PROBLEM SET #4 SOLUTIONS

(1) CKD 6.1

$$k(T) = \left(\mu/2\pi k_B T\right)^{3/2} \int_0^\infty v\,\sigma_R(v)\,e^{-\mu v^2/2k_BT} \cdot 4\pi^2 v^2\,dv \quad (6\text{-}5a)$$

OR

$$k(T) = \frac{1}{k_B T}\left(8/\pi\mu k_B T\right)^{\frac{1}{2}} \int_0^\infty E\,\sigma_R(E)\,e^{-E/k_BT}\,dE \quad (6\text{-}5b)$$

a) $\sigma_R(v) = \pi d^2$

$$k(T) = \pi d^2 \left(\frac{8 k_B T}{\pi\mu}\right)^{1/2}$$

b) $\sigma_R(E) = \sigma_0(1 - e^{-aE})$

$$k(T) = \sigma_0 \left(8k_BT/\pi\mu\right)^{1/2}\left(1 - \left(\frac{1}{ak_BT+1}\right)^2\right)$$

c) $\sigma_R(E) = \sigma_0(1 - e^{-a(E-E_0)})$; $E_0 > 0$; min ENERGY threshold

$\sigma_R(E) = 0$ for $E < E_0$

$$k(T) = \sigma_0\left(8/\pi\mu k_BT\right)^{1/2} \underline{\underline{e^{-E_0/k_BT}}} \left[E_0 + k_BT - \frac{1}{ak_BT+1}\left(E_0 + k_BT/ak_BT+1\right)\right]$$

↑ Arrhenius-like temperature dependence.

d) $\sigma_R(v) = \sigma_0 \exp(-A/v)$

Solve numerically w/ appropriate values.

(2) CKO 8.8

a) k @ $T = 1000, 1500, 2000\,K$

$\mu = 10$ daltons ; $d = 0.1\,nm$; $E_0 = 100\,kJ\,mol^{-1}$

$$k = \left(\frac{8\pi k_B T}{\mu}\right) d^2 \exp\left[-E_0/k_BT\right]$$

$k\ (Ls^{-1})$	$T\ (K)$
2.74×10^{-19}	1000
1.86×10^{-17}	1500
1.58×10^{-16}	2000

Plot $\ln K$ vs. $1/T$; slope $= -E_0/k_B$

$E_0 \sim 105.6\,kJ/mol$ $\qquad = 7.27 \times 10^{+4}$

close to original value of ~100 kJ/mole for E_0. Graph demonstrates Arrhenius behavior, as expected from eqn for k.

4. CKD 10.6

$$A = \frac{L^{\neq} k_B T}{h} \left(\frac{Q^{\neq}}{Q_{reactants}}\right)_{rot} \left(\frac{Q^{\neq}}{Q_{reactants}}\right)_{trans}$$

Low T $\Rightarrow$ $\left(Q^{\neq}/Q_{reactants}\right)_{vib} \sim 1$

a) $H_2 + F_2 \rightarrow 2HF$

$$A \propto T \left(\frac{T^{3/2}}{T \cdot T}\right)\left(T^{-3/2}\right)$$

$$\boxed{A \propto T^{-1}}$$

b) $NO_2 + F_2 \rightarrow NO_2F + F$

$$A \propto T\left(T^{3/2}/T^{3/2} \cdot T\right)\left(T^{-3/2}\right)$$

$$\boxed{A \propto T^{-3/2}}$$

c) $2\,NOCl \rightarrow 2NO + Cl_2$

$$A \propto T\left(T^{3/2}/T^{3/2} \cdot T^{3/2}\right)\left(T^{-3/2}\right)$$

$$\boxed{A \propto T^{-2}}$$

e) $C_2H_4 + HCl \rightarrow C_2H_5Cl$

$$A \propto T\left(\frac{T^{3/2}}{T^{3/2} \cdot T}\right)\left(T^{-3/2}\right)$$

$$\boxed{A \propto T^{-3/2}}$$

/3

(5) CED 10.9

$$H + H_2 \rightleftharpoons H_3^{\ddagger} \rightarrow H_2 + H$$

$$k_{TST} = \frac{k_B T}{h} \left(\frac{Q^{\ddagger}}{Q_H Q_{H_2}} \right) e^{-E_0/k_B T} \cdot L^{\ddagger} \text{ (symmetry number)}$$

