MTS723 F97 Homework 1 Solution J. J. Weimer 28.Sept.97

Constants

```
> No := 6.022e23: kb := 1.3805e-23: R := 8.314: me :=9.1091e-31: JpeV := 1.602e-19:
```

Common Formula

mean velocity in gas   gas number density

$$> vm_{gas} := \sqrt{\frac{8\,R\,T}{\pi\,M_{gas}}};\ \rho_{gas} := \frac{P}{kb\,T}$$

Problem 1

part a

The mean free path could be calculated from the formula $lm = \frac{kb\,T}{\sqrt{2}\,P\,dc^2\,\pi}$

This requires the value for the collision diameter of N2. Instead of this approach, I will use the table in my handbook that gives values for lm*P at T = 0 oC.

The value of lm*P is given as m mbar .....

```
> lmP[0] := 5.9e-5:
```

at 1 bar (1000 mbar) and 25 oC, lm is (in m)

```
> lma := lmP[0]*(25+273.15)/(273.15*1000);
```

$$lma := .6439996338\ 10^{-7}$$

```
> lmb := lma*1000/1e-9;
```

$$lmb := 64399.96338$$

<u>At 1 bar, lm is 64 nm. At 10e-9 mbar, lm is 64 km</u>

<u>Physical Chemistry, G. M. Barrow gives lm as 66 nm at 1 bar pressure and 25 oC.</u>

Collision times are determined by dividing the mean velocity by the mean free path. The mean velocity of the gas is only dependent on temperature and molar mass as given above

```
> T := 25 + 273.15:
> vmN2 := evalf(subs(M[gas]=(2*14.01/1000),vm[gas]),3);
```

$$vmN2 := 475.$$

Determine the collision times at the two pressures

```
> tca := evalf(lma/vmN2,3); tcb := evalf(lmb/vmN2,3);
```

$$tca := .136\ 10^{-9}$$

$$tcb := 136.$$

<u>At 1 bar, tc is 0.14 ns. At 10e-9 mbar, tc is 140 s.</u>

part b

Let's first determine what KE the electron has when traveling at the mean velocity of the N2.

```
> KEe := me*vmN2^2/2: evalf(KEe/JpeV,3);
```

$$.643\ 10^{-6}$$

The electron would only need to have a kinetic energy of 0.6 micro-eV to be traveling as fast as the N2 molecules. Therefore, for all intents and purposes, electrons in any spectroscopic analysis are traveling far faster than the background gas.

The mean free path of the electron is determined by the formula given in class.

```
> lmea := evalf(4*sqrt(2)*lma,3); lmeb := evalf(4*sqrt(2)*lmb,3);
```

$$lmea := .364\ 10^{-6}$$

$$lmeb := 364000.$$

At 1 bar, lme is 0.3 micron. At 10e-9 mbar, lme is 364 km.

The collision times must be affected by the velocity of the gas molecules since this also determines the mean free path. Therefore

```
> tcea := evalf(lmea/vmN2,3); tceb := evalf(lmeb/vmN2,3);tceb/60;
```

$$tcea := .766\ 10^{-9}$$

$$tceb := 766.$$

$$12.76666667$$

At 1 bar, tce is 0.77 ns. At 10e-9 mbar, tce is 13 min.

Problem 2

The monolayer time and impingement rate are given as

$$> tm := \frac{nsites}{s\ Za};\ Za := \frac{\rho_{gas}\ vm_{gas}}{4}$$

First find the number density of Ni sites on the Ni(111) surface. Ni is FCC, and the (111) surface is the close packed surface. We will have 2 Ni atoms in an equilateral triangle with sides of length l = 4r, where r is the atomic radius of an Ni atom. One O2 molecule occupies two Ni atoms, therefore it occupies the triangle.

```
> letriangle := 4*rNi: Aetriangle := sqrt(3)*letriangle^2/4: nsites[Ni] := 1/Aetriangle;
```

$$nsites_{Ni} := \frac{1}{12}\frac{\sqrt{3}}{rNi^2}$$

The sticking coefficient is unity. The radius of a Ni atom is 0.124 nm (from a periodic table reference).

```
> s :=1: rNi := 0.124e-9: T := 25 + 273.15:
> evalf(nsites[Ni]/100^2,3);
```

$$.936\ 10^{15}$$

The Ni surface has about 1 x 10e15 sites per cm2 (this is the typical number for a metal surface).

