

CHM 3400 – Fundamentals of Physical Chemistry
Final Exam

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

R = 0.08206 L·atm/mole·K	$N_A = 6.022 \times 10^{23}$	
R = 0.08314 L·bar/mole·K	1 L·atm = 101.3 J	
R = 8.314 J/mole·K	1 atm = 1.013 bar = 1.013×10^5 N/m ²	
F = 96485. C/mol	$h = 6.626 \times 10^{-34}$ J·s	1 eV = 1.602×10^{-19} J
$c = 2.998 \times 10^8$ m/s	$1 \text{ cm}^{-1} = 1.986 \times 10^{-23}$	$m_e = 9.11 \times 10^{-31}$ kg

Thermodynamic data for several substances are given below, at T = 298. K and p = 1.000 bar. The data may be useful in doing problems 1, 2, and 3.

Substance	M (g/mol)	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)	S° (J/mol·K)	$C_{p,m}$ (J/mol·K)
Cl ₂ (g)	70.91	0.00	0.00	223.07	33.91
P(s)	30.97	0.00	0.00	41.09	23.840
P ₄ (g)	123.90	58.91	24.44	279.98	67.15
PCl ₃ (g)	137.33	- 287.0	- 267.8	311.78	71.84
PCl ₅ (g)	208.24	- 374.9	- 305.0	364.6	112.8

1. (24 points) The temperature of 1.000 mol of chlorine gas (Cl₂(g)) is changed from an initial value $T_i = 250.0$ K to a final temperature $T_f = 350.0$ K. The process is carried out reversibly at a constant pressure p = 0.500 bar. For the conditions of the problem you may assume that chlorine gas behaves ideally, and that the value for the constant pressure molar heat capacity is independent of temperature.

Find q, w, ΔU , ΔH , ΔS_{sys} , ΔS_{surr} , and ΔS_{univ} for the above process, or briefly explain why there is insufficient information to find the quantity requested.

2. (32 points) The element phosphorus is unusual in that the most stable form of the element in the gas phase is P₄, a molecule with tetrahedral geometry.

a) What is the rms average speed of a P₄ molecule in the gas phase at T = 298. K? Give your final answer in units of m/s.

b) What is the vapor pressure of solid phosphorus at T = 298. K? Give your final answer in units of torr.

c) The heat capacity of solid phosphorus in the vicinity of absolute zero is given by the expression

$$C_{p,m} = aT^3 + bT^4 \quad (2.1)$$

where $a = 1.04 \times 10^{-3}$ J/mol·K⁴ and $b = - 8.0 \times 10^{-6}$ J/mol·K⁵. Find the value for ΔH° and ΔS° when the temperature of 1.00 mol of solid phosphorus is changed from an initial value T = 0.0 K to a final value T = 20.0 K reversibly and at constant pressure.

3. (30 points) In a system containing chlorine gas (Cl₂) an equilibrium is established between phosphorus trichloride (PCl₃) and phosphorus pentachloride (PCl₅) by the process



a) Give the expression for K for reaction 3.1 in terms of reactant and product activities.

b) Give the expression for K for reaction 3.1 assuming ideal behavior for all reactants and products.

c) Give the numerical value for K for reaction 3.1 at T = 298. K

d) Give the numerical value for K for reaction 3.1 at T = 373. K. State any assumptions made in finding the value for K at this temperature.

4. (24 points) The density of a mixture of carbon monoxide (CO, $M = 28.01$ g/mol) and propane (C_3H_8 , $M = 44.11$ g/mol) was measured at $T = 29.3$ °C and $p = 1.045$ atm, and found to be $\rho = 1.324$ g/L.

a) Based on this above information, and assuming the gases obey the ideal gas law, find X_{CO} , the mole fraction of CO in the gas mixture.

b) How many rotational motions does a molecule of C_3H_8 possess?

c) How many vibrational motions does a molecule of C_3H_8 possess?

5. (30 points) Hypochlorous acid (HOCl) plays an important role in stratospheric ozone chemistry. The following question explores some of the properties of this molecule.

a) Write the correctly balanced formation reaction for HOCl(g).

