

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.

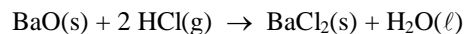
b) By considering the general behavior of real gases it is possible to find an expression for the value for the constant a in eqn 2.1. Briefly explain how this can be done, and give the expression for a . Note that your expression for a should not require knowledge of the values for the constants b and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

Solutions.

$$1) \quad a) \quad (\partial p / \partial T)_{V,n} = \frac{nR}{(V - nb)} \quad (\partial p / \partial V)_{T,n} = - \frac{nRT}{(V - nb)^2} + \frac{2an^2}{V^3}$$

b) Substitution into the van der Waals equation gives

$$p = \frac{(0.500 \text{ mol})(0.08206 \text{ L}\cdot\text{atm/mol}\cdot\text{K})(300.0 \text{ K})}{[0.4000 \text{ L} - (0.500 \text{ mol})(0.0516 \text{ L/mol})]} - \frac{(4.081 \text{ L}^2\cdot\text{atm/mol}^2)(0.500 \text{ mol})^2}{(0.400 \text{ L})^2}$$
$$= 32.89 \text{ atm} - 6.38 \text{ atm} = 26.51 \text{ atm}$$

2) a) The process is reversible (so $p_{\text{ex}} = p$) and isothermal (so T is constant). So

$$w = - \int_i^f p_{\text{ex}} dV = - \int_i^f p dV = - \int_i^f \left\{ \frac{a}{V} + \frac{b}{V^2} + \frac{c}{V^3} \right\} dV$$
$$= - \left\{ a \ln(V_f/V_i) - b \left[\frac{1}{V_f} - \frac{1}{V_i} \right] - \frac{c}{2} \left[\frac{1}{V_f^2} - \frac{1}{V_i^2} \right] \right\}$$

b) All gases behave like ideal gases in the limit $V \rightarrow \infty$. So we may say

$$\frac{a}{V} + \frac{b}{V^2} + \frac{c}{V^3} = \frac{nRT}{V} \quad \text{in the limit } V \rightarrow \infty.$$

If we multiply both sides of the above by V , we get

$$a + \frac{b}{V} + \frac{c}{V^2} = nRT \quad \text{in the limit } V \rightarrow \infty.$$

But as V becomes large the second and third terms on the left side of the equation become negligible, and so in this limit

$$a = nRT$$

3) Since little specific information is given about the process we must carefully focus on what we do know. We cannot assume the process is isothermal, or constant volume, or constant pressure, or that the substance is ideal, or anything else, because there is nothing in the problem suggesting these are good assumptions to make.

Both processes have the same initial and final state for the system, and so the change in value for any state function for the system will be the same. Therefore ΔU and ΔH will be the same for the reversible and irreversible processes. Based on this, we may say

$$B = + 895. \text{ J} \quad E = + 1034. \text{ J}$$

From the first law, $\Delta U = q + w$. Since we know ΔU and w for the reversible process, it follows that

$$w = \Delta U - q = 895. \text{ J} - (1511. \text{ J}) = - 616. \text{ J} \quad \text{So } A = - 616. \text{ J}$$

The first law also applies to the irreversible process, but we only know the value for ΔU . Since we don't know either q or w for this process, neither one can be found. So for C and D we cannot tell what the values are.

$$4) \quad a) \quad \Delta H^\circ_{\text{rxn}} = [\sum \Delta H^\circ_f(\text{products})] - [\sum \Delta H^\circ_f(\text{reactants})]$$

$$= [\Delta H^\circ_f(\text{BaCl}_2(\text{s})) + \Delta H^\circ_f(\text{H}_2\text{O}(\text{l}))] - [\Delta H^\circ_f(\text{BaO}(\text{s})) + 2 \Delta H^\circ_f(\text{HCl}(\text{g}))]$$

$$= [(- 858.6 \text{ kJ/mol}) + (- 285.83 \text{ kJ/mol})] - [(- 553.5 \text{ kJ/mol}) + 2 (- 92.31 \text{ kJ/mol})]$$

$$= (- 1144.43 \text{ kJ/mol}) - (- 738.12 \text{ kJ/mol}) = - 406.3 \text{ kJ/mol}$$

b) To a good first approximation we may say

$$\Delta H^\circ_{\text{rxn}} \cong \Delta U^\circ_{\text{rxn}} + \Delta n_g RT$$

