

**Chemistry 271, Section 21xx
General Chemistry and Energetics
Final Exam (200 points total)**

**University of Maryland, College Park
Prof. Jason Kahn
May 15, 2009**

You have 120 minutes for this exam.

Exams written in pencil or erasable ink will not be re-graded under any circumstances.

Explanations should be concise and clear. I have given you more space than you should need. There is extra space on the last page if you need it.

You will need a calculator for this exam. No other study aids or materials are permitted.

Partial credit will be given, *i.e.*, if you don't know, guess.

Honor Pledge: At the end of the examination time, please write out the following sentence and sign it, or talk to me about it:

"I pledge on my honor that I have not given or received any unauthorized assistance on this examination."

Your Name: _____

Key

Your SID #: _____

Viewing: Monday, May 18, 9:30-10:30 a.m., Chemistry 1346 (Wing 3)

Useful Equations:

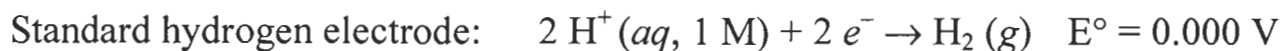
$$\Delta S - q/T \geq 0$$

$$\Delta G^\circ = -RT \ln K_{eq}$$

$$K_a = [H^+][A^-]/[HA]$$

$$^\circ C = ^\circ K - 273.15$$

$$2.303RT/\mathcal{F} = 0.0592 \text{ Volts at } 25^\circ C$$



$$\ln K_{eq} = (-\Delta H^\circ/RT + \Delta S^\circ/R) \quad \ln k = (-E_a/RT) + \ln A$$

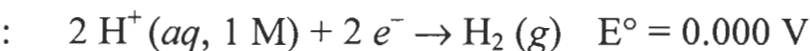
$$[A] = [A]_0 - kt$$

$$pH = -\log([H^+])$$

$$\Delta G = \Delta H - T\Delta S$$

$$n_i/n_0 = \exp[-(E_i - E_0)/kT]$$

$$R = 8.314 \text{ J/mole K}$$



$$\ln[A] = \ln[A]_0 - kt$$

$$S = k \ln W$$

$$PV = nRT$$

$$\Delta G = -n\mathcal{F}E$$

$$E = E^\circ - 2.303(RT/n\mathcal{F}) \log_{10} Q$$

$$\mathcal{F} = 96500 \text{ C(oulomb)/mole}$$

$$1 \text{ Volt} = 1 \text{ Joule/Coulomb}$$

$$1/[A] = 1/[A]_0 + 2kt$$

1. Thermodynamics and Kinetics (40 pts)

(a; 6 pts) What is the second law of thermodynamics?

The ⁺²entropy of the ⁺²universe always ⁺²increases.
 (disorder) Energy can not be destroyed = 1st law

[C.P. Snow!]

(b; 26 pts = 2 pts each) Circle True or False:

Exothermic reactions are always spontaneous	T	<input checked="" type="radio"/> F
Thermodynamics provides no constraints on rates of reaction.	T	<input checked="" type="radio"/> F
Catalysts can be developed to accelerate the same reaction in either the forward or the reverse direction selectively, without accelerating the reverse reaction.	T	<input checked="" type="radio"/> F
Free energy minimization reflects the decreasing entropy of the universe.	T	<input checked="" type="radio"/> F
Endothermic reactions are never spontaneous.	T	<input checked="" type="radio"/> F
The steady-state approximation (SSA) is useful for elementary (single-step) reactions.	T	<input checked="" type="radio"/> F
The steady-state approximation is that reactant concentration is constant.	T	<input checked="" type="radio"/> F
The SSA applies to intermediates for which there is a rapid breakdown path.	<input checked="" type="radio"/> T	F
The rate limiting step of a reaction is the one with the largest free energy of activation.	<input checked="" type="radio"/> T	F
Catalysts can change the mechanism of a reaction	<input checked="" type="radio"/> T	F
There are no fundamental limits on reaction rates	T	<input checked="" type="radio"/> F
The biochemical standard state is referenced to 1 M/1 atm everything.	T	<input checked="" type="radio"/> F
"There ain't no such thing as a free lunch" is Heinlein's restatement of the First Law of Thermodynamics.	<input checked="" type="radio"/> T	F

(c; 8 pts) Why is burning oil better than burning coal as far as global warming is concerned? (I am looking for a fundamental answer; don't worry about contaminants etc.) Why is coal a better fuel for a steam engine locomotive than wood?

