1. Multiple Choice (30 pts)

(i; 5 pts) The half life $t_{1/2}$ of a second order reaction A + A -> B

(a) = $\ln 2/k$.
(b) = $\{k([A]_0)^2\}^{-1}$. = $\frac{1}{k[A_0]^2}$
(c) = $[A]_0/k$.
(d) is shorter than the half life of a first-order reaction.
(e) none of the above

(ii; 5 pts) A first-order rate constant

(a) has units of time^{-1}.
(b) is inversely related to half-life.
(c) depends on reactant concentration.
(d) has units of $M^{-1}s^{-1}$.
(e) (a) and (b).

(iii, 5 pts) The function of Photosystem I in plants is to

(a) use light energy to oxidize carbon dioxide.
(b) use light energy to reduce $NADP^+$ to NADPH.
(c) oxidize water to provide light.
(d) re-reduce Photosystem II.
(e) oxidize water and transfer electrons to H^+.

(iv, 5 pts) Syntrophy is defined as

(a) consumption of the product of the reduction of one microbe's terminal electron acceptor by another microbe for their mutual benefit.
(b) any interaction among microorganisms that live in the same environment.
(c) microorganisms that make synthetic chemicals.
(d) [deleted bad pun on Sin Trophy]
(e) pathogens that co-infect target hosts.

(v, 5 pts) Stratification of inorganic NO_3^-, SO_4^{2-}, and other species in the water column or in sediments originates because

(a) anaerobes are heavier than aerobes so they sink.
(b) sulfate and nitrate react with metals in the soil so they are present only near the top.
(c) weathering and currents leach out different ions at different depths.
(d) at any depth, the organism that is capable of using the best available terminal electron acceptor dominates, so the other terminal electron acceptors are left alone.
(e) None of the above.

(vi, 5 pts) The fundamental condition for applicability of the Steady State Approximation is

(a) The product concentration must be zero.
(b) The concentration of the intermediate cannot change at all during the reaction.
(c) There must be a rapid pathway for decay of the steady state intermediate.
(d) The activation energy for the reaction must be smaller than the $\Delta G°$.
(e) The reaction must be second-order.

Score for the page 130

2. Short Answer (36 pts)

(a; 6 pts) Give two statements that must be true for or a substance to be called a catalyst for a reaction.

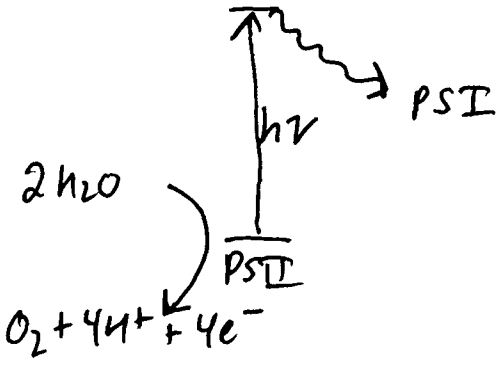
(+3 for each for max +6)
- The substance must cause the reaction to go faster than it did before.
- The catalyst is neither created nor destroyed
- The position of equilibrium does not change

(b; 6 pts) Why does www.350.org call "350" the most important number in the world?

(+3) - 350 parts per million of CO_2 in the atmosphere

(+3 for idea of climate change) - is the highest concentration that will allow a world similar to that on which civilization developed to be maintained

(c; 6 pts) The main function of Photosystem II in plants is to provide electrons to re-reduce Photosystem I. What is the oxidation half-reaction used, and why was that choice advantageous during evolution?



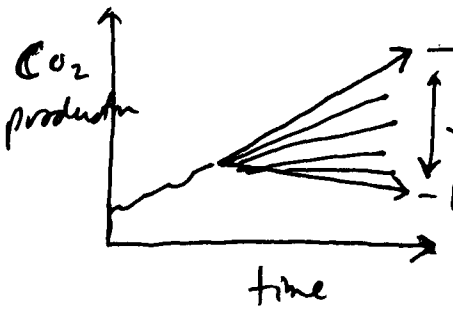
(+3) $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

(+3) Water is an inexhaustible source of electrons. That's why water oxidation catalysts are essential for artificial photosynthesis.

