Chemistry 271, Section 21xx **Your Name:**__________________________________

University of Maryland, College Park **Your SID #:**__________________________________

General Chemistry and Energetics **Prof. Jason Kahn**

Final Exam (200 points total) **May 14, 2007**

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.

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

Useful equations and schemes are given on a tear-off sheet at the end.

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."

1. Thermodynamics (50 pts)

(a; 12 pts) In the table below, fill in the signs of ΔG° and whether the reaction is spontaneous at all T, spontaneous at no T, spontaneous at low T, or spontaneous at high T. (Don't be insulted, some of the questions below are harder.)

Sign of ΔH°	**Sign of ΔS°**	**Sign of ΔG°**	**Spontaneity: circle none, one, or both**
+	+	______at low T ______at high T	low T high T
+	–	______at low T ______at high T	low T high T
–	+	______at low T ______at high T	low T high T
–	–	______at low T ______at high T	low T high T

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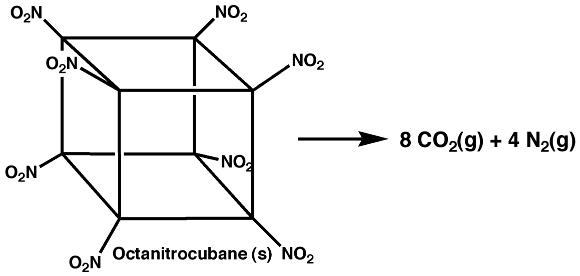
(b; 4 pts) Give an example of an exothermic ordering reaction.

(c; 4 pts) Give an example of an endothermic disordering reaction.

(d; 8 pts) What are the signs of ΔS° and ΔH° for the reaction at the right, and why?



(e; 2 pts) What does part (d) tell us about the kinetics of the octanitrocubane decomposition reaction? (A one-word answer will do.)

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Consider the reaction A <-> B -> C, where (1) the overall reaction A -> C is strongly downhill, (2) the reaction is a rapid pre-equilibrium followed by a rate-limiting step, (3) the equilibrium A <-> B is exothermic, and (d) the activation free energy for the B -> C step is temperature-independent.

(f; 8 pts) In the space below, draw a free energy reaction coordinate diagram for the reaction, at a temperature at which $K_{eq} = 1$ for A <-> B.

(g; 6 pts) On the same diagram, draw the curve observed at a higher temperature; be sure to label your curves. Assume that the free energy of the reactant A is constant (in practice, it doesn't matter -- we adopt the free energy of A as the reference state).

(h; 6 pts) With reference to your diagram, explain why we might observe an apparent negative activation free energy for the overall reaction A -> C using the standard Eyring equation to measure $\Delta G‡$.

