

CHM 3400 – Fundamentals of Physical Chemistry
First Hour Exam

There are five problems on the exam. Do all of the problems. Show your work

| | |
|---|--|
| $R = 0.08206 \text{ L}\cdot\text{atm}/\text{mole}\cdot\text{K}$ | $N_A = 6.022 \times 10^{23}$ |
| $R = 0.08314 \text{ L}\cdot\text{bar}/\text{mole}\cdot\text{K}$ | $1 \text{ L}\cdot\text{atm} = 101.3 \text{ J}$ |
| $R = 8.314 \text{ J}/\text{mole}\cdot\text{K}$ | $1 \text{ atm} = 1.013 \text{ bar} = 1.013 \times 10^5 \text{ N}/\text{m}^2$ |

1. (20 points) The van der Waals equation of state is

$$p = \frac{nRT}{(V - nb)} - \frac{an^2}{V^2} \quad (1.1)$$

a) Find the values for the following two partial derivatives for a van der Waals gas

$$(\partial p / \partial T)_{V,n} \qquad (\partial p / \partial V)_{T,n}$$

b) A 0.500 mol sample of xenon (Xe) is confined in a gas cylinder with volume $V = 400.0 \text{ mL}$ at a temperature $T = 300.0 \text{ K}$. Assuming that xenon behaves like a van der Waals gas, find the value for pressure for these conditions. Give your final answer in units of atm. For Xe, $a = 4.081 \text{ L}^2\cdot\text{atm}/\text{mol}^2$, $b = 0.0516 \text{ L}/\text{mol}$.

2. (20 points) The pressure for a real gas at constant temperature can always be written as an expansion in powers of $(1/V)$. Consider the following expression for the pressure of a real gas at constant temperature T

$$p = \frac{a}{V} + \frac{b}{V^2} + \frac{c}{V^3} \quad (2.1)$$

where a , b , and c are constants.

a) Find the value for work when the volume for a real gas obeying eqn 2.1 is changed reversibly and isothermally from an initial value V_i to a final volume V_f . Give your answer in terms of a , b , c , V_i , V_f , and/or other constants.

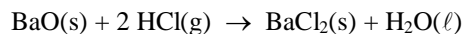
b) By considering the general behavior of real gases it is possible to find an expression for the value for the constant a in eqn 2.1. Briefly explain how this can be done, and give the expression for a . Note that your expression for a should not require knowledge of the values for the constants b and c .

3. (20 points) A partial table of thermodynamic data for two processes is given below. One process is carried out reversibly while the other process is carried out irreversibly. For both processes the system has the same initial and final state. No other information is available concerning the system. Missing entries in the table are labeled by the letters A, B, ...E.

For each missing entry provide the correct value for the entry, or, for cases where there is not sufficient information to provide the missing value, write "cannot tell" and explain why you cannot provide the value from the information given.

| | q (J) | w (J) | ΔU (J) | ΔH (J) |
|--------------|-------|---------|----------------|----------------|
| Reversible | A | + 1511. | B | + 1034. |
| Irreversible | C | D | + 895. | E |

4. (24 points) Barium oxide (BaO) will react with hydrogen chloride (HCl) by the process given below



Find the following for the above reaction.

- $\Delta H^\circ_{\text{rxn}}$, at $T = 298. \text{ K}$.
- $\Delta U^\circ_{\text{rxn}}$, at $T = 298. \text{ K}$.
- $\Delta H^\circ_{\text{rxn}}$, at $T = 373. \text{ K}$.

Data of use in answering this problem are given below for $T = 298.0 \text{ K}$

| Substance | ΔH°_f (kJ/mol) | S° (J/mol·K) | ΔG°_f (kJ/mol) | $C_{p,m}$ (J/mol·K) |
|-----------------------|--------------------------------|------------------------|--------------------------------|------------------------|
| BaCl ₂ (s) | - 858.6 | 123.68 | - 810.4 | 75.14 |
| BaO(s) | - 553.5 | 70.43 | - 525.1 | 47.78 |
| HCl(g) | - 92.31 | 186.91 | - 95.30 | 29.12 |
| H ₂ O(l) | - 285.83 | 69.91 | - 237.13 | 75.291 |

5. (16 points) The pressure of 1.000 mol of an ideal gas is changed from an initial value $p_i = 10.00 \text{ atm}$ to a final value $p_f = 1.000 \text{ atm}$, by some unspecified constant temperature process, with $T = 320.0 \text{ K}$. Note that the temperature of the surroundings is also constant and equal to 320.0 K . The constant pressure molar heat capacity of the gas is $C_{p,m} = 20.79 \text{ J/mol}\cdot\text{K}$. q for the process is 2400.0 J .

What are ΔS_{sys} , ΔS_{surr} , and ΔS_{univ} for the above process?