Columbia University in the City of New York
New York, N.Y.10027

Department of Chemistry **3109 Havemeyer Hall**
212-854-4162
Chemistry C2407x **George Flynn**

Problem Set 1

Solutions to Even Numbered and Other Problems

Oxtoby, 4.6

a) Since 76 cm difference in Hg levels is 1 atm,

$P = [(9.50) / 76.0] \times 1$ atm = 0.125 atm.

Using SI units and Pascals:

$P = \rho hg$ $\quad \rho = 13.60\ g/cm^3 \times (10^6\ cm^3 / 1\ m^3)(1\ kg / 1000\ g)$

$\rho = 13.6 \times 10^3\ kg/m^3$

$h = 9.50\ cm = 0.0950\ m$

$g = 980.7\ cm/s^2 = 9.807\ m/s^2$

$P = (13.6 \times 10^3\ kg/m^3)(0.095\ m)(9.807\ m/s^2)$

$= 1.267 \times 10^4$ Pascals $\quad$ 1 atm = 1.01325×10^5 Pascals

$P = (1.27 \times 10^4\ Pa) \times (1\ atm / 1.01325 \times 10^5\ Pa)$

$P = 0.125$ atm.

b) Pressure is same for both gauges so

$P = \rho_1 h_1 g = \rho_2 h_2 g$ or $\rho_1 h_1 = \rho_2 h_2$

$h_1 / h_2 = \rho_2 / \rho_1$ $\quad \rho_1 = 13.6 \times 10^3\ kg/m^3$

$\rho_2 = 1.045 \times 10^3\ kg/m^3$

$h_1 = 9.5\ cm = .095\ m$

$h_2 = h_1(\rho_1)/\rho_2 = (.095\ m)(13.6 / 1.045)$

$h_2 = 1.24$ meters

Oxtoby 4.10

1 atm = 760 torr = 1.01325×10^5 Pa

$(5 \times 10^{-10}\ torr) \times (1\ atm / 760\ torr) = 6.58 \times 10^{-13}$ atm

$(6.58 \times 10^{-13}\ atm) \times (1.01325 \times 10^5\ Pa / 1\ atm) = 6.67 \times 10^{-8}$ Pa

Oxtoby 4.42

$C_{rms} = (3\ kT/m)^{1/2} = (3\ RT/M)^{1/2}$

M = atomic weight of Na atoms. M = 23 gm/mole = 0.023 kg/mole. SI units here are kg and Joules for R. R = 8.314 Joules/mole-deg

T = 0.00024 deg Kelvin

$C_{rms} = ((3)(8.314\ J/mole\text{-}deg)(0.00024\ deg) / (0.023\ kg/mole))^{1/2}$

$C_{rms} = (0.260\ J/kg)^{1/2}$

$= 0.510\ m/s$

$(J = kg(m/s)^2 \rightarrow J/kg = (m/s)^2$

Oxtoby 4.48

In class we derived the (slightly oversimplified) formula for the number of collisions with an area A:

I = #/sec = (1/6)(N/V)AC

where we took $C = C_{rms} = \sqrt{3\mathbf{RT}/\mathbf{M}}$

A more rigorous treatment gives

#/sec = $(1/4)(N/V)A\bar{\mathbf{C}}$

where $\bar{\mathbf{C}}$ is the average speed = $\sqrt{8\mathbf{RT}/p\mathbf{M}}$

The 1/4 replacing the 1/6 comes from our oversimplified assumption that all atoms fly on a trajectory ⊥ to the wall.

We will calculate the value of A using both formulas. In either case we need to know the number of atoms/sec escaping from the vessel

A useful formula is $PV = nRT = (N/N_0)RT$

$N = N_0(PV/RT)$

At start P = 0.99 atm, at end (1 hr) P = 0.989 atm.

V= 200mL, T = 298 K, R 82 mL-atm/mole-deg

$N_1 = N_0(P_1V/RT) \qquad N_2 = N_0(P_2V/RT)$

$\Delta N = (N_1 - N_2) = [(P_1 - P_2)V/RT]\ N_0$

$?N = [(0.001\ atm)(200\ mL)/(82\ mL\text{-}atm/mole\text{-}deg) \times (298\ deg)\}N_0$

$?N = (8.185 \times 10^{-6}\ mole)N_0,\ N_0 = 6.023 \times 10^{23}\ /\ mole$

$?N = (8.185 \times 10^{-6})(6.023 \times 10^{23}) = 4.93 \times 10^{18}$

1 hour = 60 × 60 sec = 3600 sec

$I = ?N/t = 4.93 \times 10^{18} / 3600 = 1.37 \times 10^{15}\ sec^{-1}$

More rigorous formula $A = 4\ (?N\ /t\ )\ (V\ /\ N)\ /\ \bar{\mathbf{c}}$

$V/N = V/\ \{N_0\ (PV\ /\ RT)\} = RT\ /\ N_0P$

$V/N = (82\ cm^3\text{-}atm\ /\ mole\text{-}deg)(298\ deg)\ /\ (6.023 \times 10^{23}\ /\ mole) \times (0.99\ atm)$