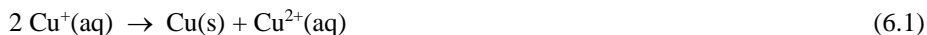
b) Using the table of bond enthalpies (Table 3.5, p 70 of Atkins) estimate the value for ΔH°_f , the enthalpy of formation, for HOCl(g).

c) The enthalpy of reaction for the process



is $\Delta H^\circ_{rxn} = -75.0$ kJ/mol at $T = 25.0$ °C. Based on this result and the data in the Appendix of Atkins, find the value for ΔH°_f , the enthalpy of formation, for HOCl(g).

6. (16 points) In a disproportionation reaction the same substance is simultaneously oxidized and reduced. The disproportionation reaction for Cu^+ ion is



Using the table of standard cell potentials in the Appendix of Atkins, determine E°_{rxn} and K , the numerical value for the equilibrium constant for the above reaction, at $T = 25.0$ °C.

7. (24 points) The initial concentration of a substance X is 0.287 mol/L. After 1000. s, the concentration of X has decreased to 0.185 mol/L. Calculate the value for concentration for X after 3600 s (1 hour) assuming

a) That the disappearance of X follows first order homogeneous kinetics, that is

$$d[X]/dt = -k[X] \quad (7.1)$$

b) That the disappearance of X follows second order homogeneous kinetics, that is

$$d[X]/dt = -k[X]^2 \quad (7.2)$$

8. (20 points) An argon ion laser provides monochromatic light at a wavelength $\lambda = 488.0$ nm.

a) How many photons are produced by the above laser when it emits a pulse of monochromatic light with total energy $E = 4.45 \times 10^{-3}$ J?

b) A low energy pulse of light from the above laser is used to illuminate a metal surface in a photoelectric effect experiment. The work function for the metal is $\Phi = 3.18$ eV. Will electrons be produced? Justify your answer. If your answer is yes, also give the maximum kinetic energy and speed of electrons that are produced.

Solutions.

1) For an ideal gas

$$\Delta H = \int_i^f n C_{p,m} dT$$

$$\Delta U = \int_i^f n C_{V,m} dT$$

$$C_{p,m} - C_{V,m} = R, \text{ so } C_{V,m} = C_{p,m} - R$$

We are told that $C_{p,m}$ is constant over the temperature range of the problem, so

$$\Delta H = \int_i^f n C_{p,m} dT = n C_{p,m} (T_f - T_i)$$

$$\Delta U = \int_i^f n C_{V,m} dT = n C_{V,m} (T_f - T_i)$$

$$C_{V,m} = (33.91 \text{ J/mol}\cdot\text{K}) - (8.314 \text{ J/mol}\cdot\text{K}) = 25.60 \text{ J/mol}\cdot\text{K}$$

So $\Delta H = (1.00 \text{ mol}) (33.91 \text{ J/mol}\cdot\text{K}) (350.0 \text{ K} - 250.0 \text{ K}) = 3391. \text{ J}$

$$\Delta U = (1.00 \text{ mol}) (25.60 \text{ J/mol}\cdot\text{K}) (350.0 \text{ K} - 250.0 \text{ K}) = 2560. \text{ J}$$

The process is carried out under conditions of constant pressure, and so

$$q = \Delta H = 3391. \text{ J}$$

From the first law

$$\Delta U = q + w$$

and so $w = \Delta U - q = (2560. \text{ J}) - (3391. \text{ J}) = - 831. \text{ J}$

Since the process is reversible, $\Delta S_{\text{univ}} = 0$.

Since $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0$, it follows that $\Delta S_{\text{surr}} = - \Delta S_{\text{sys}}$

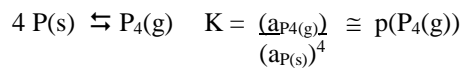
$$\Delta S_{\text{sys}} = \int_i^f (dq)_{\text{rev}}/T = \int_i^f (nC_{p,m}/T) dT = nC_{p,m} \ln(T_f/T_i)$$

So $\Delta S_{\text{sys}} = (1.00 \text{ mol}) (33.91 \text{ J/mol}\cdot\text{K}) \ln(350.\text{K}/250.\text{K}) = 11.41 \text{ J/K}$

$$\Delta S_{\text{surr}} = - 11.41 \text{ J/K}$$

2) a) $c_{\text{rms}} = (3RT/M)^{1/2} = [3(8.314 \text{ J/mol}\cdot\text{K})(298. \text{ K})/(123.90 \times 10^{-3} \text{ kg/mol})]^{1/2} = 245. \text{ m/s}$

b) We can consider the vaporization reaction as the process



So the value of the equilibrium constant is equal to the vapor pressure of solid phosphorus (in bar).