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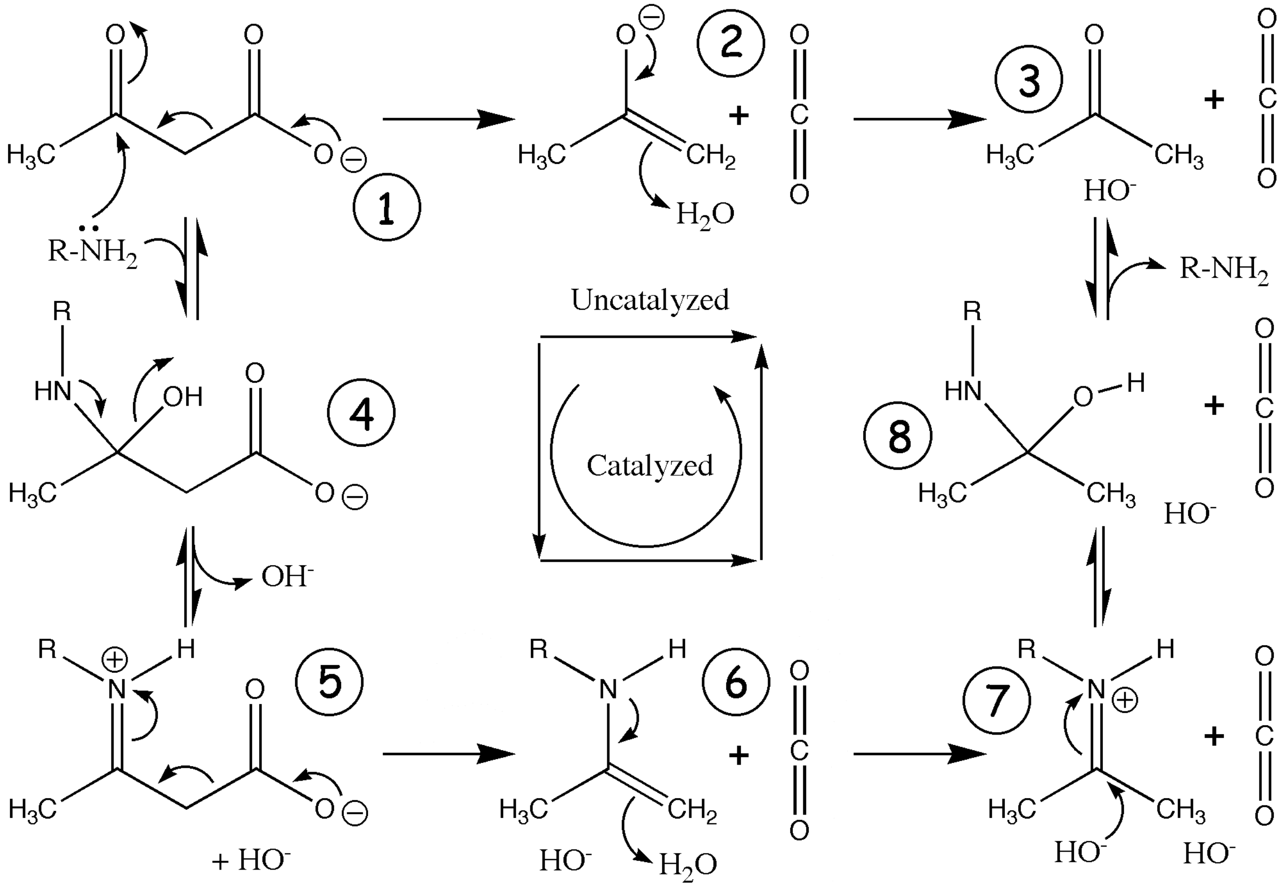
2. Acetoacetate (95 pts)

This is an extended question covering many aspects of the chemistry and biochemistry of acetoacetate. You can answer many of these questions even if you have missed those that came before. This is my idea of an integrated question, one that demonstrates that a competent chemist picks up whatever theoretical or experimental tool is appropriate to the problem at hand.

Acetoacetate is an intermediate in amino acid catabolism, and it is produced from fat in the bodies of people who are starved for glucose, or whose bodies think they are starved (diabetics). Its decarboxylation is responsible for the smell of acetone on the breath of patients with uncontrolled diabetes. Acetoacetate is oxidized to provide energy in the brains of starving people.

We are concerned first with the mechanism of acetoacetate decarboxylation, both for the uncatalyzed reaction shown along the top of the scheme below and also the reaction catalyzed by primary amines along the bottom three sides of the square. The pH is roughly 7. For your reference, the same scheme is reprinted on the last page of the exam.

$$\text{Acetoacetate}^- + H_2O \longrightarrow \text{Acetone} + CO_2 + HO^-$$



(a; 6 pts) Is there net oxidation or reduction of carbon atoms in this reaction? What is the formal oxidation state of each of the four carbons in acetone and CO_2?