$V/N = 4.1 \times 10^{-20}\ cm^3\ /\ molecule$

$\bar{\mathbf{c}} = \sqrt{8\mathbf{RT}/p\mathbf{M}} = (8\ (8.314)(298)/\pi(0.002))^{1/2}\ m/s$

$\bar{\mathbf{c}} = 1776\ m/s = 1.78 \times 10^5\ cm/s$

$A = 4(?N/t)(V/N)/\ \bar{\mathbf{c}} = 4(1.37 \times 10^{15}\ sec^{-1})(4.1 \times 10^{-20}\ cm^3)/(1.78 \times 10^5\ cm/s)$

$A = 1.26 \times 10^{-9}\ cm^2 = \pi r^2 \qquad r = 2.0 \times 10^{-5}\ cm = 2.0 \times 10^{-7}\ m$

$C_{rms} = \sqrt{3\mathbf{RT}/\mathbf{M}} = [(3)(8.314)(298)\ /\ (0.002)]^{1/2} = 1.927 \times 10^5\ cm/s$

$A = (6)(?N/t)(V/N)/C_{rms} = 1.74 \times 10^{-9}\ cm^2$

$r = 2.35 \times 10^{-5}$ cm = 2.35×10^{-7} m (this is the <u>less</u> rigorous value)

Oxtoby 4.52

(Rate Ef He) / (Rate Ef H_2) = 3 Experimental observatioin

$(R_{He} / \mathbf{R}_{\mathbf{H}_2}) = N_{He} C_{He} / \mathbf{N}_{\mathbf{H}_2} \mathbf{C}_{\mathbf{H}_2}$

$C_{He} / \mathbf{C}_{\mathbf{H}_2} = \sqrt{3\mathbf{RT}/\mathbf{M}_{\mathbf{He}}} / \sqrt{3\mathbf{RT}/\mathbf{M}_{\mathbf{H}_2}} = (\mathbf{M}_{\mathbf{H}_2} / M_{He})^{1/2}$

$R_{He} / \mathbf{R}_{\mathbf{H}_2} = (N_{He} / \mathbf{N}_{\mathbf{H}_2}) (\mathbf{M}_{\mathbf{H}_2} / M_{He})^{1/2}$

$= (N_{He} / \mathbf{N}_{\mathbf{H}_2}) (2/4)^{1/2}$

$(N_{He} / \mathbf{N}_{\mathbf{H}_2}) = \sqrt{4/2}\ (R_{He} / \mathbf{R}_{\mathbf{H}_2}) = \sqrt{2}\ (3)$

$(N_{He} / \mathbf{N}_{\mathbf{H}_2}) = 4.24$

$\mathbf{X}_{\mathbf{H}_2} = \mathbf{n}_{\mathbf{H}_2} / (\mathbf{n}_{\mathbf{H}_2} + n_{He}) = 1 / (1 + n_{He} / \mathbf{n}_{\mathbf{H}_2})$

$n_{He} / \mathbf{n}_{\mathbf{H}_2} = (N_{He} / N_0) / (\mathbf{N}_{\mathbf{H}_2} / N_0) = N_{He} / \mathbf{N}_{\mathbf{H}_2}$

[n = # moles, N = # molecules, $N_0 = 6.023 \times 10^{23}$]

$n_{He} / \mathbf{n}_{\mathbf{H}_2} = N_{He} / \mathbf{N}_{\mathbf{H}_2} = 4.24$

$\mathbf{X}_{\mathbf{H}_2} = 1/(1 + 4.24) = 0.191$

Oxtoby 7.2

P = 0.98 atm V_i = 150 mL = 0.15 liter V_f = 0.80 liter

w = -P?V = -(0.98 atm) (0.8 – 0.15 liter)

w = -0.637 l-atm

R = 8.314 Joules / mole-deg = 0.082 l-atm / mole-deg

1 = (8.314 / 0.082) Joules / l-atm

w = (-0.637 l-atm) (8.314 / 0.082 Joules/l-atm)

w = -64.6 Joules

An alternate approach is to express P, V in SI units:

P = (0.98 atm)(101325 Pascals/atm)

P = 99299 Pa ?V = 0.65 liter = $0.65 \times 10^3\ cm^3$

10^2 cm = 1 m $\rightarrow$ $10^6\ cm^3 = 1\ m^3$

$?V = 0.65 \times 10^3\ cm^3 / (10^6\ cm^3 / m^3) = 0.65 \times 10^{-3}\ m^3$

w = -P?V = (-99299 Pa)($0.65 \times 10^{-3}\ m^3$)

w = -64.5 Joules

Assigned Problem

Calculate the collision frequency for:

a) **a sample of oxygen at 1.00 atm. Pressure and 25^0 C**
b) **a molecule of hydrogen in a region of interstellar space where the number density is $1.0x10^{10}$ molecules per cubic meter and the temperature is 30 K.**

[Take the diameter of oxygen to be $2.92x10^{-10}$ meter and that of hydrogen to be $2.34x10^{-10}$ meter.]