(+1) for making O_2

Score for the page 18/18

(d; 9 pts) What is a "sustainability wedge"? Algal biofuel may provide one: what is an advantage of biofuel in general over wind/solar/nuclear energy?



- line if we do nothing different
- gap is divided into 15 wedges (# doesn't matter)
- line that preserves the climate

sporty with effect of climate

(+3) - A wedge represents an amount of CO_2 that will not be put into the atmosphere.

(+3) - We need enough wedge to reduce CO_2 emission to a level that preserves the climate [connection to climate] +2 biofuels, nuclear +1 for sustainability

- Biofuel can be used for transportation (+3) with existing vehicles/infrastructure no toxic waste like nuclear waste

(e; 9 pts) We considered the temperature dependence of rate constants in light of both the Maxwell-Boltzmann distribution and also Eyring theory. Choose one and briefly explain, qualitatively, how it rationalizes the observed form of the Arrhenius equation.

$k = Ae^{-E_a/RT}$ Arrhenius

- Maxwell Boltzmann – At high speeds, probability of a given speed is $\propto e^{-\frac{1}{2}mv^2/kT}$ (+3)
- Suppose that a reaction requires some critical velocity/energy (+4) to occur – the area under the curve to the right is $\propto e^{-\frac{1}{2}mv^2/kT}$ (+2)
- Pre-exponential A is a steric factor or just a proportionality constant

- Eyring –

(+4) Consider the TS as just another state of the system, for which we can define a K_{eq} for the TS.

(+3) $K_{eq} \propto e^{-\Delta G^\ddagger/RT}$ from the Boltzmann distribution, $G = G^\circ + RT\ln P$

(+2) Pre-exponential comes from transit time plus a van't Hoff analysis $\rightarrow e^{\Delta S^\ddagger/R}$

Score for the page_____

3. Kinetics and the Steady State Approximation (50 pts)

Consider the reaction NO_2 (g) + CO (g) -> NO (g) + CO_2 (g). It is important in understanding the atmospheric chemistry of air pollution, and it has been proposed as one step in a potential series of reactions that could be useful in catalytic converters. (eventually taking NO to N_2)

(a; 4 pts) This is a redox reaction: what is the oxidant and what is the reductant?

(+2 each) Oxidant: $NO_2 \rightarrow NO$ (+4 → +2) Reductant: $CO \rightarrow CO_2$ (+2 → +4) ox #'s

(b; 4 pts) Assuming the reaction is elementary, write the differential rate law for the production of CO_2.

$$\frac{d[CO_2]}{dt} = k[NO_2][CO]$$

(+2) for any rate law

(+2) for correct factors

(c; 8 pts) In the 1910s-1970s, the observed activation energy for this reaction was determined to be about 130 kJ/mol. If the second-order rate constant k is 64 $M^{-1}s^{-1}$ at 1000 K, what is k at 500K?

$k = Ae^{-E_a/RT}$ $R = 8.314$ J/mole K

(+3 for sub) $64 = Ae^{-(130000/8314)} = Ae^{-15.63} = A \cdot 1.619 \times 10^{-7}$

$A = \frac{64\ M^{-1}s^{-1}}{1.619 \times 10^{-7}} = 3.953 \times 10^{8}$

or just notice that this # doubles

At 500 K,

(+3 for any effort to use new T) $k = 3.953 \times 10^{8} \cdot e^{-(130000/4157)} = 3.953 \times 10^{8} e^{-31.27} = 1.036 \times 10^{-5}$ $M^{-1}s^{-1}$

$\boxed{k = 1.0 \times 10^{-5}\ M^{-1}s^{-1}}$ (+2) for answer (+1 w/out units) sig figs don't matter

