

**CH353 – Physical Chemistry I**  
Spring 2013, Unique 52575  
**Exam 5 – April 26, 2013**

Name:     Kay    

Always assume ideal gas unless directed otherwise.

You may use any material that does not have a heartbeat and does not connect to the internet or cellular network.

Honor Code:

“The core values of the University of Texas at Austin are learning, discovery, freedom, leadership, individual opportunity, and responsibility. Each member of the University is expected to uphold these values through integrity, honesty, trust, fairness, and respect toward peers and community.”

I certify that the work on this exam is entirely my own.

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Signature

Date

1. (10 points) Determine if the following statements are true or false.

- a. True False The steady-state approximation assumes that an intermediate is consumed as soon as it is formed.
- b. True False Molecules with a large value of the collision frequency also have a large value of the mean free path.
- c. True False A molecule composed of three atoms has energy partitioned through electronic and translational states only.

2. (20 points) The lowest three electronic energy levels for the neon atom have the following energies and degeneracies:

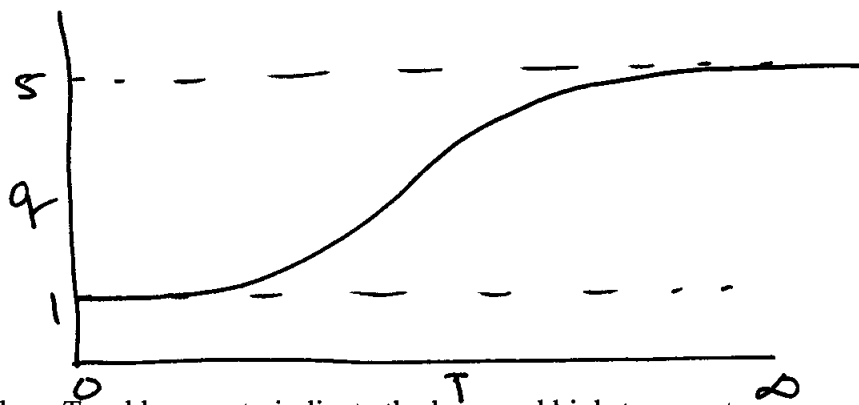
Level	Energy	Degeneracy
1	0	1
2	$\epsilon$	1
3	$3\epsilon$	3

a) Determine the partition function for this system.

$$q = \sum_i g_i e^{-\beta E_i} = e^{-\beta(0)} + e^{-\beta\epsilon} + 3e^{-\beta 3\epsilon} = 1 + e^{-\beta\epsilon} + 3e^{-\beta 3\epsilon} = q$$

b) Plot  $q$  vs.  $T$  and be sure to indicate the low- and high-temperature limits.

as  $T \rightarrow 0$ ,  $e^{-\beta\epsilon} \rightarrow 0$ ,  $q \rightarrow 1$   
 as  $T \rightarrow \infty$ ,  $e^{-\beta\epsilon} \rightarrow 1$ ,  $q \rightarrow 5$



c) Plot the probability of each level vs.  $T$  and be sure to indicate the low- and high-temperature limits.

level 1:  $p_1 = \frac{1}{1 + e^{-\beta\epsilon} + 3e^{-\beta 3\epsilon}}$

as  $T \rightarrow 0$ ,  $e^{-\beta\epsilon} \rightarrow 0$ ,  $p_1 \rightarrow \frac{1}{1} = 1$

as  $T \rightarrow \infty$ ,  $e^{-\beta\epsilon} \rightarrow 1$ ,  $p_1 \rightarrow \frac{1}{5}$

level 2:  $p_2 = \frac{e^{-\beta\epsilon}}{1 + e^{-\beta\epsilon} + 3e^{-\beta 3\epsilon}}$

as  $T \rightarrow 0$ ,  $p_2 \rightarrow 0$

as  $T \rightarrow \infty$ ,  $p_2 \rightarrow \frac{1}{5}$

level 3:  $p_3 = \frac{3e^{-\beta 3\epsilon}}{1 + e^{-\beta\epsilon} + 3e^{-\beta 3\epsilon}}$

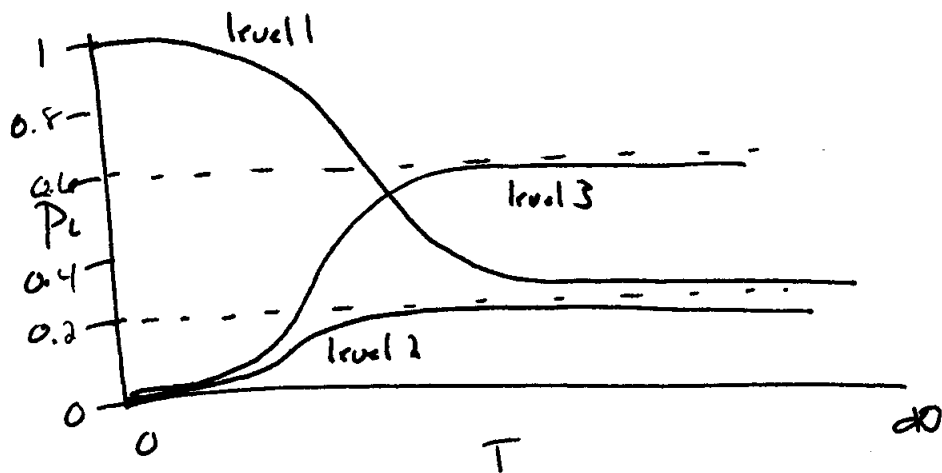
as  $T \rightarrow 0$ ,  $p_3 \rightarrow 0$

