

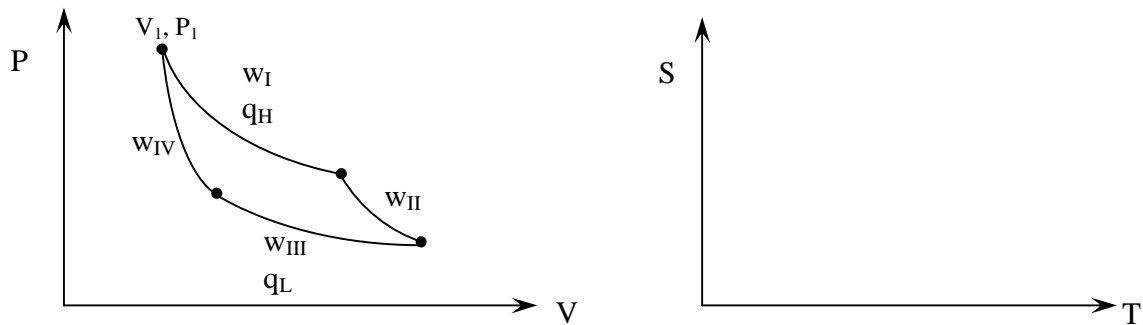
$$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1} = 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1} = 0.08314 \text{ bar L K}^{-1} \text{ mol}^{-1}$$
$$1 \text{ atm} = 1.013 \times 10^5 \text{ N m}^{-2}$$

**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?

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 <sub>sol</sub>	r <sup>2</sup> = 0.897
Model 2: activity = 2.32 + 0.61 logP - 5.61 MR	r <sup>2</sup> = 0.664

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

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

## 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  $C_v = \frac{3}{2} nR$  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  $\Delta U$  for the process.

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

[Show all steps with reasons for each step, for example: "since H is a state function", "from the definition of heat capacity", or "dividing by dP ". If you use a partial derivative relationship that has a name, if you choose not to derive the relationship, just state the corresponding relationship name. (e.g. "from the chain rule" or "from the Euler chain rule")]

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  $\text{NH}_2\text{CH}(\text{CH}_3)\text{COOH}$ . The products of the combustion are  $\text{CO}_2(\text{g})$ ,  $\text{H}_2\text{O}(\text{l})$ , and  $\text{N}_2(\text{g})$ . The enthalpy of formation of  $\text{CO}_2(\text{g})$  is  $-393.51 \text{ kJ mol}^{-1}$  and for  $\text{H}_2\text{O}(\text{l})$  is  $-285.83 \text{ kJ mol}^{-1}$ . Calculate the enthalpy of formation for alanine.

9. The standard enthalpy of combustion, at  $25.0^{\circ}\text{C}$ , of the solid amino acid alanine is  $-1623. \text{ kJ/mol}$ . The formula for alanine is  $\text{NH}_2\text{CH}(\text{CH}_3)\text{COOH}$ . The products are  $\text{CO}_2(\text{g})$ ,  $\text{H}_2\text{O}(\text{l})$ , and  $\text{N}_2(\text{g})$  (the same reaction as problem 8). Calculate the internal energy of combustion of alanine.

10. Calculate the molar entropy change for the phase transition of water liquid to water vapor at room temperature,  $298.15\text{K}$ , and one atmosphere pressure:  $\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}(\text{g})$ . The constant pressure heat capacity of liquid water is  $75.3 \text{ J K}^{-1} \text{ mol}^{-1}$  and for water vapor is  $33.6 \text{ J K}^{-1} \text{ mol}^{-1}$ . The standard enthalpy of vaporization of water at  $373.15 \text{ K}$  is  $40.7 \text{ kJ mol}^{-1}$ .

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

[Show all steps with reasons for each step, for example: "since H is a state function", "from the definition of heat capacity", or "dividing by dP ". If you use a partial derivative relationship that has a name, if you choose not to derive the relationship, just state the corresponding relationship name. (e.g. "from the chain rule" or "from the Euler chain rule")]