From class for collisions of one molecule of A with all other A's, the collision rate is z:

$z = \sqrt{2}\ (N_A/V)\pi\ \rho^{\ 2}\ c_{avge}$

$c_{avge} = (8kT / \pi\ m_A)^{1/2} = (8RT / \pi\ M_A)^{1/2}$

R = gas constant and M_A = Molecular weight

$\rho = \sigma_A + \sigma_A = 2\sigma_A = d$ (diameter of A)

$PV = nRT = (N_A/N_0)RT$

$(N_A/V) = PN_0/RT$

Part a:

$(N_A/V) = (1.00)(6.023\times10^{23})/(0.082)(298) = 2.46\times10^{22}$ molecules per liter

$(N_A/V) = 2.46\times10^{22}$ molecules per liter $\times\ 10^3$ liter/ $m^3 = 2.46\times10^{25}$ molecules/m^3

$c_{avge} = (8RT / \pi\ M_A)^{1/2} = [8\ (8.314)(298)/(\pi)(.032)]^{1/2} = 444.0$ m/sec.

$z = \sqrt{2}\ [2.46\times10^{25}$ molecules/m^3 $][(\pi)(2.92 \times 10^{-10}$ m$)^2][444.0$ m/sec$]$

$z = (1.414)\ [2.46\times10^{25}$ molecules/m^3 $][(3.1416)(8.53 \times 10^{-20}$ $m^2)]$ $[444.0$m/s$]$

$z = 4.14\times10^9$ collisions/sec

Part b:

$(N_A/V) = 1.00\times10^{10}$ molecules/ m^3

$c_{avge} = (8RT / \pi\ M_A)^{1/2} = [8\ (8.314)(30)/(\pi)(.002)]^{1/2} = 563.5$ m/sec.

$z = \sqrt{2}\ [1.00\times10^{10}$ molecules/ $m^3][(\pi)(2.34 \times 10^{-10}$ m$)^2][563.5$ m/sec$]$

$z = (1.414)\ [1.00\times10^{10}$ molecules/ $m^3][(3.1416)(5.48 \times 10^{-20}$ $m^2)]$ $[563.5$ m/s$]$

$z = 1.37\times10^{-6}$ collisions/sec

(Or, 1 collision every 728,996 sec = 1 collision every 8.44 days)

Oxtoby 13.44

From class for collisions of molecule A with itself, the total collision rate is Z_{AA} :

$Z_{AA} = (1/2)\,\pi\,\sigma_{AA}^2\ \langle u_{rel}\rangle\,(N_A / V)^2$

$u_{rel} = (8kT / \pi\,\mu)^{1/2} \qquad \mu = m_A\,m_A / (m_A + m_A) = m_A / 2$

$u_{rel} = \sqrt{2}\ (8kT / \pi\,m_A)^{1/2}$

$\sigma_{AA} = \sigma_A + \sigma_A = 2\sigma_A = d$ (diameter of A)

Using the Arrhenius model, the reaction rate R is

$R = Z_{AA}\,\mathbf{e}^{-E_A/RT}$

(Where E_A here is expressed in Joules / mole. If E_A is expressed in Joules / molecule, $R = Z_{AA}\,\mathbf{e}^{-E_A/kT}$)

$R = (1/2)\,\pi\,d^2\ \sqrt{2}\ (8kT / \pi\,m_A)^{1/2}\ \mathbf{e}^{-E_A/RT}\ (N_A / V)^2$

$R = k_R\,(N_A / V)^2$

$k_R = (1/2)\,\pi\,d^2\ \sqrt{2}\ (8kT / \pi\,m_A)^{1/2}\ \mathbf{e}^{-E_A/RT}$

$k_R = A\,\mathbf{e}^{-E_A/RT} \rightarrow$

$A \equiv (1/2)\,\pi\,d^2\ \sqrt{2}\ (8kT / \pi\,m_A)^{1/2}$

Collecting the π's, 2's, 8's together gives

$A = 2d^2\,(\pi kT / m_A)^{1/2} = 2d^2\,(\pi RT / M_A)^{1/2}$

Here the units of A are m^3 / molecule-sec

To get A in m^3 / mole-sec, multiply by Avagadro's #, 6.023×10^{23} molecules / mole

$A = 2d^2\,N_0\,(\pi RT / M_A)^{1/2}$

This is same formula as Solution's manual 13.43 except for steric factor P. P is inserted to allow for possibility that every collision at an energy E does not lead to reaction if the molecules don't have the proper orientation.

For $NO_2 + NO_2$, Table 13.1 gives P = 0.05

Problem 13.44 gives $d = 2.6 \times 10^{-10}$ m $= \sigma_A + \sigma_A = \sigma_{AA}$

$A = (0.05)(2)(2.6 \times 10^{-10}\ m)^2\,(6.023 \times 10^{23}$ / mole$) \times [(\pi)(8.314)(500)/(.046)]^{1/2}$

$A = (0.10)(6.76 \times 10^{-20}\ m^2)(6.023 \times 10^{23}$ / mole$)(532$ m/s$)$

$A = 2.17 \times 10^6\ m^3$ / mole-sec