

CHM 3400 – Fundamentals of Physical Chemistry
 First Hour Exam
 February 12, 2021

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

R = 0.082057 L·atm/mole·K	$N_A = 6.022 \times 10^{23}$
R = 0.083145 L·bar/mole·K	1 L·atm = 101.3 J
R = 8.3145 J/mole·K	1 atm = 1.013 bar = 1.013×10^5 N/m ²
	1 atm = 760 torr

1. (25 points) A sample of acetone vapor (C₃H₆O, MW = 58.08 g/mol) at T = 340.0 K has a number density of molecules $N = 4.18 \times 10^{17}$ molecule/cm³.

a) What is the pressure of acetone vapor in the sample? Give your final answer in units of torr. You may assume ideal behavior for the acetone vapor.

b) The critical pressure and temperature for acetone are $p_C = 47.1$ atm, $T_C = 508.1$ K. Based on this, find the values for the van der Waals a and b coefficients for acetone. Give you value for a in units of L²·atm/mol², and your value for b in units of L/mol.

2. (25 points) The compound 1-nonyl alcohol (C₉H₂₀O(ℓ), MW = 144.25 g/mol) is a high molecular weight alcohol.

a) Give the correctly balanced formation reaction and the correctly balanced combustion reaction for 1-nonyl alcohol.

b) The enthalpy of combustion for 1-nonyl alcohol is $\Delta H^\circ_{\text{comb}}(\text{C}_9\text{H}_{20}\text{O}(\ell)) = -5947.0$ kJ/mol. Based on this information and the data below, find the value for $\Delta H^\circ_f(\text{C}_9\text{H}_{20}\text{O}(\ell))$, the enthalpy of formation for 1-nonyl alcohol. Assume T = 25.0 °C.

Substance	ΔH°_f (kJ/mol)	ΔG°_f (kJ/mol)	S° (J/mol·K)	$C_{p,m}$ (J/mol·K)
CO ₂ (g)	- 393.51	- 394.36	213.74	37.11
O ₂ (g)	0.0	0.0	205.14	29.36
H ₂ O(ℓ)	- 285.83	- 237.13	69.91	75.29
H ₂ O(g)	- 241.82	- 228.57	188.83	33.58

3) (25 points) The compressibility factor for a gas, Z, is defined as

$$Z = \frac{pV}{nRT} \quad (3.1)$$

For moderate values of pressure the compressibility factor is often fit to the equation

$$Z = 1 + \frac{nB}{V} \quad (3.2)$$

where n is the number of moles of gas and B is a constant found from fitting experimental data to eq 3.2

For a particular gas at T = 290.0 K the value of B is B = 0.042 L/mol. Based on this, find the following:

a) The value for pressure (p) when 1.000 mol of the gas is confined in a volume V = 0.800 L at T = 290.0 K. Give your final answer in units of atm.

b) The value for work (w) when 1.000 mol of the gas is expanded reversibly and isothermally from an initial volume $V_i = 1.000$ L to a final volume $V_f = 75.00$ L. Give your final answer in units of kJ.

4. (25 points) Consider the following chemical reaction



Thermodynamic data for the substances involved in the above reaction are given below (at $T = 298.0 \text{ K}$), and may be of use in doing this problem.

Substance	ΔH°_f (kJ/mol)	ΔG°_f (kJ/mol)	S° (J/mol·K)	$C_{p,m}$ (J/mol·K)
C(s)	0.0	0.0	5.7	8.5
H ₂ (g)	0.0	0.0	130.7	28.8
HBr(g)	- 36.3	- 53.4	198.7	29.1
CHBr ₃ (ℓ)	- 22.3	- 5.0	220.9	130.7

a) What is the value for $\Delta S^\circ_{\text{rxn}}$ for reaction 4.1, at $T = 298.0 \text{ K}$? Give your final answer in units of J/mol·K.

b) What is the value for $\Delta S^\circ_{\text{rxn}}$ for reaction 4.1, at $T = 400.0 \text{ K}$? Give your final answer in units of J/mol·K. NOTE: Do not assume the value for $\Delta S^\circ_{\text{rxn}}$ is independent of temperature in this part of the problem.

