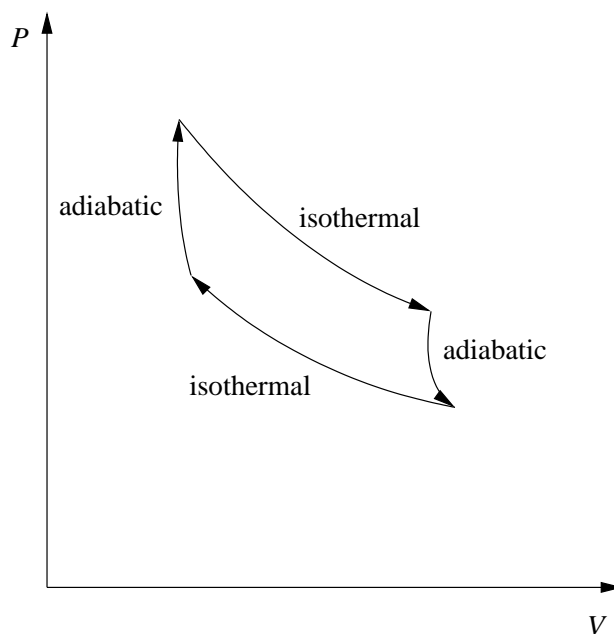


# Chemistry 2850 Spring 2007 Practice Final Examination Solutions

1. A reversible process is one which remains in equilibrium throughout.
2. No. The half-life of a second-order reaction depends on the initial concentration of reactant, so at minimum we need to know this concentration to make sense of this number.
3. The slope of a graph of  $\log_{10} k$  vs  $\sqrt{I}$  should be  $1.02z_A z_B$  at low ionic strengths. We therefore learn something about the charges of the reactants, namely the value of the product of these charges.
4. Specific acid catalysis refers to catalysis by  $H^+$ , while general acid catalysis refers to catalysis by any acid.
5. Here is my diagram:



The work done by the system is the area enclosed by the cycle.

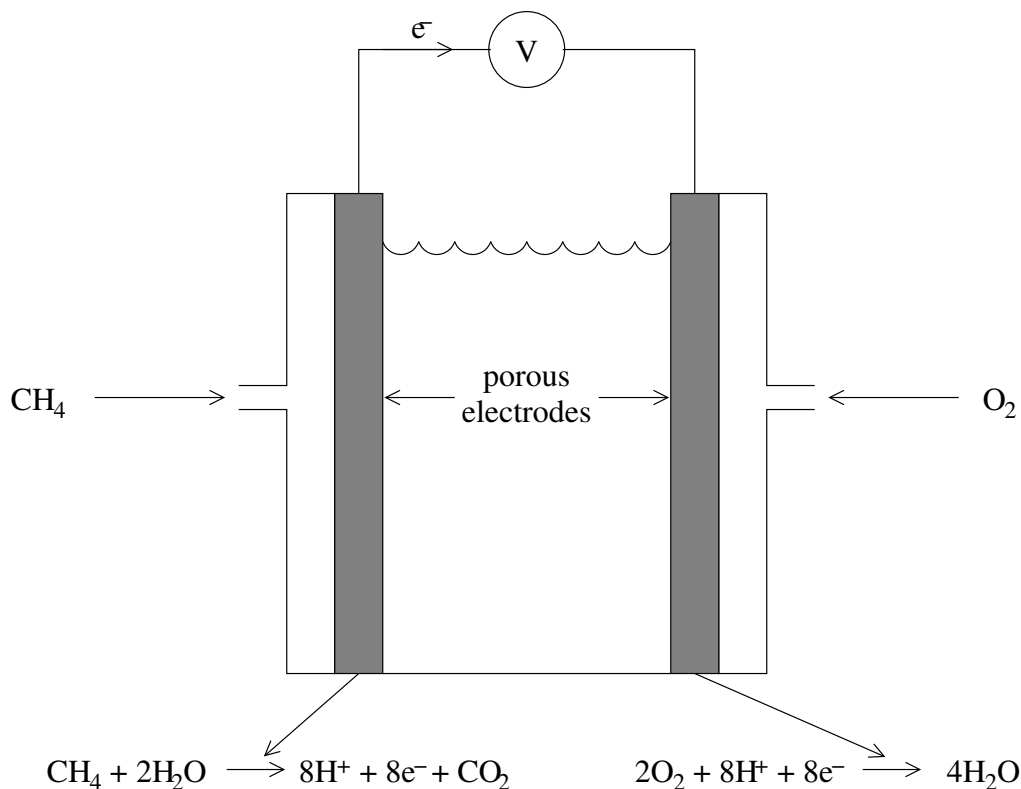
6. The comparison is perhaps best presented in the form of a table:<sup>1</sup>