...or... $k_2 = k_1 e^{-\left(\frac{E_a}{R} \cdot \left(\frac{1}{500} - \frac{1}{1000}\right)\right)}$

$= 64 e^{-15.63} = 1.0 \times 10^{-5}$ ✓

Score for the page ____/16

(d; 9 pts) At 0.010 M NO_2 and 0.050 M CO, what concentration of CO_2 is produced in 10 minutes for a rate constant $k = 2.4 \times 10^{-5}\ M^{-1}s^{-1}$? You can assume that the rate remains constant for this time; based on your answer, why is this assumption justified? [By measuring an initial rate, we avoid the need to use an integrated rate law that we didn't learn.]

1) used wrong equation

$$\frac{d[CO_2]}{dt} = 2.4\times10^{-5}\ M^{-1}s^{-1}\,[NO_2][CO] = (2.4\times10^{-5} \times 0.01 \times 0.05)\ Ms^{-1}$$

$$= 1.2\times10^{-8}\ M s^{-1}$$ (+3) for calculating a rate

$$1.2\times10^{-8}\ Ms^{-1} \cdot 600\ s = 7.2\times10^{-6}\ M\ [CO_2]$$ (+3) for a [ ]

2)

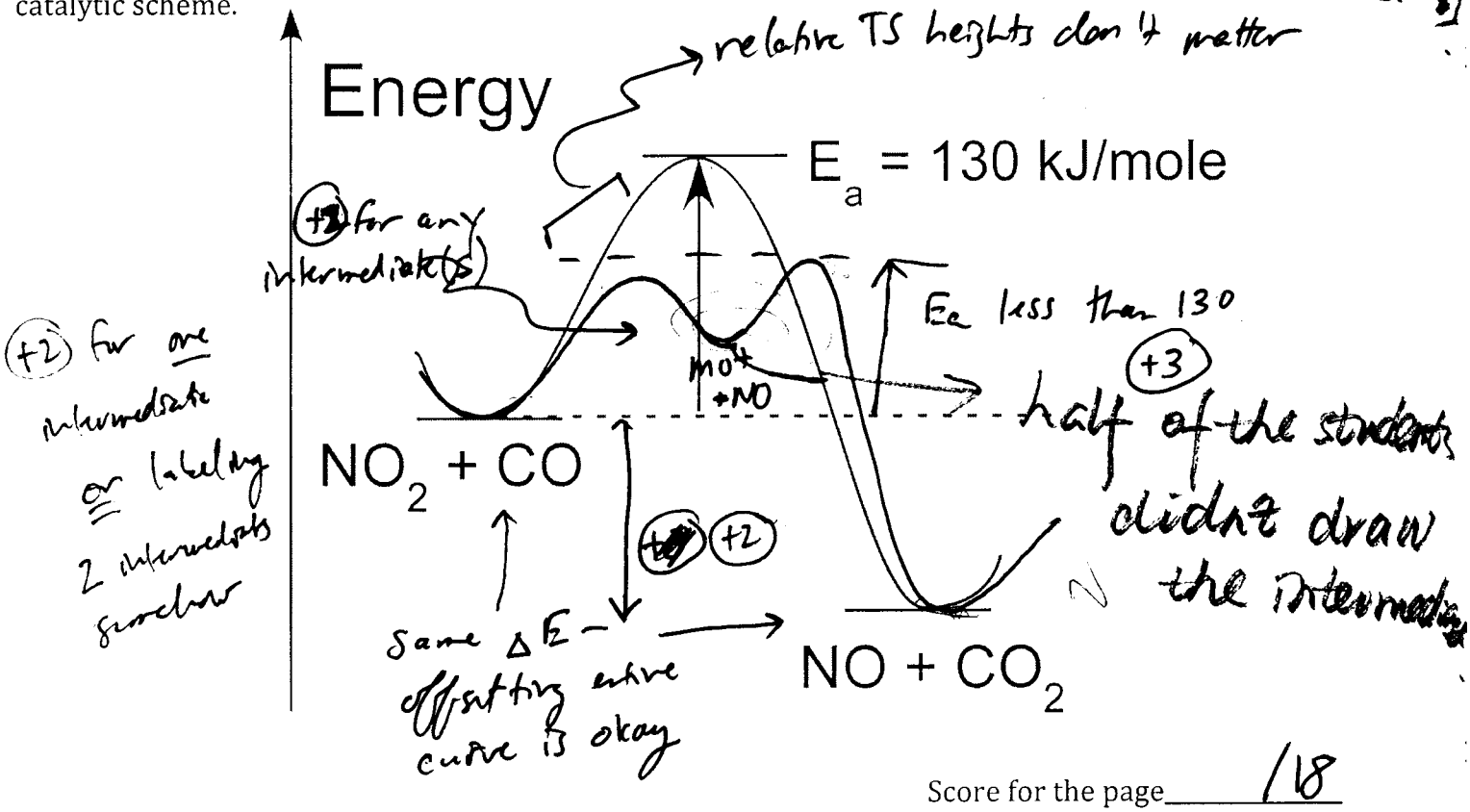
(+3) The amount of CO_2 produced is trivial, so the concentrations of CO and NO_2 have not changed and the rate is ∴ constant