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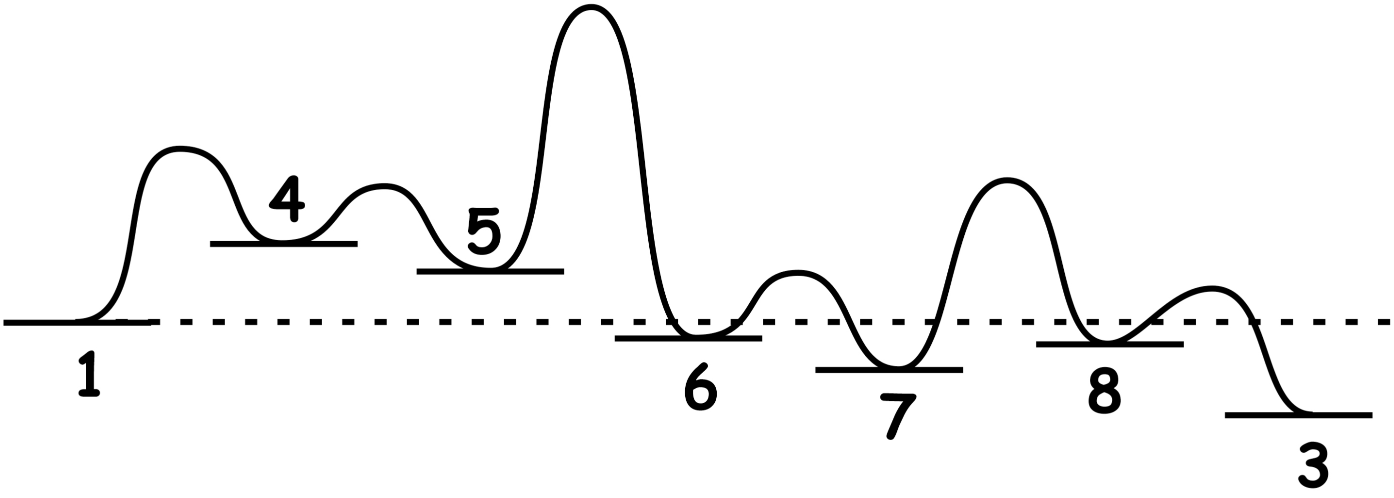
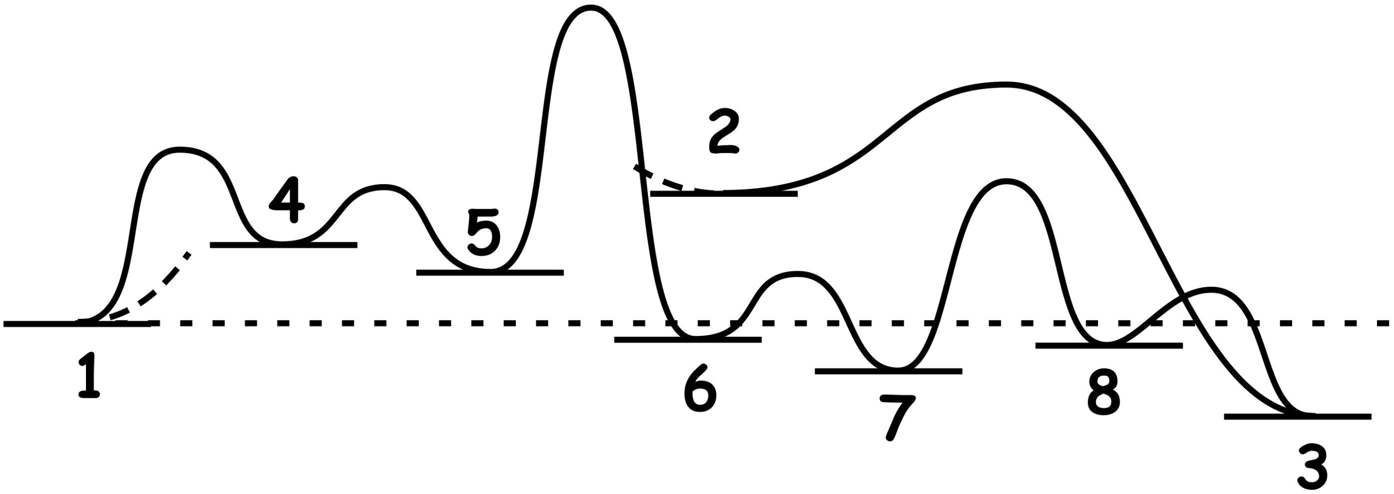
(b; 12 pts) On the free energy reaction coordinate diagram below for the catalyzed reaction, identify the rate-limiting step, and sketch in a graphical representation of ΔG‡ for the forward reaction, ΔG‡ for the reverse reaction and the thermodynamic ΔG for the reaction.



