

CHM 3400 – Fundamentals of Physical Chemistry
First Hour Exam
February 12, 2020

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

$$R = 0.082057 \text{ L}\cdot\text{atm}/\text{mole}\cdot\text{K}$$

$$R = 0.083145 \text{ L}\cdot\text{bar}/\text{mole}\cdot\text{K}$$

$$R = 8.3145 \text{ J}/\text{mole}\cdot\text{K}$$

$$N_A = 6.022 \times 10^{23}$$

$$1 \text{ L}\cdot\text{atm} = 101.3 \text{ J}$$

$$1 \text{ atm} = 1.013 \text{ bar} = 1.013 \times 10^5 \text{ N}/\text{m}^2$$

$$1 \text{ atm} = 760 \text{ torr}$$

1. (15 points) Titan, the largest moon of the planet Saturn, is the only moon in the solar system that has an appreciable atmosphere. Information about that atmosphere is given below and may be useful in answering the following problems.

$$p(\text{surface}) = 1.45 \text{ atm}$$

$$\text{mol fraction } \text{N}_2 (\text{MW} = 28.01 \text{ g}/\text{mol}) X_{\text{N}_2} = 0.984$$

$$\text{mol fraction } \text{CH}_4 (\text{MW} = 16.04 \text{ g}/\text{mol}) X_{\text{CH}_4} = 0.014$$

$$T(\text{surface}) = 94.0 \text{ K}$$

$$\text{mol fraction } \text{H}_2 (\text{MW} = 2.01 \text{ g}/\text{mol}) X_{\text{H}_2} = 0.002$$

a) What is v_{rms} , the rms average speed of a methane molecule (CH_4) at surface level for Titan? Give your final answer in units of m/s.

b) What is ρ , the density of Titans atmosphere, at surface level? Give your final answer in units of g/L.

2. (12 points) For real gases at or near room pressure and temperature, one equation of state that can be used is the following:

$$\frac{pV}{nRT} = 1 + Bp \quad (2.1)$$

where B is a constant found from fitting eq 2.1 to experimental data.

The experimental value for the molar volume of argon (Ar) at $p = 1.0000 \text{ atm}$ and $T = 273.15 \text{ K}$ is $V/n = 22.392 \text{ L}/\text{mol}$. The molar volume of an ideal gas at the same temperature and pressure is $V/n = 22.414 \text{ L}/\text{mol}$. Based on this information, find the value for B in eq 2.1. Give your final answer in units of atm^{-1} .

3. (25 points) Consider 1.000 moles of an ideal gas. The gas undergoes the following process:

$$p_i = 2.500 \text{ atm}$$

$$T_i = 440.0 \text{ K}$$

$$C_{p,m} = 29.10 \text{ J}/\text{mol}\cdot\text{K}$$

$$p_f = 1.500 \text{ atm}$$

$$T_f = 365.0 \text{ K}$$

Nothing is known about how the process is carried out, only the initial and final pressure and temperature, and the constant pressure molar heat capacity, which is assumed to be constant.

Find the value for the following, or explain why there is insufficient information to find the value: q, w, ΔU , ΔH , and ΔS .

4. (22 points) Thermodynamic data for several substances are given below (at $T = 298.0$ K), and may be of use in doing the following problem.

Substance	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)	S° (J/mol·K)	$C_{p,m}$ (J/mol·K)
C(g)	716.68	671.26	158.10	20.838
Cl ₄ (g)	267.94			
I(g)	106.84	70.25	180.79	20.786
I ₂ (g)	62.44	19.33	260.69	36.90

a) What is the value for $\Delta H_{\text{rxn}}^\circ$ (at $T = 298.0$ K) for the following reaction (which corresponds to the conversion of carbon tetraiodide into atoms in the gas phase)? Give your final answer in units of kJ/mol.



b) What is $\Delta H(\text{C-I})$, the average bond strength of a carbon-iodine single bond, in Cl₄? Give your final answer in units of kJ/mol.

c) At what temperature would you expect iodine atoms and I₂ molecules to be in equilibrium at standard pressure? Give your final answer in K (degrees Kelvin).

5. (24 points) The molar enthalpy for aluminum (Al) is given by the equation

$$H = H_0 + a(T - T_0) + b(T - T_0)^2 \quad (5.1)$$

where H_0 is a constant, $a = 24.38$ J/mol·K, $b = 0.0062$ J/mol·K², and $T_0 = 300.0$ K.

a) What is the value for ΔH° when the temperature of 1.000 mole of aluminum is changed reversibly from $T_i = 300.0$ K to $T_f = 450.0$ K at a constant pressure $p = 1.000$ atm.

b) What is the value for $C_{p,m}$ (constant pressure molar heat capacity) for the aluminum at $T = 500.0$ K

c) What is the value for ΔS° when the temperature of 1.000 mole of aluminum is changed reversibly from $T_i = 300.0$ K to $T_f = 450.0$ K at a constant pressure $p = 1.000$ atm.

Solutions.