can't get this. They usually say, "it's not dependent on the [CO] or [NO_2]"

(e; 9 pts) For use in practical systems at reasonable temperatures, catalysis of the above reaction by gas phase metal cations "M^+" has been proposed, according to this scheme:

$$M^+ + NO_2 \rightarrow MO^+ + NO$$
$$MO^+ + CO \rightarrow M^+ + CO_2$$

On the reaction coordinate diagram below, add in a reasonable curve that could represent the above catalytic scheme.



Score for the page 18

The perils of textbooks...the reaction $NO_2 + CO \rightarrow NO + CO_2$ can be found in several textbooks (and therefore on hundreds of web pages) as an example of more complicated kinetics, apparently entirely without regard to the fact that as far as I have been able to discover there is no experimental evidence for the more complicated kinetics. (Please correct me if this is wrong, and a shout out to Oxtoby for using original sources.) Be all that as it may, we will still use the reaction as an example for the application of the Steady State Approximation. Consider the proposed mechanism:

$$NO_2 + NO_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NO + NO_3 \text{ (reversible)}$$

$$NO_3 + CO \xrightarrow{k_2} NO_2 + CO_2 \text{ (irreversible)}$$

(f; 4 pts) Write down the differential rate law for $d[CO_2]/dt$ by inspection of just the second elementary reaction. It involves $[NO_3]$ among other things.

$$\frac{d[CO_2]}{dt} = k_2[NO_3][CO]$$ (+2) for any rate law (+2) for correct factors

(g; 9 pts) Apply the steady state approximation to the reactive intermediate NO_3 to obtain its concentration in terms of $[NO_2]$, $[CO]$, and $[NO]$, and substitute into your answer from (f) to obtain the overall rate law for CO_2 production.

$$\frac{d[NO_3]}{dt} = \underbrace{k_1[NO_2]^2 - k_{-1}[NO][NO_3] - k_2[NO_3][CO]}_{(+3)} = 0 \quad \text{SSA} \quad (+2)$$

$$[NO_3](k_{-1}[NO] + k_2[CO]) = k_1[NO_2]^2$$

$$[NO_3] = \frac{k_1[NO_2]^2}{k_{-1}[NO] + k_2[CO]}$$ (+2)

$$\frac{d[CO_2]}{dt} = \frac{k_1 k_2 [NO_2]^2[CO]}{k_{-1}[NO] + k_2[CO]}$$ (+2)

→ $k_1[NO_2]^2$ at ↑↑ [CO] (first step RDS) ✓

→ rapid pre-eq at very low [CO] ✓

(h; 3 pts) The textbook problems state that the observed rate is $d[CO_2]/dt = k[NO_2]^2$. How do we know that this can't possibly be true under all conditions? (Hint: what is the order of reaction with respect to CO?)