(c; 9 pts) The rate-limiting step of the uncatalyzed reaction is the same chemical transformation as for the catalyzed reaction, at least around pH 7. Given this fact, on the diagram below sketch in the remainder of the free energy reaction coordinate diagram for the uncatalyzed reaction. Briefly explain your reasoning.



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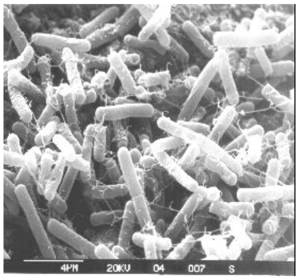
The catalyzed mechanism shown above resembles that of the enzyme acetoacetate decarboxylase, which is produced by the obligate anaerobic bacterium *Clostridium acetobutylicum* shown at the right. This bug produces acetoacetate as one product of carbohydrate metabolism, and then degrades it using acetoacetate decarboxylase in order to raise its intracellular pH. There is renewed interest in this "solventogenic" fermentation as a means of industrial production of acetone. Accompanying reactions give butanol and ethanol, so this is called ABE fermentation. Cars can run on "biobutanol."



(d; 3 pts) How does the overall reaction function to neutralize the cytoplasm of *Clostridium*?

(e; 4 pts) Would the free energy change for the reaction become more negative or more positive as pH decreases? Why?

(f; 8 pts) Fermentation was referred to in class as a means of living via rearranging the deck chairs. What did this mean in terms of redox chemistry? *Clostridium* is poisoned by oxygen, but even if it weren't it couldn't compete with aerobic bacteria living on carbohydrates. Why not?

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(g; 6 pts) Briefly, what is the thermodynamic origin of the stratification of nitrate reducers and sulfate reducers in the Black Sea?

(h; 8 pts) With reference to the global carbon cycle, explain why biofuel (like biobutanol produced as above) may be better than fossil fuel in terms of climate change. (Provided that it doesn't take too much fossil fuel energy to process the biofuel…this is one big problem with corn-based ethanol.)

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(i; 8 pts) The catalytic R-NH2 group in the acetoacetate decarboxylase enzyme is an active site lysine. The pKa of the ε-NH_3^+ group is around 6, much lower than that of the free amino acid. In general, why does burial of a lysine in the interior of a protein tend to cause a drop in its pKa? This explanation doesn't work as well in the context of a solvent-exposed active site: what other protein structural element could cause a decrease in pKa in this situation?

(j; 6 pts) The enzyme has a pH optimum around 6. According to the mechanism given, why does the rate drop off markedly as the pH decreases? (Note that this implies a change in which step is rate limiting.)

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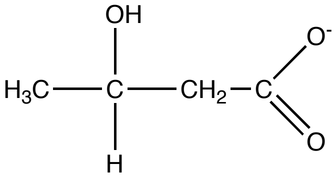

Under some conditions, acetoacetate can be reduced by NADH to give D-β-hydroxybutyrate (at right), with the half reactions and standard reduction potentials shown below.

Acetoacetate$^-$ + 2 H^+ + 2 e^- <-> D-β-hydroxybutyrate$^-$ E°′ = –0.346 V

NAD^+ + H^+ + 2 e^- <-> NADH E°′ = –0.315 V

(k; 9 pts) Calculate E°′ and ΔG°′ and show that $K_{eq} = 0.089$ at pH 7 for the reduction of acetoacetate.

(l; 16 pts) What is the equilibrium constant expression for this reduction? We will use the abbreviations BHB and Acac for brevity. If the ratio of $[NAD^+]/[NADH] = 1$, pH = 7, and [Acac] = 2 mM, what is [BHB]? If $[NAD^+]/[NADH] = 1000$ and [Acac] is 3 mM, what is [BHB]? Why have biochemists studying rat liver used an elevated ratio of [D-β-hydroxybutyrate$^-$]/[acetoacetate$^-$] as a sign of hypoxia (lack of O_2)?

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3. Redox Reactions to Live By (25 pts)

(a; 15 pts) Sketch the Z scheme for photosynthesis. You do not need to write down the names of intermediate electron acceptors. Specify what the y-axis represents, but you do not need to know the numerical values on it.