To find K we need to find $\Delta G^\circ_{\text{rxn}}$ for the above process. But

$$\Delta G^\circ_{\text{rxn}} = \Delta G^\circ_f(\text{P}_4(\text{g})) - 4 \Delta G^\circ_f(\text{P(s)}) = 24.44 \text{ kJ/mol} - 4 (0) = 24.44 \text{ kJ/mol}$$

$$\text{Since } \ln K = - \frac{\Delta G^\circ_{\text{rxn}}}{RT} = - \frac{(24440. \text{ J/mol})}{(8.314 \text{ J/mol}\cdot\text{K})(298. \text{ K})} = -9.85$$

$$K = e^{-9.85} = 5.28 \times 10^{-5}$$

$$p_{\text{vap}} = (5.28 \times 10^{-5} \text{ bar}) \frac{1 \text{ atm}}{1.013 \text{ bar}} \frac{760. \text{ torr}}{1 \text{ atm}} = 0.040 \text{ torr}$$

c) For a constant pressure reversible heating

$$\Delta H = \int_{T_i}^{T_f} (n C_{p,m}) dT = n \int_{T_i}^{T_f} (aT^3 + bT^4) dT = n \left\{ (aT^4/4) + (bT^5/5) \right\}_{T_i}^{T_f}$$

$$\Delta S = \int_{T_i}^{T_f} (n C_{p,m}/T) dT = n \int_{T_i}^{T_f} (aT^2 + bT^3) dT = n \left\{ (aT^3/3) + (bT^4/4) \right\}_{T_i}^{T_f}$$

Since $T_i = 0. \text{ K}$, we may write the above as

$$\begin{aligned} \Delta H &= n \left\{ (aT_f^4/4) + (bT_f^5/5) \right\} \\ &= (1.00 \text{ mol}) \left\{ [(1.04 \times 10^{-3} \text{ J/mol}\cdot\text{K}^4)(20. \text{ K})^4/4] + [(-8.0 \times 10^{-6} \text{ J/mol}\cdot\text{K}^5)(20. \text{ K})^5/5] \right\} \\ &= 41.60 \text{ J} + (-5.12 \text{ J}) = 36.5 \text{ J} \end{aligned}$$

$$\begin{aligned} \Delta S &= n \left\{ (aT_f^3/3) + (bT_f^4/4) \right\} \\ &= (1.00 \text{ mol}) \left\{ [(1.04 \times 10^{-3} \text{ J/mol}\cdot\text{K}^4)(20. \text{ K})^3/3] + [(-8.0 \times 10^{-6} \text{ J/mol}\cdot\text{K}^5)(20. \text{ K})^4/4] \right\} \\ &= 2.77 \text{ J/K} + (-0.32 \text{ J/K}) = 2.45 \text{ J/K} \end{aligned}$$

$$3) \quad \text{a+b)} \quad K = \frac{(a_{\text{PCl}_5})}{(a_{\text{PCl}_3})(a_{\text{Cl}_2})} = \frac{(p_{\text{PCl}_5})}{(p_{\text{PCl}_3})(p_{\text{Cl}_2})}$$

We calculate the following to help in doing parts c and d

$$\begin{aligned} \Delta G^\circ_{\text{rxn}} &= [\Delta G^\circ_f(\text{PCl}_5(\text{g}))] - [\Delta G^\circ_f(\text{PCl}_3(\text{g})) + \Delta G^\circ_f(\text{Cl}_2(\text{g}))] \\ &= [(-305.0)] - [(-267.8) + (0.0)] = -37.2 \text{ kJ/mol} \end{aligned}$$

$$\begin{aligned} \Delta H^\circ_{\text{rxn}} &= [\Delta H^\circ_f(\text{PCl}_5(\text{g}))] - [\Delta H^\circ_f(\text{PCl}_3(\text{g})) + \Delta H^\circ_f(\text{Cl}_2(\text{g}))] \\ &= [(-374.9)] - [(-287.0) + (0.0)] = -87.9 \text{ kJ/mol} \end{aligned}$$