- Oil provides ⁺³more useful energy per carbon because the carbon is more reduced (can donate more electrons to O₂). ⁺²the CO₂ is recycled the earth ⁺²no net addition of greenhouse gas to

- Coal is essentially dehydrated wood - more dense in terms of energy per gram.

⁺¹Common mistakes
 ① Coal is more reduced carbon than wood
 ② Very few mentioned 'dense'
 ③ Coal is carbohydrate or wood is hydrate carbon

Score for the page _____

2. First and Second Order Kinetics (50 pts)

(a; 6 pts) What is the half-life of a first order reaction, in terms of the rate constant for the reaction? Why is the half-life of a first-order reaction independent of the initial concentration of the reactant? Give a reason, not a recitation of the equation.

+2
$$t_{1/2} = 0.693/k = \ln 2/k$$

+4 First order reactions require only one molecule of reactant - it doesn't "know" what all the others are doing, therefore rate of rxn is the same for all, lifetime is the same for all.

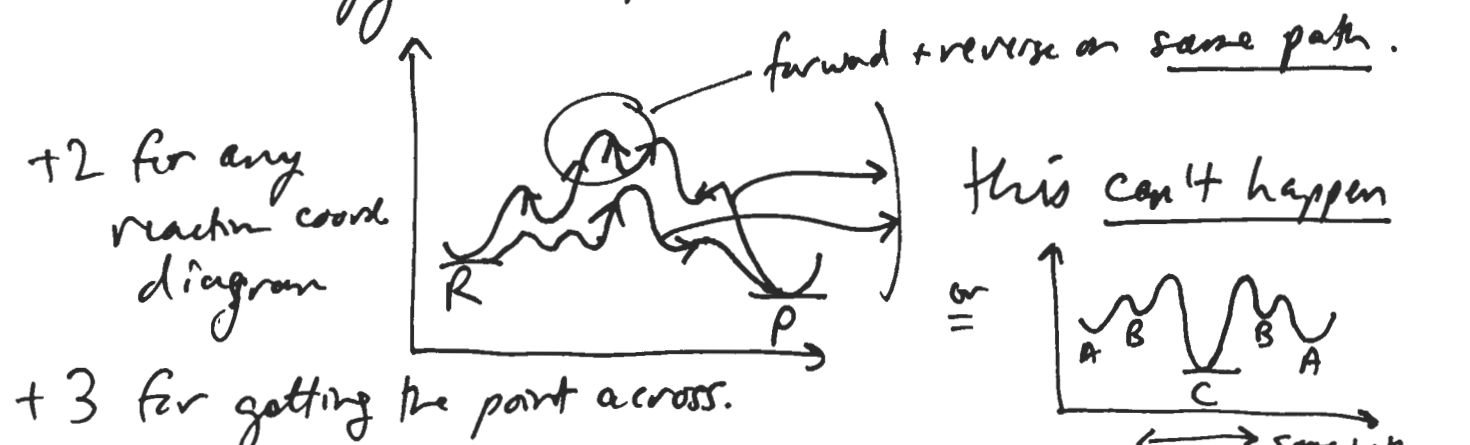
(b; 6 pts) What is the integrated rate law for a second-order reaction? Does the instantaneous rate of the reaction normalized to the amount of reactant (i.e. $-(1/2)(d[A]/dt)/[A]$), increase or decrease as the reaction progresses? (Circle one.)

+3
$$\frac{1}{[A]} - \frac{1}{[A]_0} = 2kt$$

 +2 for no "2"
$$-\frac{1}{2} \cdot \frac{d[A]}{dt} \cdot \frac{1}{[A]} = k_2 [A]$$
 decrease as rxn progresses

(c; 10 pts) What is the law of microscopic reversibility? Sketch a free energy reaction coordinate diagram to illustrate your answer.