1) a) $v_{\text{rms}} = [3RT/M]^{1/2} = [3 (8.3145 \text{ J/mol}\cdot\text{K}) (94.0 \text{ K})/16.04 \times 10^{-3} \text{ kg/mol}]^{1/2} = 382. \text{ m/s}$

b) $pV = nRT$

so $\frac{n}{V} = \frac{p}{RT}$

If we multiply both sides of this equation by M_{ave} , the average molecular mass for Titan at surface level, we get

$$\frac{nM_{\text{ave}}}{V} = \frac{m}{V} = \rho = \frac{pM_{\text{ave}}}{RT}$$

But $M_{\text{ave}} = (0.984)(28.01 \text{ g/mol}) + (0.014)(16.04 \text{ g/mol}) + (0.002)(2.01 \text{ g/mol}) = 27.79 \text{ g/mol}$

So $\rho = \frac{(1.45 \text{ atm})(27.79 \text{ g/mol})}{(0.082057 \text{ L}\cdot\text{atm/mol}\cdot\text{K})(94.0 \text{ K})} = 5.22 \text{ g/mol}$

2) $\frac{pV}{nRT} = 1 + Bp$

So $Bp = \frac{pV}{nRT} - 1 = \frac{pV_m}{RT} - 1$ where $V_m = V/n$

or $B = (1/p) [pV_m/RT - 1]$

$$\begin{aligned} &= (1/1.0000 \text{ atm}) [(1.0000 \text{ atm})(22.392 \text{ L/mol})/(0.082057 \text{ L}\cdot\text{atm/mol}\cdot\text{K})(273.15 \text{ K}) - 1] \\ &= -9.8 \times 10^{-4} \text{ atm}^{-1} \end{aligned}$$

3) Since the gas is ideal, we can use the general expressions that apply for ΔH and ΔU for ideal gases

$$\Delta H = \int_{T_i}^{T_f} n C_{p,m} dt$$

$$\Delta U = \int_{T_i}^{T_f} n C_{v,m} dT$$

$C_{p,m} = 29.10 \text{ J/mol}\cdot\text{K}$, and is constant over the temperature range of the problem.

For an ideal gas, $C_{v,m} = C_{p,m} - R = 29.10 \text{ J/mol}\cdot\text{K} - 8.3145 \text{ J/mol}\cdot\text{K} = 20.78 \text{ J/mol}\cdot\text{K}$

Since both n and $C_{p,m}$ (or $C_{v,m}$) are constant, they can be taken outside the integrals, to give

$$\Delta H = n C_{p,m} (T_f - T_i) = (1.000 \text{ mol}) (29.10 \text{ J/mol}\cdot\text{K}) (365.0 \text{ K} - 440.0 \text{ K}) = -2182. \text{ J}$$

$$\Delta U = n C_{v,m} (T_f - T_i) = (1.000 \text{ mol}) (20.78 \text{ J/mol}\cdot\text{K}) (365.0 \text{ K} - 440.0 \text{ K}) = -1558. \text{ J}$$

We have no information about the process used to go between the initial and final state. Since the values for q and w are path dependent (as these are not state functions) their values cannot be found.

Since entropy is a state function, any pathway connecting the same initial and final state will have the same value for ΔS . Consider the following two step process:

Step 1: Isothermal reversible expansion of the gas, from $p_i = 2.500$ atm to $p_f = 1.500$ atm, at $T = 440.0$ K

Step 2: Constant pressure cooling of the gas, from $T_i = 440.0$ K to $T_f = 365.0$ K, at $p = 1.500$ atm

$$\text{For step 1, } \Delta S_1 = \int_{p_i}^{p_f} (\delta q)_{\text{rev}}/T = q/T$$

The process is isothermal and the gas is ideal, and so $\Delta U = 0 = q + w$, $q = -w$

For an isothermal reversible change in pressure of an ideal gas, the value for work is

$$w = - \int_{p_i}^{p_f} p_{\text{ex}} dV = - \int_{p_i}^{p_f} (nRT/V) dV = - nRT \ln(V_f/V_i) = + nRT \ln(p_f/p_i) ; q = - nRT \ln(p_f/p_i)$$

where we have used Boyle's law ($p_i V_i = p_f V_f$ for an ideal gas as constant T)

$$\text{So } \Delta S_1 = \frac{q}{T} = - nR \ln(p_f/p_i) = - (1.000 \text{ mol})(8.3145 \text{ J/mol}\cdot\text{K})\ln(1.500 \text{ atm}/2.500 \text{ atm}) = + 4.25 \text{ J/K}$$

$$\begin{aligned} \text{For step 2, } \Delta S_2 &= \int_{T_i}^{T_f} (\delta q)_{\text{rev}}/T = \int_{T_i}^{T_f} (nC_{p,m} dT)/T = n C_{p,m} \ln(T_f/T_i) \\ &= (1.000 \text{ mol})(29.10 \text{ J/mol}\cdot\text{K}) \ln(365.0 \text{ K}/440.0 \text{ K}) = - 5.44 \text{ J/K} \end{aligned}$$