$$\left(\frac{Q^{\ddagger}}{Q_H Q_{H_2}} \right)_{total} = \left(\frac{Q^{\ddagger}}{Q_H Q_{H_2}} \right)_{tran} \left(\frac{Q^{\ddagger}}{Q_{H_2}} \right)_{rot} \left(\frac{Q^{\ddagger}}{Q_{H_2}} \right)_{vib} \left(\frac{Q^{\ddagger}}{Q_H Q_{H_2}} \right)_{elec.}$$

Q_{vib} only temp. dependent quantity

a) $Q_{trans} = 3.05 \times 10^{-31}\ m^3$ $\qquad L^{\ddagger} = 2$

$Q_{rot} = 6.29$

$Q_{vib} = 1.02$ (300 K)

1.84 (1000 K)

@ 300 K

$4.24 \times 10^{-12}\ cm^3 s^{-1} = k_{TST}$

@ 1000 K

$k_{TST} = 1.60 \times 10^{-12}\ cm^{+3} s^{-1}$

MEASURED $k \Rightarrow 2.1 \pm 0.6 \times 10^{-12}\ cm^{+3} s^{-1}$

b) USING OLD-COLLISION THEORY

$$k_{coll} = \pi d^2 \left(8 k_B T / \pi \mu \right)^{1/2} e^{-E/k_B T}$$

$$\mu = \frac{m_H(m_H + m_H)}{m_H + m_H + m_H} = 1.11 \times 10^{-27}\ kg$$

$$A_{300K} = \pi (2.5 \times 10^{-10} m)^2 \left(8 k_B \cdot 300K / \pi (1.11 \times 10^{-27} kg) \right)^{1/2}$$

$$= 6.05 \times 10^{-10}\ cm^3 s^{-1}$$

$$A_{1000K} = 1.11 \times 10^{-9}\ cm^3 s^{-1}$$

$$k_{300K, coll} = 1.72 \times 10^{-16}\ cm^3 s^{-1}$$

$$k_{1000K, coll} = 1.21 \times 10^{-11}\ cm^3 s^{-1}$$

$k_{collision-theory}$ are much larger than k_{TST} (~ 4 x's)

> reaction every collision ~~is~~ not as accurate of a description of the situation as the fundamentals of transition-state theory. <

c) WIGNER TUNNELING CORRECTION

(p. 299)

corrections can be found in book, or calculated of an estimated ν_s, the imaginary frequency of the transition state @ the top of the barrier. $Q_{TUNNEL} = 1 - \frac{1}{24}\left(\frac{h\nu_s}{k_B T}\right)^2 \left(1 + \frac{k_B T}{E_0}\right)$

c) ctd.

depending of V_s you choose (related to calculation), you would get a correction factor between 1 and 5 for both 300 K and 1000 K.

d) @ 300K

$k \sim 7 \times 10^{7}$ L mole^{-1} s^{-1} $\rightarrow$ $\sim 1.20 \times 10^{-16}$ cm^{+3} s^{-1}

@ 1000K

$k \sim 2 \times 10^{9}$ L mole^{-1} s^{-1} $\rightarrow$ $\sim$ **3** $\times 10^{-12}$ cm^{3} s^{-1}

These values are all in pretty good agreement w/ calculated values using TST. Collision theory deviates a bit more, but still not too far consider experimental uncertainties associated w/ ~~these~~ this reaction. Good agreement → so who is right?