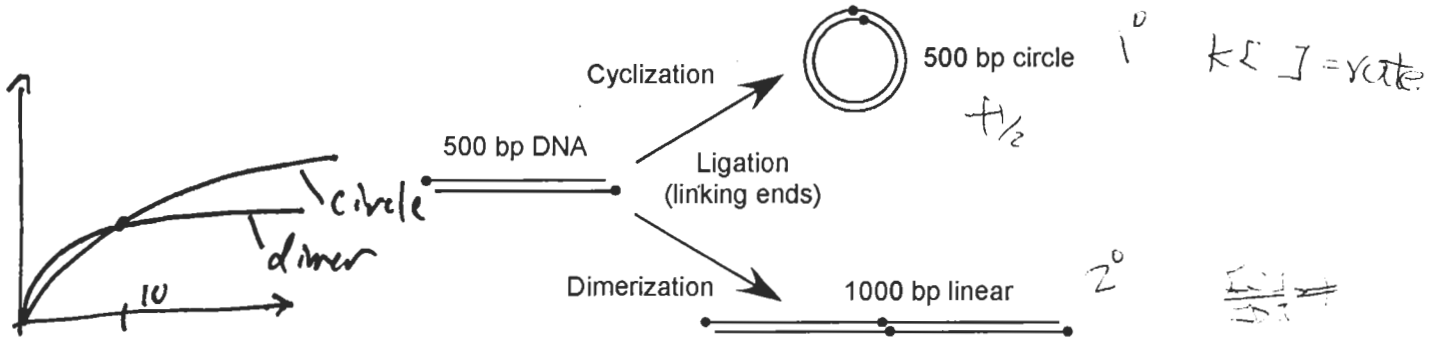
+3 - The mechanism of the backward reaction is exactly the reverse of the forward reaction - note this does not mean that the r.l.s. is the same!
 +2+3 - They exist on the same free energy landscape



Note dynamic equilibrium \neq microscopic reversibility

(d; 28 pts) Consider the pair of competing reactions sketched below: the first-order cyclization of linear DNA fragments to circular products, competing with second-order ligation of the same fragment to give dimeric linear products.

Assume that at a starting DNA concentration of 10 nM, in a 100 μl reaction mixture, after 10 minutes of reaction, you observe a 50:50 mixture of circular and dimeric DNA products as well as unreacted monomeric DNA.



For the following four different situations, state whether the ratio of circular to dimeric products is > 1 , $= 1$, or < 1 , and briefly explain your reasoning. (7 pts each)

(1) The same reaction mixture as above, but after 60 minutes of reaction, when it has gone mostly to completion.

(+3) > 1 (+2) cyclization rate is constant throughout (first order)
 = 1 (+2) dimerization slows down - after 10 min. rate \uparrow
 The reaction is completed. therefore the ratio does not change.

(2) A second reaction performed at 20 nM starting [DNA] but otherwise identical, after 10 minutes.

(+3) < 1 (+2) +3 The rate of the 2nd order reaction increases
 more than that of the first order rxn.

The first order reaction (+3) is independent on concentration.

(3) A 20 μL aliquot of the same reaction mixture, otherwise identical, after 10 minutes. (Not a trick question.)

(+3) = 1 (+4) Most of them answer correctly.
 it's identical - nothing depends on V, only [DNA]
 (should have had double degrees.)

(4) A longer piece of DNA, for which ΔS^\ddagger for cyclization is much more negative than for the shorter piece of DNA shown, but ΔH^\ddagger is unchanged, otherwise identical conditions, after 10 minutes

(+1) (ok if implicit) (+2)
 $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$ becomes more positive, so cyclization
 becomes ~~more~~ less favorable.

So ~~the~~ cyclization decreases \rightarrow see $\frac{[C]}{[D]} < 1$
 The ~~order~~ of dimer is smaller than circular.
 Based on 2 rule of thermodynamic, circular would
 be less than dimer.
 = (+3)