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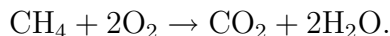
<sup>1</sup>Note that there is plenty of scope to disagree with my classification of similarities and differences, or to add other points.

	<b>Relaxation</b>	<b>Flash Photolysis</b>
Similarity:	<ul style="list-style-type: none"> <li>• Reactants premixed</li> </ul>	<ul style="list-style-type: none"> <li>• Reactants premixed</li> </ul>
Difference:	<ul style="list-style-type: none"> <li>• Reaction allowed to go to equilibrium</li> </ul>	<ul style="list-style-type: none"> <li>• No reaction occurs after mixing</li> </ul>
Similarity:	<ul style="list-style-type: none"> <li>• System disturbed by a sudden change in conditions (temperature, pressure)</li> </ul>	<ul style="list-style-type: none"> <li>• System disturbed by a light flash</li> </ul>
Difference:	<ul style="list-style-type: none"> <li>• Disturbance changes the equilibrium point</li> </ul>	<ul style="list-style-type: none"> <li>• Disturbance initiates the reaction</li> </ul>
Difference:	<ul style="list-style-type: none"> <li>• System starts close to the new equilibrium</li> </ul>	<ul style="list-style-type: none"> <li>• System starts as far from equilibrium as we want (controlled by initial concentrations)</li> </ul>
Similarity:	<ul style="list-style-type: none"> <li>• A system property (e.g. absorbance at a particular wavelength) is followed to the new equilibrium</li> </ul>	<ul style="list-style-type: none"> <li>• A system property (e.g. absorbance at a particular wavelength) is followed to equilibrium</li> </ul>
Difference:	<ul style="list-style-type: none"> <li>• Obtain the relaxation time from the data</li> </ul>	<ul style="list-style-type: none"> <li>• Data treatment depends on kinetics, just as in a normal kinetics experiment</li> </ul>
Applies to:	<ul style="list-style-type: none"> <li>• Any kind of reaction</li> <li>• Usually solution-phase kinetics</li> </ul>	<ul style="list-style-type: none"> <li>• Only reactions which can be initiated by an injection of energy but where the reactants can otherwise be mixed without reacting</li> <li>• Gas- or solution-phase kinetics</li> </ul>

7.



The overall reaction is



Note that I've written the two half-reactions so that they add up to the overall reaction. Accordingly, we have  $z = 8$ .

$$\begin{aligned} \Delta G^\circ &= \Delta_f G_{\text{CO}_2}^\circ + 2\Delta_f G_{\text{H}_2\text{O}}^\circ - (\Delta_f G_{\text{CH}_4}^\circ + 2\Delta_f G_{\text{O}_2}^\circ) \\ &= -394.37 + 2(-237.140) - (-50.72) \text{ kJ/mol} = -817.93 \text{ kJ/mol}. \\ \therefore E &= -\frac{\Delta G^\circ}{zF} = -\frac{-817.93 \times 10^3 \text{ J/mol}}{8(96485.3383 \text{ C/mol})} \\ &= 1.0597 \text{ V}. \end{aligned}$$

8. Heat isn't a state function, so it doesn't make sense to talk of "the change in heat". To put it another way, bodies don't contain heat so the heat evolved during a process can't be thought of as the change of a property.

9. We use the equation<sup>2</sup>

$$k = \frac{k_B T}{h} e^{\Delta^\ddagger S^\circ / R} e^{-\Delta^\ddagger H^\circ / (RT)}.$$

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<sup>2</sup>Given the repetitive nature of this calculation, I just programmed this formula into my calculator to fill out the table. In an ideal world, I would show a sample calculation, but if you're reasonably sure you got the calculation right, feel free to just give your values as I did here.