So
$$\Delta U^\circ_{\text{rxn}} = \Delta H^\circ_{\text{rxn}} - \Delta n_g RT = - 406.3 \text{ kJ/mol} - (- 2)(8.314 \times 10^{-3} \text{ kJ/mol}\cdot\text{K})(298. \text{ K})$$

$$= - 406.3 \text{ kJ/mol} + 4.96 \text{ kJ/mol} = - 401.3 \text{ kJ/mol}$$

c) In general

$$\Delta H^\circ_{\text{rxn}}(T_2) = \Delta H^\circ_{\text{rxn}}(T_1) + \int_{T_1}^{T_2} \Delta C_p dT$$

If we can assume ΔC_p is independent of temperature, then ΔC_p can be taken outside of the integral, to give

$$\Delta H^\circ_{\text{rxn}}(T_2) = \Delta H^\circ_{\text{rxn}}(T_1) + \int_{T_1}^{T_2} \Delta C_p dT = \Delta H^\circ_{\text{rxn}}(T_1) + \Delta C_p (T_2 - T_1)$$

$$\Delta C_p = [\sum C_p(\text{products})] - [\sum C_p(\text{reactants})]$$

$$= [C_{p,m}(\text{BaCl}_2(\text{s})) + C_{p,m}(\text{H}_2\text{O}(\text{l}))] - [C_{p,m}(\text{BaO}(\text{s})) + 2 C_{p,m}(\text{HCl}(\text{g}))]$$

$$= [(75.14 \text{ J/mol}\cdot\text{K}) + (75.291 \text{ J/mol}\cdot\text{K})] - [((47.78 \text{ J/mol}\cdot\text{K}) + 2 (29.12 \text{ J/mol}\cdot\text{K}))]$$

$$= (150.431 \text{ J/mol}\cdot\text{K}) - (106.02 \text{ J/mol}\cdot\text{K}) = 44.41 \text{ J/mol}\cdot\text{K}$$

And so
$$\Delta H^\circ_{\text{rxn}}(373. \text{ K}) = \Delta H^\circ_{\text{rxn}}(298. \text{ K}) + \Delta C_p (373. \text{ K} - 298 \text{ K})$$

$$= - 406.3 \text{ kJ/mol} + (44.41 \times 10^{-3} \text{ kJ/mol}\cdot\text{K})(373. \text{ K} - 298. \text{ K})$$

$$= - 406.3 \text{ kJ/mol} + 3.33 \text{ kJ/mol} = - 403.0 \text{ kJ/mol}$$

5) To find ΔS_{sys} , we need a reversible process with the same initial and final state as the unspecified process in the problem. A reversible isothermal expansion from $p_i = 10.00 \text{ atm}$ to $p_f = 1.00 \text{ atm}$ is such a process. For that process

$$\Delta S_{\text{sys}} = \int_i^f (\delta q)_{\text{rev}}/T.$$
 The process being used to find ΔS_{sys} is isothermal and reversible, and so we can take T outside the integral, to get

$$\Delta S_{\text{sys}} = (1/T) \int_i^f (\delta q)_{\text{rev}} = q_{\text{rev}}/T$$

For an isothermal reversible expansion of an ideal gas, $q_{\text{rev}} = nRT \ln(p_i/p_f)$

And so
$$\Delta S_{\text{sys}} = (1/T) [nRT \ln(p_i/p_f)] = nR \ln(p_i/p_f) = (1.00 \text{ mol}) (8.314 \text{ J/mol}\cdot\text{K}) \ln(10.0/1.00)$$

$$= 19.14 \text{ J/K}$$

$$\Delta S_{\text{surr}} = - q_{\text{sys}}/T = - 2400.\text{J}/320.0 \text{ K} = - 7.50 \text{ J/K}$$
 (Note that moving 2400. J of heat from the system to the surroundings is reversible from the point of view of the surroundings, even if the process taking place is irreversible from the point of view of the system.)

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 19.14 \text{ J/K} + (- 7.50 \text{ J/K}) = 11.64 \text{ J/K}$$