(b; 10 pts) Some photosynthetic bacteria lack Photosystem II (the left half of the Z scheme), and the electron donated by the PS I chromophore eventually returns to it. Obviously, these bugs can't use those electrons to fix CO_2 the way plants do. By analogy with oxidative phosphorylation, what benefit do they derive from this cyclic electron transfer?

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4. Kinetics (30 pts)

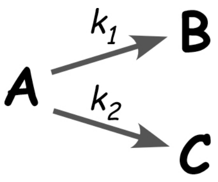
This question has not changed significantly from Exam II except I have added part (g).

Kinetic partitioning describes the distribution of products for reactions under kinetic control, such as correct and incorrect base incorporation by DNA polymerases.

For the elementary reaction A -> B, the differential rate law is $-d[A]/dt = k[A]$.

(a; 3 pts) What is the integrated rate law for a the first-order reaction A -> B assuming that we start with 100 % A at concentration $[A]_0$ (not a trick question)?

(b; 6 pts) Given that all of the starting material that starts out as A can always be found as either A or B at any time during the reaction, derive an integrated rate law expression for the amount of B as a function of time.



(c; 6 pts) Now consider the scheme at the right, where A can be converted to either B or C.

What are the differential rate laws for loss of [A], gain of [B], and gain of [C]? Remember, k_1 and k_2 just indicate which reaction is which. The subscripts do not refer to reaction order.

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(d; 3 pts) B and C are always produced at a constant ratio (in other words, for every mole of B we get x moles of C. From your answer to (c), what is $[C]/[B] = x$?

(e; 3 pts) By analogy with your answer in (a) for A -> B, what is the integrated rate law for the concentration of A as a function of time?

(f; 6 pts) The total concentration of products is given by $[B] + [C] = [A]_0 - [A]$ as in (b) above. Use your answers to (d) and (e) to derive the integrated rate law for the total amount of [B] as a function of time.

(g; 3 pts) What is $t_{1/2}$ for this reaction?

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Tear-off Sheet of Useful Equations and Schemes:

$\Delta S - q/T \geq 0$	$\mathrm{pH} = -\log([\mathrm{H}^+])$	$E = mc^2$
$S = k\ln W$	$\Delta G = \Delta H - T\Delta S$	$PV = nRT$
$K_a = [\mathrm{H}^+][\mathrm{A}^-]/[\mathrm{HA}]$	$\Delta G° = -RT\ln K_{eq}$	$e^{i\pi} + 1 = 0$
$\mathrm{W} = \mathrm{N}!/(\prod n_i!)$	$n_i/n_0 = \exp[-(E_i\text{-}E_0)/kT]$	$\mathrm{T_m} = \Delta\mathrm{H}°/[\Delta\mathrm{S}°+\mathrm{R}\ln(\mathrm{C_t}/4)]$
$°\mathrm{C} = °\mathrm{K} - 273.15$	$\mathrm{R} = 8.314$ J/mole K	$\mathrm{E} = \mathrm{E}° - 2.303(\mathrm{RT}/n\mathcal{F})\log_{10}\mathrm{Q}$

$2.303\mathrm{RT}/\mathcal{F} = 0.0592$ Volts at 25 °C $\qquad \Delta\mathrm{G} = -n\mathcal{F}\mathrm{E}$

$\mathcal{F} = 96500$ C(oulomb)/mole $\quad 1\ \mathrm{V} = 1\ \mathrm{J/C} \qquad a^2 + b^2 - 2ab\cos C = c^2$