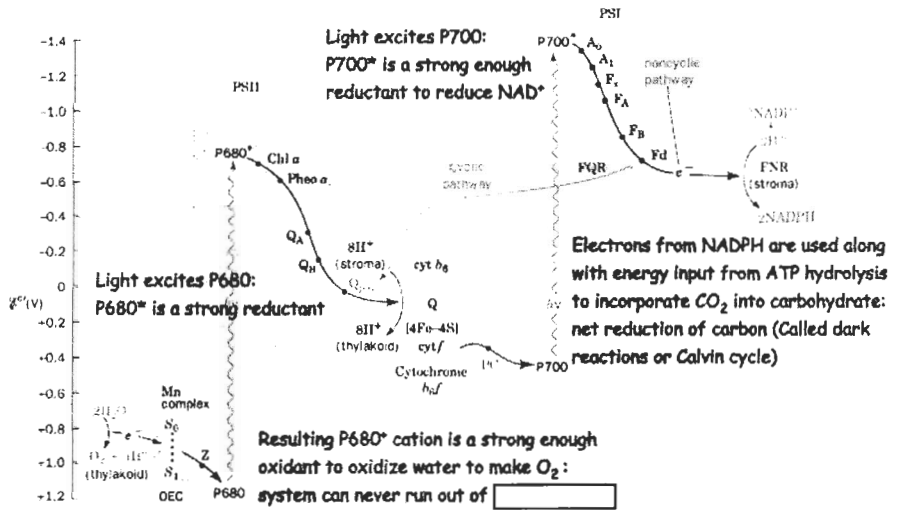
3. Redox Reactions to Live By (75 pts)

(a; 4 pts) We suggested a rationale for the sequential transfer of electrons through several intermediate electron acceptors on the way from NADH to O₂ in the electron transport system. Why not just transfer the electron directly and harvest the liberated free energy in one step?

+4 It's like catching a bowling ball - the energy can't be captured in a single elementary step or one molecule like ATP.

Common mistakes It's more efficient to transfer the energy/electrons through several intermediate acceptors

(b; 4 pts) Two photosystems in photosynthesis might seem like one too many. What evolutionary advantage accrued to plants with the development of PSII? (Hint: the word that was in the box in the picture.)



+4 plants can never run out of electrons to replenish PSI (as long as there's H₂O around)

Common mistakes O₂, H₂O, reductant.

We discussed the idea that microbes are usually on the edge of starvation. Anaerobic metabolism (other than fermentation) is based on living off the downhill flow of electrons. Microbes need both a source of electrons and a place to dump them. So do we.

(c; 3 pts) What do we call the final destination of the electrons?

+3 terminal electron acceptor or terminal oxidant

(d; 3 pts) What particularly unappealing source of electrons for humans did we discuss in regards to the Siege of Leningrad? (In class I misidentified the city as Stalingrad.)

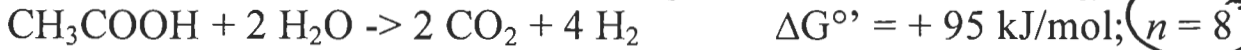
+3 wall paper paste (or rats +3)

Wrong, but written:

Fossil fuels	detritus	fire	urea
Methane (CH ₄)	poop	bird food source	sulfur
Feces	urine	the smog in the air	soil
N ₂	waste	Teletubies	alcohol
Mustard Gas	cow poop	fertilizer	Very bad, not tasty food
	excrement / food waste	smog & pollutants	E. coli

Score for the page _____

The oxidation of acetic acid shown below has a small but positive standard-state free energy change:



(e, 10 pts) Write the two half-reactions that make up the above reaction, one for the oxidation of acetic acid and one for the reduction of protons. Balance with water or protons as needed.

update +1 for each idea if answer is wrong

balance charge

balance oxygen

balance H

note it's given!

1. Some don't know electrons gain or lose in half-reactions

2. Some don't balance the equations

+5 $\text{CH}_3\text{COOH} + 2 \text{H}_2\text{O} \rightarrow 2 \text{CO}_2 + 8 \text{H}^+ + 8 \text{e}^-$

+5 $8 \text{e}^- + 8 \text{H}^+ \rightarrow 4 \text{H}_2$ [*+3 for any $\text{H}^+ \rightarrow \text{H}_2$ reduction*]

$\text{CH}_3\text{COOH} + 2 \text{H}_2\text{O} \rightarrow 2 \text{CO}_2 + 4 \text{H}_2 \checkmark$

(f; 6 pts) Calculate E° for this reaction. Why does the reaction initially seem like a poor choice on which to base a metabolism?

most of them got this right

It's not a spontaneous reaction!

some of them didn't convert kg/mol to J/mol

+2

$$E^\circ = -\frac{\Delta G^\circ}{nF} = -\frac{95000 \text{ J/mol}}{8 \cdot 96500 \text{ C/mol}} = -0.123 \text{ V}$$

+2

+2 *+1* *Some forget this and get the positive E*

(g; 12 pts) Calculate E at 100 mM CH_3COOH , 0.0004 atm CO_2 , 0.0001 atm H_2 . Thus, how is it that the bug (*Geobacter*) can actually survive by using this reaction to make energy?