(6) CKD 11.10

a) HNC : degrees of freedom

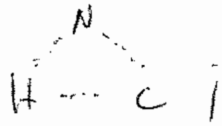
rotational → 2

vibrational → 4 (3N−5)

translation → 3

9 TOTAL DOF.

HCN HNC



translation → 3

rotational → 3

vibrational → 3 (3N − 6)

9 total D.O.F.

b) $Q^{\ddagger} = \left(Q^{\ddagger}_{trans}/V\right)\left(Q^{\ddagger}_{rot}\right)\left(Q^{\ddagger}_{vib}\right)\left(Q^{\ddagger}_{elec}\right)$

(1) (2) (3) (4)

(1) $\frac{(2\pi m k_B T)^{3/2}}{h^3} \sim 8.35 \times 10^{32}\ m^{-3}$

(2) $\frac{\pi^{1/2}}{\sigma}\left(\frac{8\pi^2 k_B T}{h^2}\right)^{3/2}(I_x \cdot I_y \cdot I_z)^{1/2} \sim 5.32 \times 10^3$

(3) $\prod_i \frac{1}{1-\exp(-h\nu_i/k_BT)}$ $\nu_i = 1{,}000\ cm^{-1}, 2000\ cm^{-1}, 3000\ cm^{-1}$

$Q^{\ddagger}_{vib} = 1.4$

(4) $Q^{\ddagger}_{elec} = 1$

$Q^{\ddagger} = 6.3 \times 10^{36}\ m^{-3}$

DO THE SAME FOR HNC

$Q_{HNC} = 1.04 \times 10^{36}\ m^{-3}$

/7

(7) CKD 11.12

a) Good idea to use a program like MATLAB to do the work for you.

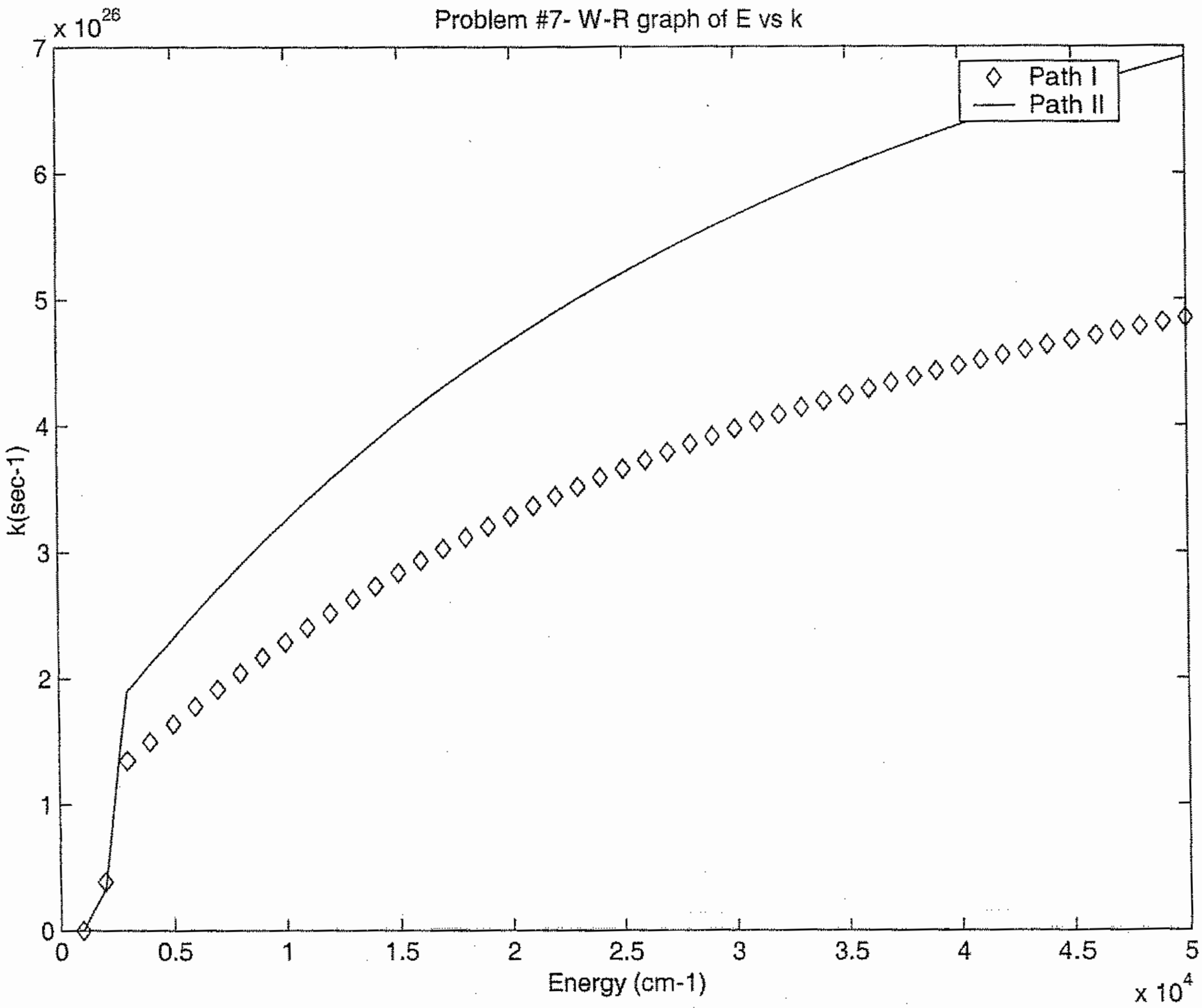
The script used here is provided by Huzeifa Ismail.