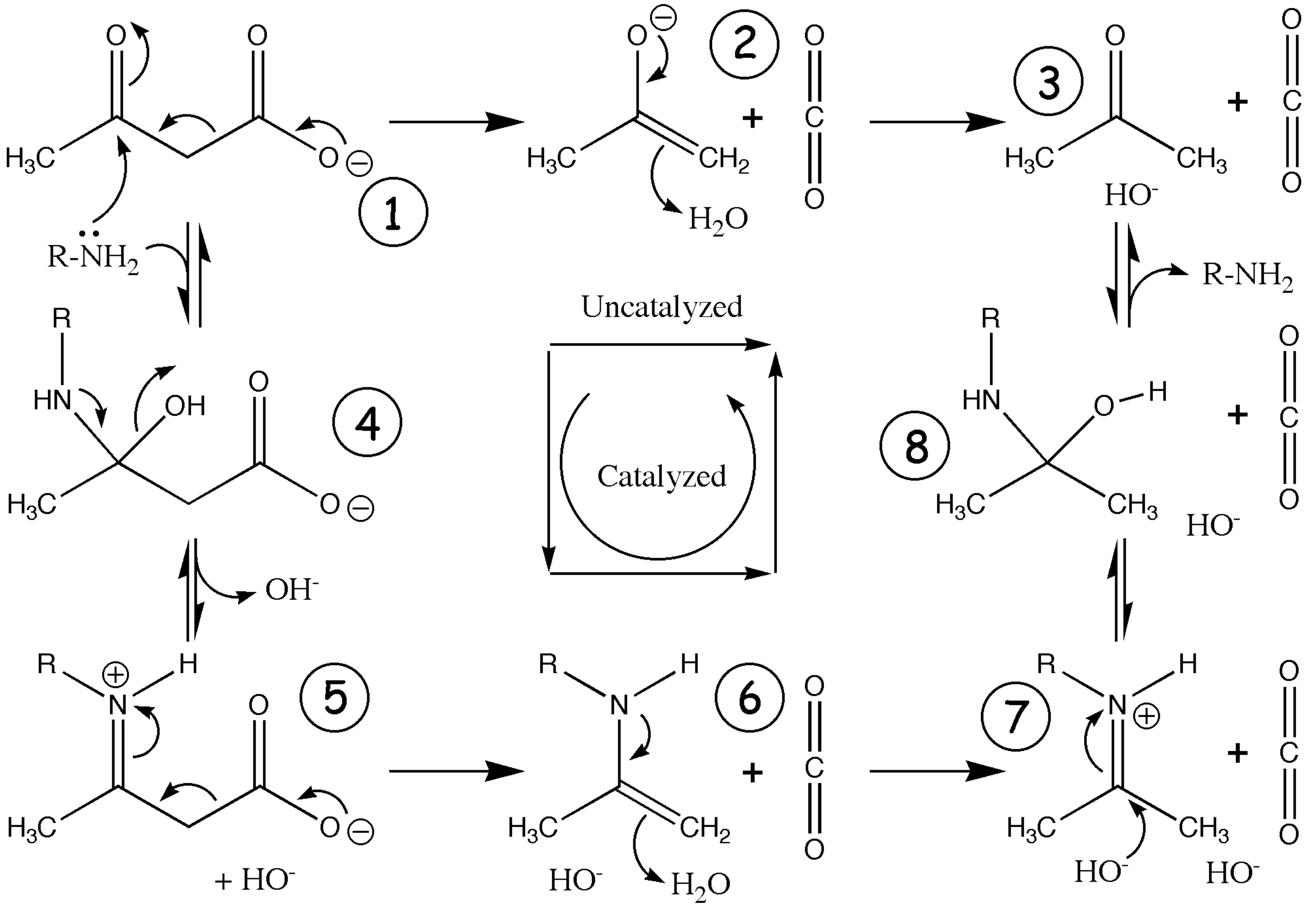
Chemical standard state: 1M solutes, pure liquids, 1 atm gases

Biochemical standard state: pH 7, all species in the ionic form found at pH 7

$\ln K_{eq} = (-\Delta\mathrm{H}°/\mathrm{RT} + \Delta\mathrm{S}°/\mathrm{R}) \qquad \ln k = (-\mathrm{Ea}/\mathrm{RT}) + \ln \mathrm{A}$

$[\mathrm{A}] = [\mathrm{A}]_0 - kt \qquad \ln[\mathrm{A}] = \ln[\mathrm{A}]_0 - kt \qquad 1/[\mathrm{A}] = 1/[\mathrm{A}]_0 + 2kt$

$$\text{Acetoacetate}^- + \mathrm{H_2O} \longrightarrow \text{Acetone} + \mathrm{CO_2} + \mathrm{HO}^-$$



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