as  $T \rightarrow \infty$ ,  $p_3 \rightarrow \frac{3}{5}$

Over  $\rightarrow$

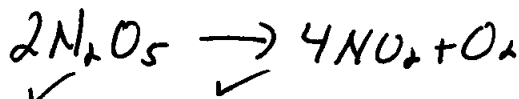
2. continued at both  $T \rightarrow 0$  and  $T \rightarrow \infty$ ,  $p_1 + p_2 + p_3 = 1$

This is good.



3. (70 points)  $N_2O_5$  gas decomposes to  $NO_2$  gas and  $O_2$  gas.

a) Write the stoichiometrically balanced overall reaction equation.



$$d(N_2O_5) = 3A^0$$

$$P = 1 \text{ bar} = 1.01 \times 10^5 \text{ Pa}$$

b) What is the velocity, collision frequency, and mean free path of  $N_2O_5$  at room temperature?

$$FW(N_2O_5) = 108 \text{ g/mol} = 0.108 \text{ kg/mol}$$

$$T = 298 \text{ K}$$

$$c = \left( \frac{3RT}{FW} \right)^{1/2} = \left( \frac{3(8.314 \text{ J/K mol})(298 \text{ K})}{(0.108 \text{ kg/mol})} \right)^{1/2} = (6.88 \times 10^4 \text{ J/kg})^{1/2} = \boxed{262 \text{ m/s} = c}$$

$$c_{rel} = \sqrt{2}c = 371 \text{ m/s} \quad Z_{coll} = \frac{\sigma c_{rel} P}{k_B T} = \frac{\pi (3.0 \times 10^{-10} \text{ m})^2 (371 \text{ m/s}) (1.01 \times 10^5 \text{ Pa})}{(1.38 \times 10^{-23} \text{ J/K})(298 \text{ K})}$$

$$Z_{coll} = 2.6 \times 10^9 \text{ s}^{-1}$$

$$\lambda = \frac{c_{rel}}{Z_{coll}} = \frac{371 \text{ m/s}}{2.6 \times 10^9 \text{ s}^{-1}} = \boxed{1.4 \times 10^{-7} \text{ m} = \lambda}$$

So the molecule moves ~1000x its diameter before colliding

c) You are interested in the rate of this decomposition reaction. You measure the initial rate ( $v_0$ ) of decay of a freshly prepared sample of  $N_2O_5$  and collect the following data:

$[N_2O_5]$ (mol L <sup>-1</sup> )	$v_0$ (mol L <sup>-1</sup> s <sup>-1</sup> )
1.4	$2.1 \times 10^4$
1.7	$2.5 \times 10^4$
4.1	$6.1 \times 10^4$
10.9	$1.6 \times 10^5$

$$v(t) = k_{obs} [N_2O_5]^n$$

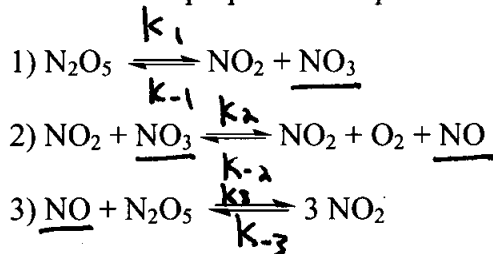
Determine the rate law and rate constant of this reaction, assuming integer reaction orders.

$$n = \frac{\ln \left( \frac{v_1}{v_2} \right)}{\ln \left( \frac{[N_2O_5]_1}{[N_2O_5]_2} \right)} = \frac{\ln \left( \frac{2.1 \times 10^4}{2.5 \times 10^4} \right)}{\ln \left( \frac{1.4}{1.7} \right)} = \frac{-0.17}{-0.19} \approx 1$$

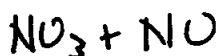
(you can also tell by inspection that  $[N_2O_5]$  and  $v_0$  increase proportionally)

$$k_{obs} = \frac{v_1}{[N_2O_5]_1} = \frac{2.1 \times 10^4 \text{ mol/L s}}{1.4 \text{ mol/L}} = \boxed{1.5 \times 10^4 \text{ s}^{-1} = k_{obs} \text{ units!}}$$

The following mechanism has been proposed to explain this reaction:



d) What are the intermediates of this mechanism?



e) The remaining questions will be significantly simpler if you are able to ignore the back reactions of elementary steps 2 and 3 in the proposed mechanism. Provide a physical justification for doing so, in clear comprehensible English.

The back reactions for steps 2 + 3 are both termolecular; i.e. they require the collision of 3 molecules:

$$v(t) = k_{-2} [\text{NO}_2] [\text{O}_2] [\text{NO}]$$

$$v(t) = k_{-3} [\text{NO}_2]^3$$

this is going to be very unlikely on the time scale of  $k_1, k_{-1}, k_2$ , and  $k_3$ .