$$\begin{aligned} S^\circ_{\text{rxn}} &= [S^\circ(\text{PCl}_5(\text{g}))] - [S^\circ(\text{PCl}_3(\text{g})) + S^\circ(\text{Cl}_2(\text{g}))] \\ &= [(364.6)] - [(311.78) + (223.07)] = -170.2 \text{ J/mol}\cdot\text{K} \end{aligned}$$

c) At $T = 298. \text{ K}$

$$\ln K = - \frac{\Delta G^\circ_{\text{rxn}}}{RT} = - \frac{(-37200. \text{ J/mol})}{(8.314 \text{ J/mol}\cdot\text{K})(298. \text{ K})} = 15.02$$

$$K = e^{15.02} = 3.3 \times 10^6$$

d) At $T = 373. \text{ K}$, and assuming $\Delta H^\circ_{\text{rxn}}$ and $\Delta S^\circ_{\text{rxn}}$ are independent of temperature

$$\Delta G^\circ_{\text{rxn}} = \Delta H^\circ_{\text{rxn}} - T\Delta S^\circ_{\text{rxn}} = (-87.9 \text{ kJ/mol}) - (-170.2 \times 10^{-3} \text{ kJ/mol}\cdot\text{K})(373. \text{ K}) = -24.4 \text{ kJ/mol}$$

$$\ln K = -\frac{\Delta G^\circ_{\text{rxn}}}{RT} = -\frac{(-24400. \text{ J/mol})}{(8.314 \text{ J/mol}\cdot\text{K})(373. \text{ K})} = 7.87$$

$$K = e^{7.87} = 2.6 \times 10^3$$

4) a) $pV = nRT$, and so

$$\frac{V}{n} = \frac{p}{RT} = \frac{(1.045 \text{ atm})}{(0.08206 \text{ L}\cdot\text{atm/mol}\cdot\text{K})(302.4)} = 0.04211 \text{ mol/L}$$

Since we know the density of the gas mixture, we can now find the average molecular mass

$$M_{\text{ave}} = \frac{\rho}{(V/n)} = \frac{(1.324 \text{ g/L})}{(0.04211 \text{ mol/L})} = 31.44 \text{ g/mol}$$

But $M_{\text{ave}} = X_{\text{CO}} M_{\text{CO}} + X_{\text{C}_3\text{H}_8} M_{\text{C}_3\text{H}_8}$

Since $X_{\text{CO}} + X_{\text{C}_3\text{H}_8} = 1$, $X_{\text{C}_3\text{H}_8} = 1 - X_{\text{CO}}$

$$M_{\text{ave}} = X_{\text{CO}} M_{\text{CO}} + (1 - X_{\text{CO}}) M_{\text{C}_3\text{H}_8} = X_{\text{CO}} M_{\text{CO}} + M_{\text{C}_3\text{H}_8} - X_{\text{CO}} M_{\text{C}_3\text{H}_8}$$

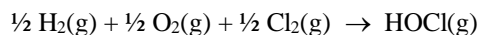
Solving for X_{CO} gives

$$X_{\text{CO}} = \frac{(M_{\text{C}_3\text{H}_8} - M_{\text{ave}})}{(M_{\text{C}_3\text{H}_8} - M_{\text{CO}})} = \frac{(44.11 - 31.44)}{(44.11 - 28.01)} = 0.797$$

b) Molecule is non-linear, so there are 3 rotations.

c) Molecule is non-linear, and so there are $3(11) - 6 = 27$ vibrations.

5) a) Formation reaction is



b) We may estimate $\Delta H^\circ_{\text{rxn}}$ by keeping track of the bonds broken and formed

bonds broken

$$\frac{1}{2} (\text{H-H}) = \frac{1}{2} (436)$$

$$\frac{1}{2} (\text{O=O}) = \frac{1}{2} (497)$$

$$\frac{1}{2} (\text{Cl-Cl}) = \frac{1}{2} (242)$$

$$587.5 \text{ kJ/mol}$$

bonds formed

$$1 (\text{O-H}) = 1 (463)$$

$$1 (\text{O-Cl}) = 1 (203)$$

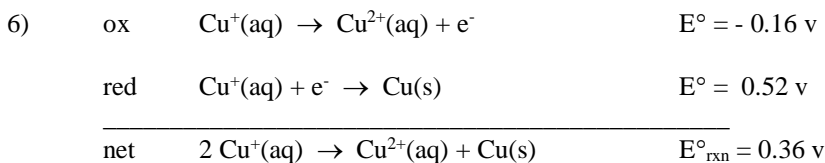
$$666.0 \text{ kJ/mol}$$

$$\Delta H^\circ_{\text{rxn}} \cong (\text{bonds broken}) - (\text{bonds formed}) = (587.5 \text{ kJ/mol}) - (666.0 \text{ kJ/mol}) = -78. \text{ kJ/mol}$$