Solutions.

1) a) $pV = nRT$

So $p = \frac{nRT}{V}$ But $n/V = N/N_A$, where N_A is Avogadro's number

And so $p = (N/N_A)RT$

$$\frac{N}{N_A} = \frac{4.18 \times 10^{17} \text{ molecules}}{\text{cm}^3} \frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ molecule}} \frac{1000. \text{ cm}^3}{\text{L}} = 6.941 \times 10^{-4} \text{ mol/L}$$

So $p = (6.941 \times 10^{-4} \text{ mol/l}) (0.082057 \text{ L}\cdot\text{atm/mol}\cdot\text{K}) (340.0 \text{ K})$

$$= 0.01937 \text{ atm} \frac{760. \text{ torr}}{1 \text{ atm}} = 14.72 \text{ torr}$$

b) The equations for p_c and T_c are

$$p_c = \frac{a}{27b^2}$$

$$T_c = \frac{8a}{27Rb}$$

If we solve each of these equations for a, we get

$$\text{From } p_c \quad a = 27b^2p_c$$

$$\text{From } T_c \quad a = \frac{27RbT_c}{8}$$

If we set these two expressions equal to one another, we get

$$27b^2p_c = \frac{27RbT_c}{8}$$

If we divide both sides of this equation by $27bp_c$, we get

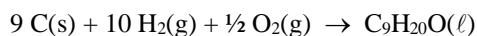
$$b = \frac{27RbT_c}{8} \frac{1}{27bp_c} = \frac{RT_c}{8p_c} = \frac{(0.082057 \text{ L}\cdot\text{atm/mol}\cdot\text{K})(508.1 \text{ K})}{8(47.1 \text{ atm})} = 0.1107 \text{ L/mol}$$

We can then substitute into the expression for a found from the equation for p_c , to get

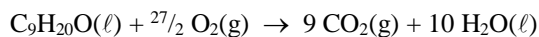
$$a = 27b^2p_c = 27 (0.1107 \text{ L/mol})^2 (47.1 \text{ atm}) = 15.57 \text{ L}^2\cdot\text{atm/mol}^2$$

Note – This is often the way values for the van der Waals a and b coefficients are actually obtained, since as we saw previously the values for a and b found from these expressions are close to those found from experiment when a comparison can be done.

2) a) Formation reaction



Combustion reaction



b) Using the general method for finding $\Delta H^\circ_{\text{rxn}}$, we may say for the combustion reaction that

$$\Delta H^\circ_{\text{rxn}} = \Delta H^\circ_{\text{comb}} = [9 \Delta H^\circ_f(\text{CO}_2(\text{g})) + 10 \Delta H^\circ_f(\text{H}_2\text{O}(\ell))] - [\Delta H^\circ_f(\text{C}_9\text{H}_{20}\text{O}(\ell)) + {}^{27}/_2 \Delta H^\circ_f(\text{O}_2(\text{g}))]$$

And so $\Delta H^\circ_f(\text{C}_9\text{H}_{20}\text{O}(\ell)) = [9 \Delta H^\circ_f(\text{CO}_2(\text{g})) + 10 \Delta H^\circ_f(\text{H}_2\text{O}(\ell))] - [\Delta H^\circ_{\text{comb}}(\text{C}_9\text{H}_{20}\text{O}(\ell)) + {}^{27}/_2 \Delta H^\circ_f(\text{O}_2(\text{g}))]$

$$= [9(-393.51) + 10(-285.83)] - [(-5947.0) + {}^{27}/_2(0.0)]$$

$$= -452.9 \text{ kJ/mol}$$

3) a) Setting the two expressions for Z equal to one another gives

$$\frac{pV}{nRT} = 1 + \frac{nB}{V}$$

or $p = \frac{nRT}{V} \left[1 + \frac{nB}{V} \right] = \frac{nRT}{V} + \frac{n^2RTB}{V^2}$