$k_{\infty} \sim 40\,s^{-1}$ ✓

predicted ratio : $\frac{[HCl]_{\infty}}{[DCl]_{\infty}} \sim 3$ ✓

SCRIPT + RELEVANT INFO TO FOLLOW.

/8



Problem #7- W-R graph of E vs k
x 10^26
7
6
5
4
3
2
1
0
k(sec-1)
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
5
Energy (cm-1)
x 10^4
Path I
Path II

```
%huzeifa Ismail
%problem #7

clear;

h=6.6262*10^-34;
c=3*10^10;

vi1=[2940 2940 2940 2940 2160 1340 1340 1340 1340 1340 1270 1270 960 960 96↙
0 720 720 330 200];
vi2=[3000 3000 3000 2200 2200 1380 1380 1115 960 960 960 960 960 850 820 64↙
5 403];
vi3=[3000 3000 3000 3000 2088 1380 1100 960 960 960 960 850 850 850 750 570↙
 501];

tem1=c*vi1;
tem2=c*vi2;
tem3=c*vi3;

s1=18;
s2=17;
s3=17;

vi2_1=vi1.^2;
vi2_2=vi2.^2;
vi2_3=vi3.^2;


z=0;
for energy=50000:-1000:0
    sumvi1=0;
    sumvi2_1=0;
    Ndenom1=1;
    for i=1:length(vi1)
        if(vi1(i)<=energy)
            sumvi1=sumvi1+vi1(i);
            sumvi2_1=sumvi2_1+vi2_1(i);
            Ndenom1=Ndenom1*vi1(i)*c;
        end
    end
    Ez1=sumvi1*c/2;
    beta1=((s1-1)/s1)*sumvi2_1/sumvi1^2;
    sumvi2=0;
    sumvi2_2=0;
    Gdenom2=1;
    for i=1:length(vi2)
        if(vi2(i)<=energy)
            sumvi2=sumvi2+vi2(i);
            sumvi2_2=sumvi2_2+vi2_2(i);
```