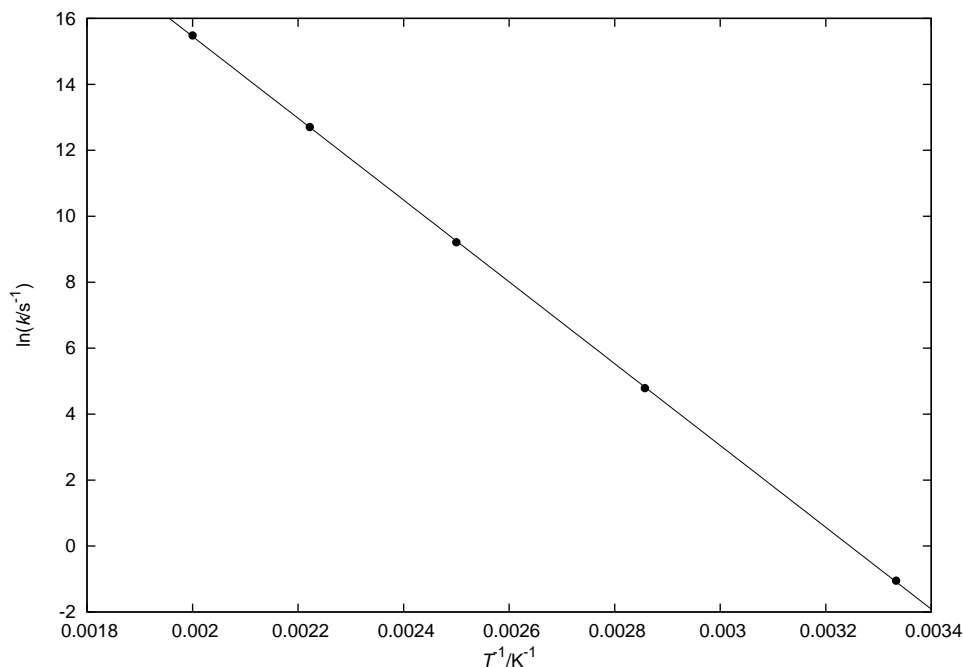


Figure 1: Arrhenius plot for question 9.

$T/\text{K}$	300	350	400	450	500
$k/\text{s}^{-1}$	0.35	$1.2 \times 10^2$	$1.0 \times 10^4$	$3.3 \times 10^5$	$5.3 \times 10^6$

The Arrhenius plot is perfectly linear (figure 1). The slope and intercept are as follows:

$$\begin{aligned} \text{slope} &= -12\,404 \text{ K}, \\ \text{intercept} &= 40.26. \end{aligned}$$

From the slope and intercept, we calculate

$$\begin{aligned} E &= -R(\text{slope}) = -(8.314\,472 \text{ J K}^{-1}\text{mol}^{-1})(-12\,404 \text{ K}) \\ &= 103 \text{ kJ/mol.} \\ A &= e^{\text{intercept}} = e^{40.26} \\ &= 3.1 \times 10^{17} \text{ s}^{-1}. \end{aligned}$$

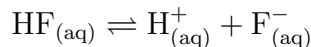
On the other hand, working directly from the entropy and enthalpy of activation, we

would calculate

$$\begin{aligned}
 E &= \Delta^\ddagger H^\circ + RT \\
 &= 100 \text{ kJ/mol} + (8.314 472 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1})(300 \text{ K}) \\
 &= 102 \text{ kJ/mol.} \\
 A &= \frac{k_B T}{h} e^{1 + \Delta^\ddagger S^\circ / R} \\
 &= \frac{(1.380 650 3 \times 10^{-23} \text{ J/K})(300 \text{ K})}{6.626 068 8 \times 10^{-34} \text{ J/Hz}} \exp \left( 1 + \frac{80 \text{ J K}^{-1} \text{ mol}^{-1}}{8.314 472 \text{ J K}^{-1} \text{ mol}^{-1}} \right) \\
 &= 2.6 \times 10^{17} \text{ s}^{-1}.
 \end{aligned}$$

These values are very similar to those we got from the graph. The small differences are attributable to a combination of factors: rounding in the intermediate steps of the calculation, and the somewhat arbitrary choice of 300 K for the transition-state theory calculations. The conclusion we can reach is that the dependence of the preexponential factor and activation energy on  $T$  predicted by transition-state theory are unimportant over temperature ranges of a few hundred Kelvin.