part a

Determine the gas density and mean velocity of molecules at 1 bar (1 x 10e5 Pa).

```
> rhoO2a := subs(P=1e5,rho[gas]); vmO2 :=
  evalf(subs(M[gas]=(2*16.01/1000),vm[gas]),3);
```

$$rhoO2a := .2429566414\ 10^{26}$$

$$vmO2 := 444.$$

Determine the impingement rate and monolayer time.

```
> ZaO2a := evalf(rhoO2a*vmO2/4,3); tmO2a := evalf(nsites[Ni]/(s*ZaO2a),3);
```

$$ZaO2a := .270\ 10^{28}$$

$$tmO2a := .346\ 10^{-8}$$

We have about 3.5 ns until the surface is covered with a monolayer of gas at 1 bar.

part b

Repeat the above calculations for 10e-9 mbar (10e-7 Pa)

```
> rhoO2b := subs(P=1e-7,rho[gas]);
```

$$rhoO2b := .2429566414\ 10^{14}$$

```
> ZaO2b := evalf(rhoO2b*vmO2/4,3); tmO2b := evalf(nsites[Ni]/(s*ZaO2b),3);
  tmO2b/60;
```

$$ZaO2b := .270\ 10^{16}$$

$$tmO2b := 3460.$$

$$57.66666668$$

We have about 1 h until the surface is covered with a monolayer of gas at 1e-9 mbar.

part c

Find the collision rate of O2 in number per cm2 per second at a pressure of 10e-6 Torr.

```
> rhoO2c := subs(P=1e-6*133.32,rho[gas]);
```

$$rhoO2c := .3239097943\ 10^{17}$$

```
> ZaO2c := evalf(rhoO2c*vmO2/4,3); evalf(ZaO2c/100^2,3);
```

$$ZaO2c := .360\ 10^{19}$$

$$.360\ 10^{15}$$

The collision rate is 3.6 x 10e14 molecule/cm2 s.

The number of Langmuirs needed to give a monolayer coverage is the site density divided by this collision rate.

```
> nLangmuirs := evalf(nsites[Ni]/ZaO2c,3);
```

$$nLangmuirs := 2.60$$

We need 2.6 Langmuirs of O2 dose to reach monolayer.

Problem 3

The lower cutoffs for the flow ranges are defined as follows (P in Pa and dtube in m)

```
> Pviscous := 0.6/dtube; PKnudsen := 1e-2/dtube;
```

$$Pviscous := \frac{.6}{dtube}$$

$$PKnudsen := \frac{.01}{dtube}$$

For a 0.5 m diameter chamber (pressures in mbar and Torr)

```
> dtube := 0.5: Pviscous*1e-2; Pviscous*750.06e-5; PKnudsen*1e-2;
  PKnudsen*750.06e-5;
```

```
.01200000000

.009000720000

.0002000000000

.0001500120000
```

The cutoff of viscous flow is 1.2 x 10e-2 mbar or 9.0 x 10e-3 Torr.

The cutoff of Knudsen flow is 2.0 x 10e-4 mbar or 1.5 x 10e-4 Torr.

For a 2.5 cm diameter tube (pressures in mbar and Torr)

```
> dtube := 2.5e-2: Pviscous*1e-2; Pviscous*750.06e-5; PKnudsen*1e-2;
  PKnudsen*750.06e-5;
```

```
.2400000000

.1800144000

.004000000000

.003000240000
```

The cutoff of viscous flow is 0.24 mbar or 0.18 Torr.

The cutoff of Knudsen flow is 4.0 x 10e-3 mbar or 3.0 mTorr.