10

```
            Gdenom2=Gdenom2*vi2(i)*c;
        end
    end
    Ez2=sumvi2*c/2;
    beta2=((s2-1)/s2)*sumvi2_2/sumvi2^2;
    sumvi3=0;
    sumvi2_3=0;
    Gdenom3=1;
    for i=1:length(vi3)
        if(vi3(i)<=energy)
            sumvi3=sumvi3+vi3(i);
            sumvi2_3=sumvi2_3+vi2_3(i);
            Gdenom3=Gdenom3*vi3(i)*c;
        end
    end
    Ez3=sumvi3*c/2;
    beta3=((s3-1)/s3)*sumvi2_3/sumvi3^2;
    z=z+1;
    Ene(z)=energy*c;%*h;

    Eprime1(z)=Ene(z)/Ez1;
    Eprime2(z)=Ene(z)/Ez2;
    Eprime3(z)=Ene(z)/Ez3;

    if Eprime1(z) < 1
       w1=(1/(3.51+(5*Eprime1(z))+(2.73*Eprime1(z)^.5)));
       dw1=-(5+(1.365/Eprime1(z)^.5))/((3.51+(2.73*Eprime1(z)^.5)+(5*Eprime↙
1(z)))^2);
   else
       w1=exp(-2.4191*Eprime1(z)^.25);
       dw1=-24191/40000/(Eprime1(z))^(3/4)/Ez1*exp(-24191/10000*(Eprime1(z)↙
)^(1/4));
   end

    if Eprime2(z) < 1
       w2=(1/(3.51+(5*Eprime2(z))+(2.73*Eprime2(z)^.5)));
   else
       w2=exp(-2.4191*Eprime2(z)^.25);
   end

   if Eprime3(z) < 1
       w3=(1/(3.51+(5*Eprime3(z))+(2.73*Eprime3(z)^.5)));
   else
       w3=exp(-2.4191*Eprime3(z)^.25);
   end
   a1=1-beta1*w1;
   a2=1-beta2*w2;
   a3=1-beta3*w3;
```

10

```
    N1(z)=(((Ene(z) + a1*Ez1)^(s1-1))/Ndenom1)*(1-beta1*dw1);
    G2(z)=((Ene(z) + a2*Ez2)^s2)/Gdenom2;
    G3(z)=((Ene(z) + a3*Ez3)^s3)/Gdenom3;
    K1(z)=G2(z)/N1(z);
    K2(z)=G3(z)/N1(z);
end

E=[50000:-1000:0];
plot(E, K1,'d');
hold on;
plot (E, K2);
```

Continued on next page....

```
%huzeifa ismail
%prob 7b

kb=1.381e-23;
h=6.626e-34;
c=3e10;
T=1000;
g=[4 1 4 2 3 2 1 1];
v=[2940 2160 1340 1270 960 720 330 200];

E0=232.7e3/6.022e23;
TS_g=[3 2 2 1 5 1 1 1 1];
TS_v=[3000 2200 1380 1115 960 850 820 645 403];

E02=237.9e3/6.022e23;
TS2_g=[4 1 1 1 4 3 1 1 1];

TS2_v=[3000 2088 1380 1100 960 850 750 570 501];

k1=0.33/0.25*kb*T/h*exp(-E0/(kb*T))*(prod(g.*(1-exp(-h*c*v/(kb*T))))/prod(T↙
S_g.*(1-exp(-h*c*TS_v/(kb*T)))));

k2=0.33/0.497*kb*T/h*exp(-E02/(kb*T))*(prod(g.*(1-exp(-h*c*v/(kb*T))))/prod↙
(TS2_g.*(1-exp(-h*c*TS2_v/(kb*T)))));

k=k1+k2
Ratio=k1/k2
```

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PROBLEM 3. GAUSSIAN CALCULATION

$$k = \frac{L^{\neq} k_B T}{h} \frac{Q^{\neq}}{Q_1 Q_2} e^{-E_0 / k_B T}$$

<The following solution is provided by Joanna Yu.>
(w/ added commentary)

The rates for the forward & reverse rxns are a bit large, but the ratio looks ok.

Set up a spreadsheet and get the values from Gaussian into a readable user-friendly format.

Do the calculations for the partition functions and you can get to k.