The order of reaction w.r.t. CO is 0. (+1)

There's no such thing as a true zero-order reaction at low enough [CO] it must appear in the rate expression. (+2)

(rate = $k[NO_2]^2$ assumes $k_2[CO] \gg k_{-1}[NO]$)

Score for the page ____/16

4. Ecological Electrochemistry (30 pts) no need to calculate in (a)

Hydrogenosomes are organelles related to mitochondria. They transfer electrons from NADH to protons to produce hydrogen. Tiny but multicellular crustaceans that use hydrogenosomes instead of mitochondria have recently been discovered in the Mediterranean.

(a; 15 pts) Write the two half-reactions and the balanced chemical reaction for oxidation of NADH by protons and determine "*n*." E°′ for this reaction is –0.106 V. One of the half-reactions is the SHE, but the standard reduction potential we use for it is ~~–0.424~~ –0.421 V instead of 0.000 V – why?

(+3) NADH oxidation: $NADH \rightarrow NAD^+ + H^+ + 2e^-$ | $E_0' = +0.315$

(+3) proton reduction (SHE): $2H^+ + 2e^- \rightarrow H_2$ | $E_0' = -0.421$

(+3) overall reaction: $NADH + H^+ \rightarrow NAD^+ + H_2$ | $E_0' = -0.106\ V$ calc not needed

(+2) $n = 2$

(+2) The SHE is 0.000 V at the chemical standard state $[H^+] = 1\ M$ or $pH = 0$

(+2) At the biochemical standard state (the ′), $[H^+] = 10^{-7}$ and the reduction is much less favorable.

(b; 15 pts) Assuming [NADH] = 2 mM, [NAD⁺] = 1 mM, and pH = 6, use the Nernst equation to calculate the maximum possible partial pressure of H_2 [$P(H_2)$] that a hydrogenosome can produce, i.e. the $P(H_2)$ at which the reaction grinds to a halt. In light of your answer, why might it be advantageous to make the final destination of one's electrons a volatile gas?

(+1) Nernst $E = E^{o\prime} - \frac{0.0592}{n} \log Q$ referenced to biochemical standard state

(+3) substitution $E = -0.106 - \frac{0.0592}{2} \log \frac{[NAD^+](P_{H_2})}{[NADH][[H^+]/10^{-7}]}$ → +1 if this is wrong but then carry through

$E = -0.106 - \frac{0.0592}{2} \log \frac{P_{H_2}}{2 \times 10^{-6}/10^{-7}} = -0.106 - 0.0296 \log \frac{P_{H_2}}{20}$

(low P_{H_2} → ⊕V ✓)

(+3) The reaction stops at $E = 0$

(+3) math – OK if ↑ is wrong $0.106 = -0.0296 \log (P_{H_2}/20)$ } +3 for any expression containing only P_{H_2} and #'s

$\log (P_{H_2}/20) = -\frac{0.106}{0.0296} = -3.58$

(+3) H_2 being a volatile gas it can escape to drive the reaction forward.

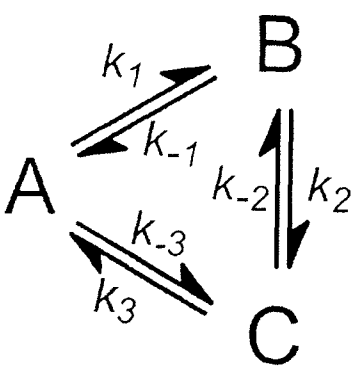
$P_{H_2} = 20 \times 10^{-3.58} = 0.00525$