$$c) \quad \Delta H^{\circ}_{\text{rxn}} = [\Delta H^{\circ}_{\text{f}}(\text{H}_2\text{O}(\text{g})) + \Delta H^{\circ}_{\text{f}}(\text{Cl}_2(\text{g}))] - [\Delta H^{\circ}_{\text{f}}(\text{HOCl}(\text{g})) + \Delta H^{\circ}_{\text{f}}(\text{HCl}(\text{g}))]$$

So
$$\Delta H^{\circ}_{\text{f}}(\text{HOCl}(\text{g})) = [\Delta H^{\circ}_{\text{f}}(\text{H}_2\text{O}(\text{g})) + \Delta H^{\circ}_{\text{f}}(\text{Cl}_2(\text{g}))] - [\Delta H^{\circ}_{\text{rxn}} + \Delta H^{\circ}_{\text{f}}(\text{HCl}(\text{g}))]$$

$$= [(-241.82) + (0.)] - [(-75.0) + (-92.31)] = -74.51 \text{ kJ/mol}$$



From reworking the Nernst equation, we may say

$$\ln K = \frac{nFE^{\circ}_{\text{rxn}}}{RT} = \frac{(1)(96485 \text{ C/mol})(0.36 \text{ v})}{(8.314 \text{ J/mol}\cdot\text{K})(298 \text{ K})} = 14.02$$

$$K = e^{14.02} = 1.23 \times 10^6$$

7) a) For a first order reaction

$$\ln([A]_0/[A]_t) = kt$$

$$k = (1/t) \ln([A]_0/[A]_t) = (1/1000.) \ln(0.287/0.185) = 4.39 \times 10^{-4} \text{ s}^{-1}$$

After 3600. s, the concentration will be

$$[A]_t = [A]_0 e^{-kt} = (0.287 \text{ mol/L}) \exp[-(4.39 \times 10^{-4} \text{ s}^{-1})(3600. \text{ s})] = 0.059 \text{ mol/L}$$

b) For a first order reaction

$$[(1/[A]_t) - (1/[A]_0)] = kt$$

$$k = (1/t) [(1/[A]_t) - (1/[A]_0)]$$

$$= (1/1000. \text{ s}) [(1/0.185 \text{ mol/L}) - (1/0.287 \text{ mol/L})] = 1.92 \times 10^{-3} \text{ L/mol}\cdot\text{s}$$

After 3600. s, the concentration will be

$$[A]_t = \frac{[A]_0}{(1 + kt[A]_0)} = \frac{(0.287 \text{ mol/L})}{[1 + (1.92 \times 10^{-3} \text{ L/mol}\cdot\text{s})(3600. \text{ s})(0.287 \text{ mol/L})]}$$

$$= 0.096 \text{ mol/L}$$

8) a) The energy of one photon from the laser is

$$E_{\gamma} = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ J}\cdot\text{s})(2.998 \times 10^8 \text{ m/s})}{(488.0 \times 10^{-9} \text{ m})} = 4.071 \times 10^{-19} \text{ J}$$

Since the energy of the laser pulse is $4.45 \times 10^{-3} \text{ J}$, the number of photons produced is

$$\# \text{ photons} = \frac{4.45 \times 10^{-3} \text{ J}}{4.071 \times 10^{-19} \text{ J/photon}} = 1.09 \times 10^{16} \text{ photons}$$

b) For the photoelectric effect

$$E_{\gamma} = E_{K,\max} + \Phi$$

or $E_{K,\max} = E_{\gamma} - \Phi$

where a negative value for E_K means no electrons are produced.

The work function for the metal is $\Phi = 3.18 \text{ eV} (1.602 \times 10^{-19} \text{ J/eV}) = 5.094 \times 10^{-19} \text{ J}$

The energy of one photon of light is $E_{\gamma} = 4.071 \times 10^{-19} \text{ J}$

If we insert these values into the equation for $E_{K,\max}$, we get a negative number, which is not physically possible. What this means is that electrons will not be produced by light at this wavelength.