. Show that $\left(\frac{\partial H}{\partial V}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T + P - \frac{1}{\kappa_T}$

Answer: Assume that the H in the numerator is the "misplaced" variable, since U is a function of T and V, not H. Using the definition of the enthalpy H ≡ U + PV and the product rule:

$$\left(\frac{\partial H}{\partial V}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T + P\left(\frac{\partial V}{\partial V}\right)_T + V\left(\frac{\partial P}{\partial V}\right)_T$$

Then $(\partial V/\partial V)_T = 1$. The definition of the isothermal compressibility is:

$$\kappa_T \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \qquad \text{giving} \qquad \left(\frac{\partial P}{\partial V}\right)_T = -\frac{1}{V\kappa_T} \qquad 7.6.9$$

Substitution of the isothermal compressibility gives:

$$\left(\frac{\partial H}{\partial V}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T + P - \frac{1}{\kappa_T}$$