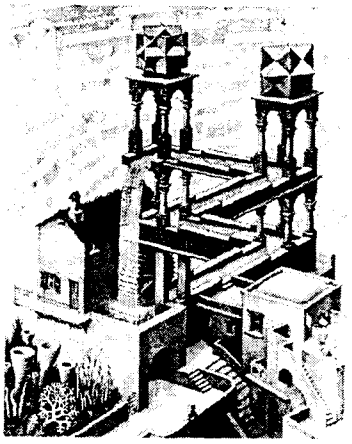
(+2) answer $\boxed{P_{H_2} = 5 \times 10^{-3}\ atm}$

$P_{H_2} = 2.62 \times 10^{-4} \cdot 2 \times 10^{-6} = 5.25 \times 10^{-10}$ if chemical ss is used

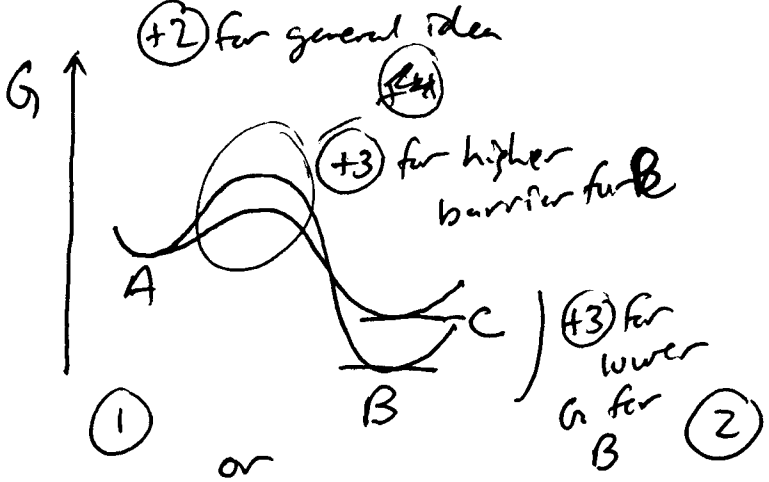
Score for the page ____/30

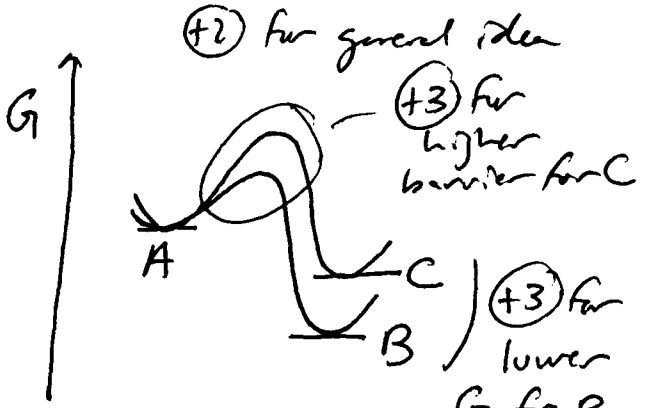
5. Chemistry, Art, and Imagination (34 pts)
Consider the elementary reactions among A, B, and C sketched at the right.