Most of them got this equation right

some miss those

+4 $E = E^\circ - \frac{0.0592 \text{ V}}{n} \log \frac{P_{\text{CO}_2}^2 P_{\text{H}_2}^4}{[\text{CH}_3\text{COOH}]}$

+2 $E = -0.123 \text{ V} - \frac{0.0592 \text{ V}}{8} \log \frac{(0.0004)^2 (0.0001)^4}{0.100}$

$E = -0.123 \text{ V} - 0.0074 \text{ V} \log(16 \times 10^{-23})$

+3 $E = \textcircled{+} 0.038 \text{ V}$ $\underbrace{\hspace{10em}}_{+0.161 \text{ V}}$

- Since reactants are in excess over products, (presumably $\text{CO}_2 + \text{H}_2$ are released), the actual E is positive, so the overall reaction becomes spontaneous, albeit pretty pathetic.

If they get $+E$, then they explain it well.
 If they get $-E$, then they may not do it well.

(h; 8 pts) *Geobacter* may also be useful in bioremediation of uranium contamination in groundwater. *Geobacter* can oxidize the acetic acid and pass the electrons to soluble U^{+6} , converting it to U^{+4} , which then precipitates out of the water and can be removed as solid waste. This process is carried out by injecting acetate into the water table to support *Geobacter* growth. Why is it important to maintain anoxic conditions when this is done? How is this related to the observed stratification of nitrate-reducers and sulfate-reducers in sediments or the water column?

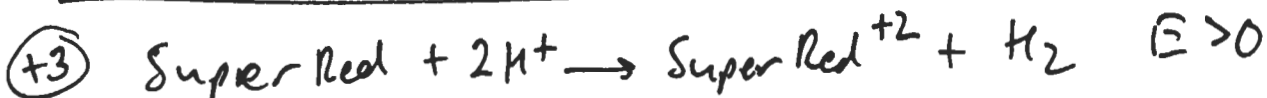
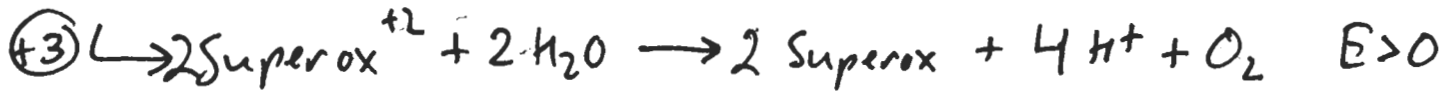
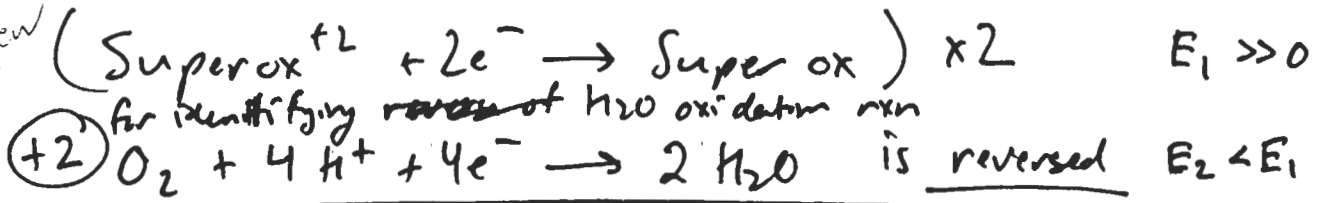
(+4) - If there is O_2 around, *Geobacter* or some other bug will use it as the terminal electron acceptor and ignore the U^{+6} .
 common error: *Geobacter* dies when exposed to O_2

Most knew these → (+2) - Stratification occurs because the bug that can use the best oxidant can make the best use of available food (reductant) - sulfate reducers (+2) can thrive only when nitrate has all been exhausted.