10. (a)



$$\begin{aligned}
 \Delta_r G^\circ &= -RT \ln K_a \\
 &= -(8.314 472 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K}) \ln(6.6 \times 10^{-4}) \\
 &= 18.2 \text{ kJ/mol.}
 \end{aligned}$$

$$\begin{aligned}
 \text{But } \Delta_r G^\circ &= \Delta_f G_{\text{H}^+}^\circ + \Delta_f G_{\text{F}^-}^\circ - \Delta_f G_{\text{HF}}^\circ. \\
 \therefore \Delta_f G_{\text{HF}}^\circ &= \Delta_f G_{\text{H}^+}^\circ + \Delta_f G_{\text{F}^-}^\circ - \Delta_r G^\circ \\
 &= 0 + (-281.52) - 18.2 \text{ kJ/mol} = -299.7 \text{ kJ/mol.}
 \end{aligned}$$

(b)

$$\begin{aligned}
 K_a &= \frac{(a_{\text{H}^+})(a_{\text{F}^-})}{a_{\text{HF}}} \\
 &= \frac{\gamma_{\pm}^2 [\text{H}^+][\text{F}^-]}{[\text{HF}]}.
 \end{aligned}$$

In this last last equation, I left out factors of the standard concentration. We would guess that the dissociation of water would not be very significant here. Thus  $[\text{H}^+] \approx [\text{F}^-]$ . Furthermore,  $[\text{HF}] = 0.10 - [\text{H}^+]$ . Thus, if we knew  $\gamma_{\pm}$ , we could calculate  $[\text{H}^+]$  by solving the quadratic equation

$$\gamma_{\pm}^2 [\text{H}^+]^2 - K_a (0.10 - [\text{H}^+]) = 0.$$

The solution of this quadratic equation is

$$[\text{H}^+] = \frac{1}{2\gamma_{\pm}^2} \left\{ -K_a + \sqrt{K_a^2 + 4(0.10)K_a\gamma_{\pm}^2} \right\}. \quad (1)$$

We also have

$$\log_{10} \gamma_{\pm} = -0.51|z_+z_-|\sqrt{I}$$

and

$$I = \frac{1}{2} ([\text{H}^+](1)^2 + [\text{F}^-](-1)^2) = [\text{H}^+].$$

Since  $z_+ = 1$  and  $z_- = -1$ , we get

$$\log_{10} \gamma_{\pm} = -0.51\sqrt{[\text{H}^+]}. \quad (2)$$

We will start with a guess for  $\gamma_{\pm}$  ( $\approx 1$ ), then use equation 1 to calculate  $[\text{H}^+]$ , then calculate  $\gamma_{\pm}$  using equation 2, then use our improved estimate of  $\gamma_{\pm}$  in equation 1 to calculate an improved estimate of  $[\text{H}^+]$ , and so on. Here are my results, again obtained with my programmable calculator

$\gamma_{\pm}$	$[\text{H}^+]/\text{mol L}^{-1}$
1	0.0078
0.9015	0.0086
0.8967	0.0087
0.8965	0.0087
0.8965	0.0087

Therefore,  $[\text{H}^+] = [\text{F}^-] = 0.0087 \text{ mol/L}$ .

(c)

$$\begin{aligned} \text{pH} &= -\log_{10} a_{\text{H}^+} \\ &= -\log_{10} (\gamma_{\pm}[\text{H}^+]) \\ &= -\log_{10} (0.8965(0.0087)) = 2.11. \end{aligned}$$

11. (a) i.  $\text{A} \rightarrow \text{P}$   
 ii. B is an intermediate. Apply the steady-state approximation:

$$\begin{aligned} \frac{d[\text{B}]}{dt} &= k_1[\text{A}]^2 - k_{-1}[\text{B}] - k_2[\text{A}][\text{B}] \approx 0. \\ \therefore [\text{B}] &\approx \frac{k_1[\text{A}]^2}{k_{-1} + k_2[\text{A}]}. \end{aligned}$$