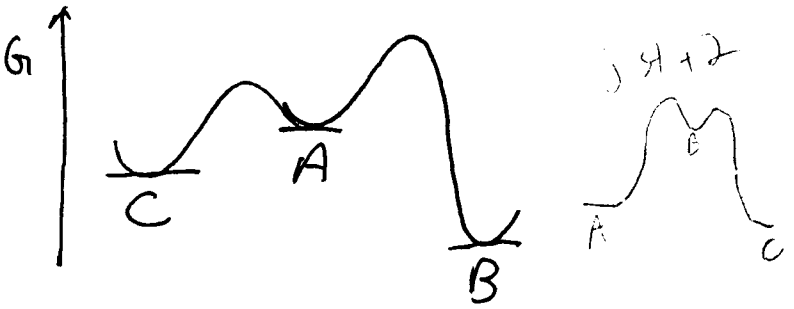


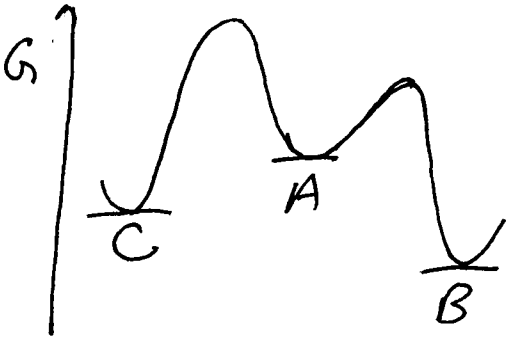


(a; 16 pts) Sketch <u>two</u> free energy reaction coordinate diagrams below that <u>each</u> illustrate the <u>two</u> reactions of reactant A. On the first diagram show <u>B as the thermodynamic product and C as the kinetic product</u>. On the second diagram show <u>B as both the kinetic and the thermodynamic product</u> (they are often the same!). You do not need to show the equilibration of B and C with each other.









(b; 4 pts) Experimentally, how does one attempt to obtain the kinetic product of a reaction as opposed to the thermodynamic product?

(+2) Do the reaction at <u>low T</u> or with hindered base so that ~~only~~ it can only go over the lower barrier, and so that there is not enough energy available

(+2) to <u>reverse</u> the formation of kinetic product

preventing it from reversing
Keeping it from reversing

Score for the page_____ /20

(c; 4 pts) If we know the equilibrium constants $K_1 > 1$ and $K_2 > 1$ for the ABC cycle shown, what is the value and magnitude (circle one: >1 or <1) of K_3?

+2

$A \rightleftharpoons B \quad K_1$

$B \rightleftharpoons C \quad K_2$

$A \rightleftharpoons C \quad 1/K_3$

b/c it's drawn as a cycle

So $\boxed{K_3 = \frac{1}{K_1 K_2} < 1}$ +2

note during exam that $K_3 = k_3/k_{-3}$ so K_3 is Keq for $C \rightleftharpoons A$

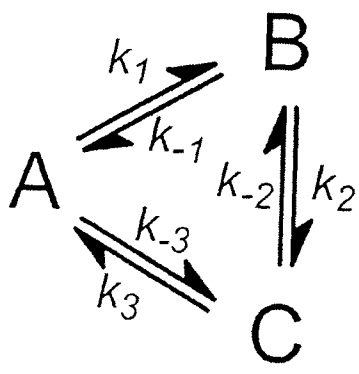
(d; 4 pts) If we know k_1, k_2, and k_3 but not the K_{eq}'s, what do we know about k_{-1}, k_{-2}, and k_{-3}?

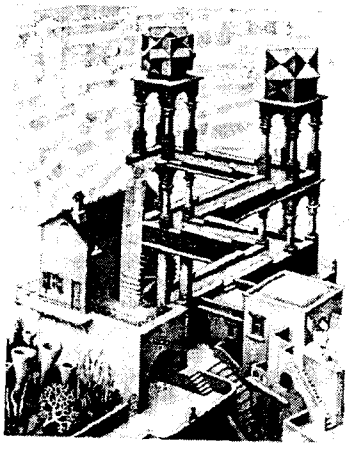
$k_1 k_2 k_3 = k_{-1} k_{-2} k_{-3}$ because $K_1 K_2 K_3 = 1$

+4

(e; 6 pts) If K_3 also had a value >1 (hopefully an answer different than the one you just derived), what law of nature would be violated? (Hint: consider the analogous M.C. Escher waterfall print shown.) What sort of forbidden machine could we make if the corresponding reaction cycle or waterfall could exist?