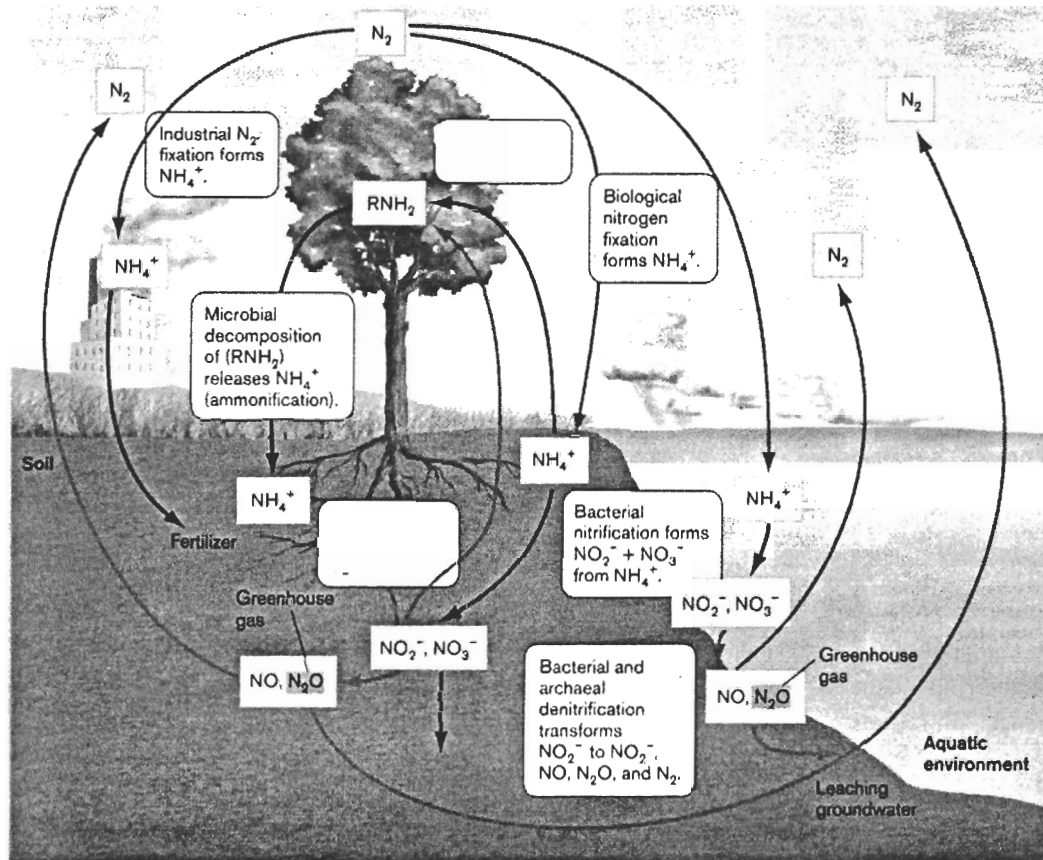
(i; 10 pts) We discussed the idea that stable biochemical oxidants cannot be stronger than oxygen, because if they were they would eventually rip electrons out of water. Write down the redox reaction that expresses this idea, given " $SuperOx^{+2} + 2e^- \rightarrow SuperOx$," with large and positive E, as one half-reaction. A different redox reaction limits the strength of stable aqueous reducing agents. Write down the redox reaction that would be carried out by the two-electron reductant "*SuperRed*."

less than

10% knew any of this



Biogeochemistry: The picture shows the nitrogen cycle in the atmosphere (from Slonczewski and Foster):



(j; 4 pts) Identify a dissimilatory reduction of a nitrogen compound.

Reduction of NO_3^- , NO_2^- , or N_2O to N_2 about 2/3 got this

(k; 4 pts) Identify an assimilatory reduction of a nitrogen compound.

Nitrogen fixation: NO_3^- or $N_2 \rightarrow NH_3$ (or NH_4^+)

(l; 7 pts) Where is the Haber process in the picture? Growing corn requires nitrogen fertilizer; why is the use of ethanol from corn not really helpful from the standpoint of ameliorating global climate change?

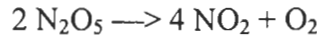
(+3) In the factory on the left ... belching smoke. Less than half knew this... if they got this, they get the rest

(+2) Growing corn for ETOH requires burning fossil fuel b/c the Haber process requires a lot of energy to run.