From the reaction stoichiometry, we have

$$v = \frac{d[\text{P}]}{dt}.$$

From the mechanism,

$$\begin{aligned} d[\text{P}]/dt &= 3k_2[\text{A}][\text{B}]. \\ \therefore v &\approx \frac{3k_1k_2[\text{A}]^3}{k_{-1} + k_2[\text{A}]}. \end{aligned}$$

iii. If  $k_2[A] \ll k_{-1}$ , we get

$$v = \frac{3k_1k_2}{k_{-1}}[A]^3,$$

i.e. a simple third-order rate law with an observed rate constant  $k = 3k_1k_2/k_{-1}$ .

(b)

$$\begin{aligned}\frac{d[A]}{dt} &= -k[A]^3 \\ \therefore \frac{d[A]}{[A]^3} &= -k dt \\ \therefore \int_{[A]_0}^{[A]} \frac{da}{a^3} &= -k \int_0^t dt' \\ \therefore -kt &= \int_{[A]_0}^{[A]} a^{-3} da \\ &= \frac{1}{1-3} a^{1-3} \Big|_{[A]_0}^{[A]} \\ &= -\frac{1}{2} \left( \frac{1}{[A]^2} - \frac{1}{[A]_0^2} \right) \\ \therefore \frac{1}{[A]^2} &= kt + \frac{1}{[A]_0^2}\end{aligned}$$

(c) According to our integrated rate law, we should plot  $1/[A]^2$  vs  $t$  to test for third-order kinetics. My graph is shown as figure 2. The graph is linear. We therefore conclude that the data are consistent with third-order kinetics. The slope should be  $k$ . We find, by linear regression,

$$k = 0.040 \times 10^6 \text{ L}^2\text{mol}^{-2}\text{min}^{-1} = 4.0 \times 10^4 \text{ L}^2\text{mol}^{-2}\text{min}^{-1}.$$

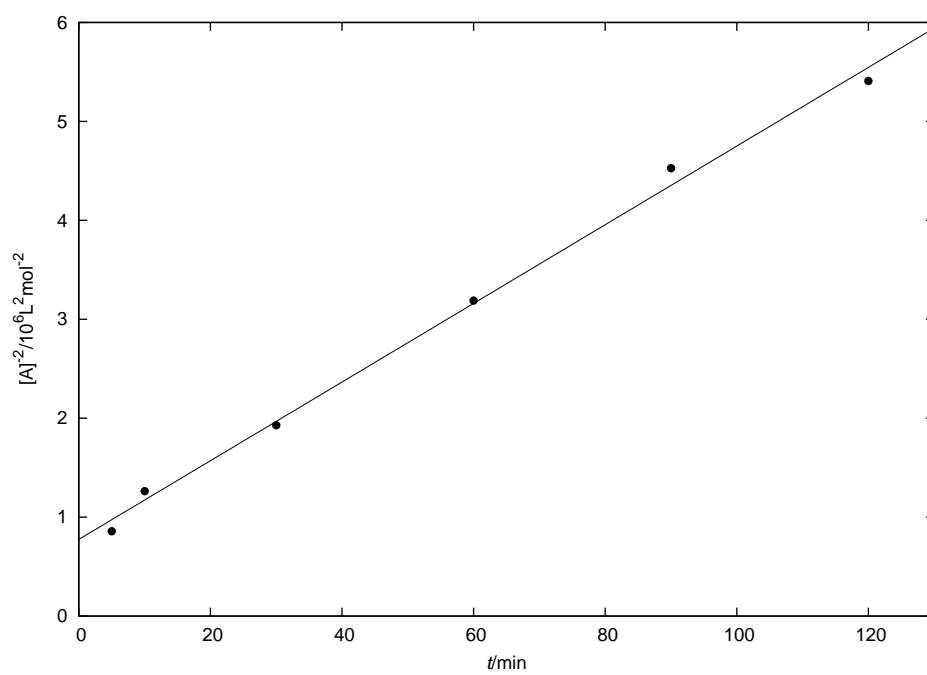


Figure 2: Test of third-order kinetics for problem 11c.