- The principle of microscopic reversibility (or detailed balance), b/c we would have $A \rightleftharpoons A$ with $K_{eq} \neq 1$, cyclic rxn +3





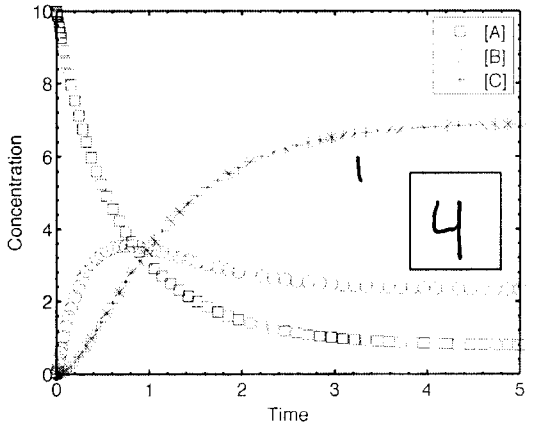
- We could make a perpetual motion machine +3 - the water always runs downhill

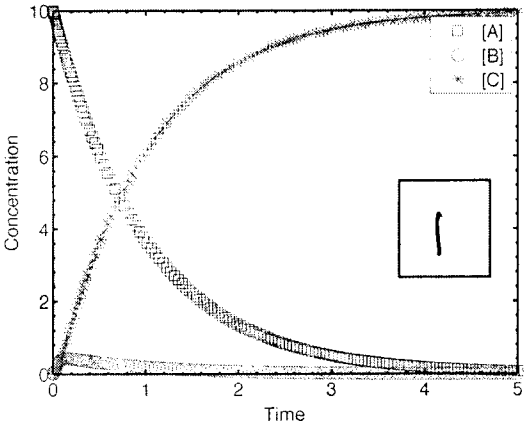
Score for the page 14

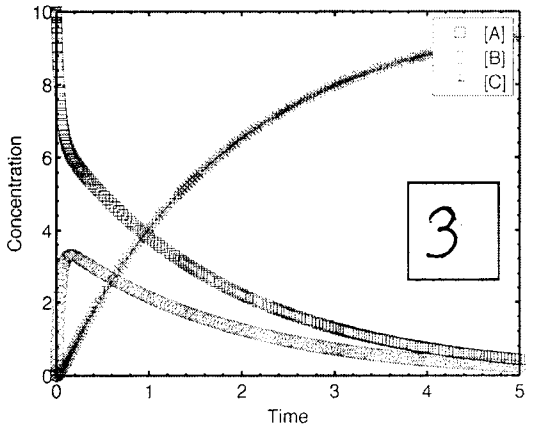
6. Kinetic patterns (20 pts)

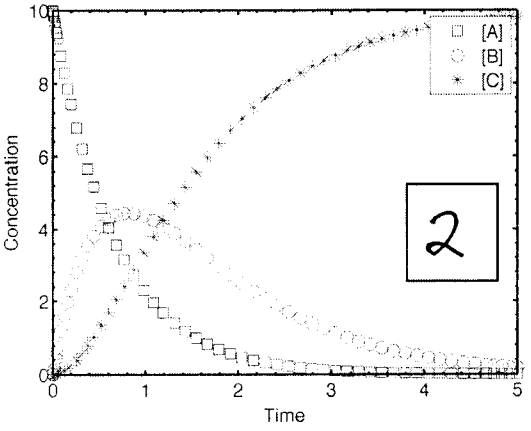
The progress curves below represent three different A ⇌ B → C reactions and one A ⇌ B ⇌ C reaction. Identify with a (①) in the box on the appropriate graph the one that shows a rate-determining first step, (②) the one with two steps of comparable speed, (③) a rapid pre-equilibrium, and (④) the one with the A ⇌ B ⇌ C reaction. Give the number of one A ⇌ B → C graph which is clearly not well-described by the steady-state approximation 2 +4

+4 each









Page	Score
2	/30
3	/18
4	/18
5	/16
6	/18
7	/16
8	/30
9	/20
10	/14
11	/20
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