Therefore, $\Delta S = \Delta S_1 + \Delta S_2 = (+ 4.25 \text{ J/K}) + (- 5.44 \text{ J/K}) = - 1.18 \text{ J/K}$

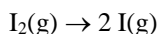
$$4) \quad a) \Delta H^\circ_{\text{rxn}} = [\Delta H^\circ_f(\text{C}(\text{g})) + 4 \Delta H^\circ_f(\text{I}(\text{g}))] - [\Delta H^\circ_f(\text{C}_2\text{I}_4(\text{g}))]$$

$$= [(716.68 \text{ kJ/mol}) + 4 (106.84 \text{ kJ/mol})] - [267.94 \text{ kJ/mol}] = 876.10 \text{ kJ/mol}$$

b) The process taking place corresponds to breaking four C-I bonds in the gas phase, and so

$$\Delta H(\text{C-I}) = 876.10 \text{ kJ/mol}/4 = 219.0 \text{ kJ/mol}$$

c) The process in this part of the problem is



At equilibrium, for standard conditions, $\Delta G^\circ_{\text{rxn}} = 0.0 \text{ kJ/mol}$

If we assume the values for $\Delta H^\circ_{\text{rxn}}$ and $\Delta S^\circ_{\text{rxn}}$ are independent of temperature, then

$$\Delta G^\circ_{\text{rxn}} = 0 = \Delta H^\circ_{\text{rxn}} - T \Delta S^\circ_{\text{rxn}}$$

$$T_{\text{eq}} \cong \frac{\Delta H^\circ_{\text{rxn}}}{\Delta S^\circ_{\text{rxn}}}$$

$$\text{But } \Delta H^\circ_{\text{rxn}} = 2 \Delta H^\circ_f(\text{I}(\text{g})) - \Delta H^\circ_f(\text{I}_2(\text{g})) = 2 (106.84 \text{ kJ/mol}) - (62.44 \text{ kJ/mol}) = 151.24 \text{ kJ/mol}$$

$$\Delta S^\circ_{\text{rxn}} = 2 S^\circ(\text{I}(\text{g})) - S^\circ(\text{I}_2(\text{g})) = 2 (180.79 \text{ J/mol}\cdot\text{K}) - (260.69 \text{ J/mol}\cdot\text{K}) = 100.89 \text{ J/mol}\cdot\text{K}$$

$$\text{And so } T_{\text{eq}} \cong (151.24 \text{ kJ/mol})(1000. \text{ J/kJ}) / (100.89 \text{ J/mol}\cdot\text{K}) = 1499. \text{ K}$$

5) a) $\Delta H^\circ = H(450.0 \text{ K}) - H(300.0 \text{ K})$

$$H(450.0 \text{ K}) = H_0 + (24.38 \text{ J/mol}\cdot\text{K}) (450.0 \text{ K} - 300.0 \text{ K}) + 0.0062 \text{ J/mol}\cdot\text{K}^2 (450.0 \text{ K} - 300.0 \text{ K})^2$$

$$= H_0 + 3796. \text{ J/mol}$$

$$H(300.0 \text{ K}) = H_0 \text{ (since all of the other terms drop out when } T = T_0 = 300.0 \text{ K)}$$

So $\Delta H^\circ = H(450.0 \text{ K}) - H(300.0 \text{ K}) = (H_0 + 3796. \text{ J/mol}) - H_0 = 3796. \text{ J/mol}$

b) At constant pressure, $C_{p,m} = (\partial H/\partial T)_p$

So $C_{p,m} = (\partial/\partial T)_p [H_0 + a(T - T_0) + b(T - T_0)^2] = a + 2b(T - T_0)$

At $T = 500.0 \text{ K}$ $C_{p,m} = (24.38 \text{ J/mol}\cdot\text{K}) + 2 (0.0062 \text{ J/mol}\cdot\text{K}^2)(500.0 \text{ K} - 300.0 \text{ K}) = 26.86 \text{ J/mol}\cdot\text{K}$

c) For the constant pressure heating of a pure chemical substance, and in the absence of any phase transitions

$$\Delta S^\circ = \int_{T_i}^{T_f} \frac{C_{p,m} dT}{T} = \int_{T_i}^{T_f} [\frac{a + 2b(T - T_0)}{T}] dT = (a - 2bT_0) \ln(T_f/T_i) + 2b (T_f - T_i)$$

$$= [(24.38 \text{ J/mol}\cdot\text{K}) - 2 (0.0062 \text{ J/mol}\cdot\text{K}^2) (300.0 \text{ K})] \ln(450.0 \text{ K}/300.0 \text{ K})$$

$$+ 2 (0.0062 \text{ J/mol}\cdot\text{K}^2)(450.0 \text{ K} - 300.0 \text{ K})$$

$$= 8.377 \text{ J/mol}\cdot\text{K} + 1.860 \text{ J/mol}\cdot\text{K} = 10.24 \text{ J/mol}\cdot\text{K}$$