We therefore will ignore  $k_{-2} + k_{-3}$ .

f) The first step of this mechanism is believed to be rate-determining and the intermediates have never been observed experimentally. Using all of the information either given or inferred, prove that this mechanism is correct and determine  $k_{obs}$  in terms of the elementary reaction rate constants.

SSA  $\leftarrow$

$$\frac{d[\text{NO}_2]}{dt} = k_1 [\text{N}_2\text{O}_5] - k_{-1} [\text{NO}_2] [\text{NO}_3] + k_2 [\text{NO}_3] [\text{NO}_2] + 3k_3 [\text{NO}] [\text{N}_2\text{O}_5]$$

$$\frac{d[\text{NO}_3]}{dt} = k_1 [\text{N}_2\text{O}_5] - k_{-1} [\text{NO}_3] [\text{NO}_2] - k_2 [\text{NO}_2] [\text{NO}_3] = 0$$

$$[\text{NO}_3] = \frac{k_1 [\text{N}_2\text{O}_5]}{(k_{-1} + k_2) [\text{NO}_2]}$$

$$\frac{d[\text{NO}]}{dt} = k_2 [\text{NO}_2] [\text{NO}_3] - k_3 [\text{NO}] [\text{N}_2\text{O}_5] = 0$$

$$[\text{NO}] = \frac{k_2 [\text{NO}_2] [\text{NO}_3]}{k_3 [\text{N}_2\text{O}_5]}$$

plug intermediates into  $\frac{d[\text{NO}_2]}{dt}$ :

$$\frac{d[\text{NO}_2]}{dt} = k_1 [\text{N}_2\text{O}_5] - k_{-1} [\text{NO}_2] \left( \frac{k_1 [\text{N}_2\text{O}_5]}{(k_{-1} + k_2) [\text{NO}_2]} \right) + k_2 [\text{NO}_2] \left( \frac{k_1 [\text{N}_2\text{O}_5]}{(k_{-1} + k_2) [\text{NO}_2]} \right)$$

$$+ 3k_3 [\text{N}_2\text{O}_5] \left( \frac{k_2 [\text{NO}_2]}{k_3 [\text{N}_2\text{O}_5]} \left( \frac{k_1 [\text{N}_2\text{O}_5]}{(k_{-1} + k_2) [\text{NO}_2]} \right) \right)$$

over  $\rightarrow$

3f) continued

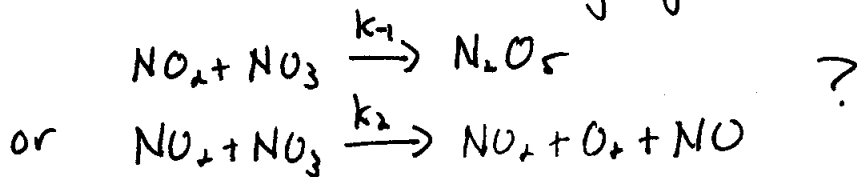
$$\frac{d[\text{NO}_2]}{dt} = k_1[\text{N}_2\text{O}_5] - \frac{k_{-1}k_1[\text{N}_2\text{O}_5]}{(k_{-1} + k_2)} + \frac{k_2k_1[\text{N}_2\text{O}_5]}{(k_{-1} + k_2)} + \frac{3k_1k_2[\text{N}_2\text{O}_5]}{(k_{-1} + k_2)}$$

i.e. rate =  $v(t) = [\text{N}_2\text{O}_5]k' - [\text{N}_2\text{O}_5]k'' + [\text{N}_2\text{O}_5]k''' + [\text{N}_2\text{O}_5]k''''$

$$v(t) = (k' - k'' + k''' + k''') [\text{N}_2\text{O}_5]$$

- We have demonstrated that the rxn. is 1st order in  $[\text{N}_2\text{O}_5]$  as expected.

- The value of  $k_{\text{obs}}$  depends on what you assume from here. We could leave  $k_{\text{obs}}$  as is, or make a further simplifying assumption. If SSA is true, then either  $k_{-1}$  or  $k_2$  must be very large. So



- No additional information is given in the problem, although the  $k_2$  rxn.

will have a larger increase in entropy (2 moles  $\rightarrow$  3 moles, instead of 2 moles  $\rightarrow$  2 moles).

You therefore might want to assume that  $k_2 \gg k_{-1}$ , and simplify the above equation:

$$\frac{d[\text{NO}_2]}{dt} = k_1 \left( \frac{k_2}{k_2} \right) [\text{N}_2\text{O}_5] - \frac{k_{-1}k_1}{k_2} [\text{N}_2\text{O}_5] + \frac{k_2k_1}{k_2} [\text{N}_2\text{O}_5] + \frac{3k_1k_2}{k_2} [\text{N}_2\text{O}_5]$$

$$\frac{d[\text{NO}_2]}{dt} = \left( \frac{k_1k_2 - k_{-1}k_1 + k_1 + 3k_1}{k_2} \right) [\text{N}_2\text{O}_5]$$