T (K)	
300	

	forward	backward
L_{TS}	2	
EF_0 (kJ/mo	27.68	126.01
EF_0/R (K)	3.33E+03	1.52E+04

	CH_3			C_2H_4			TS			$CH_3CH_2CH_2$		
m (kg)	2.49E-26			4.65E-26			7.14E-26			7.14E-26		
rotational co	285.28	284.86	142.53	1.47E+02	30.05	24.95	2.78E+01	6.06	5.54	31.26	8.79	7.90
θ_{rot} (K)	136.88	136.67	68.39	7.05E+01	14.42	11.97	13.32	2.91	2.66	15.00	4.22	3.79
E (hartree)	-39.84			-78.59			-118.42			-118.47		
Eo (kJ/mol)	-1.04E+05			-2.06E+05			-3.10E+05			-3.11E+05		
q_{vib}			0.000			4.03E-24			1.51E-38			0.000
	ν (cm-1)	θ_{vib}	q_{vib}	ν (cm-1)	θ_{vib}	q_{vib}	ν (cm-1)	θ_{vib}	q_{vib}	ν (cm-1)	θ_{vib}	q_{vib}
	454.42	653.63	0.38	834.59	1200.46	0.14	-375.62	-540.29	-0.49	77.97	112.15	2.66
	1430.80	2058.04	0.03	955.62	1374.55	0.10	91.17	131.14	2.27	254.65	366.28	0.77
	1431.87	2059.58	0.03	975.37	1402.96	0.10	216.48	311.38	0.92	334.95	481.79	0.56
	3142.26	4519.78	0.00	1069.50	1538.35	0.08	346.16	497.91	0.54	522.65	751.77	0.31
	3316.34	4770.17	0.00	1247.83	1794.85	0.05	476.45	685.32	0.36	753.10	1083.24	0.17
	3317.21	4771.42	0.00	1396.01	2008.00	0.04	495.85	713.23	0.34	899.88	1294.37	0.12
				1494.29	2149.36	0.03	782.24	1125.16	0.16	901.50	1296.70	0.12
				1720.82	2475.20	0.02	826.02	1188.13	0.14	1034.49	1488.00	0.08
				3154.24	4537.00	0.00	866.40	1246.21	0.13	1104.82	1589.16	0.07
				3169.01	4558.25	0.00	944.47	1358.51	0.11	1209.31	1739.46	0.06
				3223.92	4637.24	0.00	1026.45	1476.43	0.09	1323.25	1903.34	0.04
				3249.45	4673.96	0.00	1247.65	1794.60	0.05	1343.94	1933.11	0.04
							1326.26	1907.67	0.04	1426.02	2051.17	0.03
							1446.16	2080.13	0.03	1491.96	2146.00	0.03
							1451.78	2088.22	0.03	1514.68	2178.70	0.03
							1488.87	2141.56	0.03	1524.92	2193.43	0.03
							1616.31	2324.87	0.02	1536.91	2210.66	0.03
							3123.43	4492.69	0.00	3025.42	4351.71	0.00
							3158.37	4542.95	0.00	3043.78	4378.13	0.00
							3168.03	4556.85	0.00	3060.84	4402.66	0.00
							3230.33	4646.45	0.00	3111.75	4475.89	0.00
							3255.70	4682.94	0.00	3120.62	4488.64	0.00
							3277.51	4714.32	0.00	3160.23	4545.63	0.00
							3288.94	4730.76	0.00	3256.75	4684.46	0.00

Translational

	forward	backward
Q_{trans} (m^3)	3.353E-32	1.000E+00
Q_{trans} (m^3)	1.742E-28	1.000E+00

Rotational

	forward	backward
Q_{rot}	1.643E+04	6.550E-01
Q_{rot}	8.539E+07	6.550E-01

Vibrational

	forward	backward
Q_{vib}	0.142	98.529

Electronic

Q_{elec}	1

	forward	backward
A	9.772E-16	1.035E+14 → BUT OK
k (m^3/s)	1.49E-20	4.70E-08
k (cm^3/s)	1.49E-14	4.70E-02 → A BIT LARGE, BUT RATIO IS ABOUT RIGHT

Literature	forward	backward	T range (K)	Source	Data type
k (cm^3/s)	1.54E-18		300-600	Baulch, D.L et al.	Extensive literature review
k (cm^3/s)	1.33E-18		300-2500	Tsang, W.; Hampson, R.F	Extensive literature review
k (s^{-1})		1.20E-09	300-2500	Tsang, W.	Extensive literature review
		9.05E-10	300-800	Tsang, W.	Derived from detailed balance/reverse rate

25

/25