(+2) Therefore the net reduction of CO_2 flux to the atmosphere is small or unfavorable.

4. Steady State approximation (35 pts)

The thermal decomposition of gaseous N_2O_5 to form NO_2 and O_2 is a classic reaction which we oversimplify here. The equation is



The observed rate law is

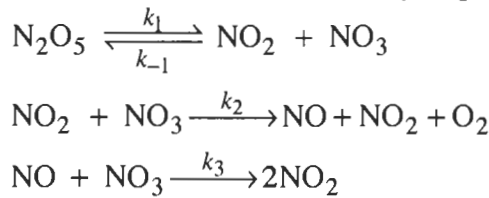
$$\text{Rate} \equiv d[O_2]/dt = k[N_2O_5]$$

where k is an empirically observed first-order rate constant.

(a; 5 pts) This rate law immediately tells us that the reaction is not a single elementary step as was initially believed 90 years ago. Why? Common mistake - saying it involves $[NO_2]$ or $[O_2]$. No mention of $[NO_2]$ or $[O_2]$. No mention of $[NO_2]$ or $[O_2]$. No mention of $[NO_2]$ or $[O_2]$.

If it were elementary it would be 2nd-order - the observed rate law is inconsistent w/ the proposed mechanism, so the mechanism must be wrong. (+3)

Ogg's proposed mechanism (1947) in terms of a set of elementary steps is as follows:



We can apply the SSA to both of the reactive intermediates NO_3 and NO . First we work with NO_3 . The rate of production of NO_3 is

$$\frac{d[NO_3]}{dt} = k_1[N_2O_5]$$

(b; 10 pts) What is the rate of decay of NO_3 ? You do not need to solve for $[NO]$. (+2)

too many!

(!) $[\text{Decay of } NO_3 = k_2 [NO_2] [NO_3] + k_3 [NO] [NO_3] + k_{-1} [NO_2] [NO_3]]$ (+2)

$= [NO_3] ([NO_2] (k_{-1} + k_2) + [NO] k_3)$ (+2)

all ~~both~~ signs \ominus is okay

+2 for no other rxns

+2 for all signs the same

- most did well. Some set it to steady state, (including $k_1[N_2O_5]$)

+ also some were confused about which direction it was \leftarrow want eg $k_{-1}[NO_2]$

Applying the SSA to NO gives a steady state concentration of $[NO] = (k_2/k_3)[NO_2]$. Setting the rates of production and decay of NO_3 equal and substituting this value of $[NO]$, we obtain

$$[NO_3] = \frac{k_1[N_2O_5]}{k_{-1}[NO_2] + 2k_2[NO_2]}$$

and again...

$$[\text{NO}_3] = \frac{k_1[\text{N}_2\text{O}_5]}{k_{-1}[\text{NO}_2] + 2k_2[\text{NO}_2]}$$

(c; 15 pts) Show that this expression for $[\text{NO}_3]$ along with the reaction mechanism above gives us the observed overall rate law for the production of O_2 , and write an expression for the overall empirical rate constant k in terms of the rate constants for elementary steps.

overall rate = $\frac{d[\text{O}_2]}{dt} = k_2 [\text{NO}_2] [\text{NO}_3]$ (+3)

- either they get it, or the worked out rate equation late bud

$\frac{d[\text{O}_2]}{dt} = k_2 \cdot \frac{k_1 [\text{N}_2\text{O}_5]}{k_{-1} [\text{NO}_2] + 2k_2 [\text{NO}_2]} \cdot [\text{NO}_2]$ (+2)

+4 for identifying the connection

+4 for rate law

$\frac{d[\text{O}_2]}{dt} = \frac{k_1 k_2}{k_{-1} + 2k_2} [\text{N}_2\text{O}_5]$

= empirical first-order rate constant

(d; 5 pts) Why do we say that a proposed mechanism can be disproved but never proven?

- A proposed mechanism must be consistent with

+3 all experimental kinetic data ... including results that have not yet been obtained!

Most get some credit, though many neglected to mention mechanisms were disproven experimentally

- So one inconsistent result ~~can~~ can disprove

+2 a mechanism, but one can never know whether the next piece of data will destroy it.

(+5 for getting the general idea across that 1 experiment can disprove)

Page	Score
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