$$= \frac{(1.000 \text{ mol})(0.082057 \text{ L}\cdot\text{atm/mol}\cdot\text{K})(290.0 \text{ K})}{(0.800 \text{ L})} \left[1 + \frac{(1.000 \text{ mol})(0.042 \text{ L/mol})}{(0.800 \text{ L})} \right]$$

$$= (29.746 \text{ atm})(1.0525) = 31.31 \text{ atm}$$

b) The process is reversible and isothermal, and so

$$w = -\int_i^f p_{\text{ex}} dV = -\int_i^f p dV = -\int_i^f \left\{ \frac{nRT}{V} + \frac{n^2RTB}{V^2} \right\} dV$$

$$= -\left\{ nRT \ln(V_f/V_i) - n^2RTB \left[\frac{1}{V_f} - \frac{1}{V_i} \right] \right\}$$

$$= -\left\{ (1.000 \text{ mol})(8.3145 \text{ J/mol}\cdot\text{K})(290.0 \text{ K}) \ln(75.00/1.00) \right.$$

$$\left. - (1.000 \text{ mol})^2 (8.3145 \text{ J/mol}\cdot\text{K})(290.0 \text{ K})(0.042 \text{ L/mol}) \left[\frac{1}{75.00 \text{ L}} - \frac{1}{1.00 \text{ L}} \right] \right\}$$

$$= -\left\{ (10410 \text{ J}) - (-99.9 \text{ J}) \right\} = -10510 \text{ J}$$

4) a) At $T = 298.0 \text{ K}$

$$\Delta S^\circ_{\text{rxn}} = [S^\circ(\text{CHBr}_3(\ell)) + S^\circ(\text{H}_2(\text{g}))] - [S^\circ(\text{C}(\text{s})) + 3 S^\circ(\text{HBr}(\text{g}))]$$

$$= [(220.9) + (130.7)] - [(5.7) + 3(198.7)] = -250.2 \text{ J/mol}\cdot\text{K}$$

b) To find the value for $\Delta S^\circ_{\text{rxn}}$ we may use the relationship

$$\Delta S^\circ_{\text{rxn}}(T_2) = \Delta S^\circ_{\text{rxn}}(T_1) + \int_{T_1}^{T_2} \Delta C_{p,m}/T dT$$

$$\Delta C_{p,m} = [C_{p,m}(\text{CHBr}_3(\ell)) + C_{p,m}(\text{H}_2(\text{g}))] - [C_{p,m}(\text{C}(\text{s})) + 3 C_{p,m}(\text{HBr}(\text{g}))]$$

$$= [(130.7) + (28.8)] - [(8.5) + 3(29.1)] = 63.7 \text{ J/mol}\cdot\text{K}$$

Since $\Delta C_{p,m}$ is independent of temperature (based on the information available to us)

$$\begin{aligned}\Delta S^{\circ}_{\text{rxn}}(T_2) &= \Delta S^{\circ}_{\text{rxn}}(T_1) + \Delta C_{p,m} \int_{T_1}^{T_2} dT/T \\ &= \Delta S^{\circ}_{\text{rxn}}(T_1) + \Delta C_{p,m} \ln(T_2/T_1)\end{aligned}$$

If we let $T_1 = 298.0 \text{ K}$, $T_2 = 400.0 \text{ K}$, then

$$\begin{aligned}\Delta S^{\circ}(400.0 \text{ K}) &= -250.2 \text{ J/mol}\cdot\text{K} + (63.7 \text{ J/mol}\cdot\text{K}) \ln(400.0/298.0) \\ &= -250.2 \text{ J/mol}\cdot\text{K} + 18.75 \text{ J/mol}\cdot\text{K} = -231.4 \text{ J/mol}\cdot\text{K}\end{aligned}$$