Chemistry 112-2014 Name: ANSWER KEY

Exam #2, Section 4

1. For each pair, choose the species with the greater entropy: $NO(g)$ or $NO_2(g)$

$H_2O(g)$ or $H_2O(l)$

NO_2 > NO because of containing more atoms.

$H_2O(g) > H_2O(l)$ because gases have greater freedom of movement.

a. NO and $H_2O(g)$ b. NO and $H_2O(l)$

c. $NO_2(g)$ and $H_2O(g)$ d. $NO_2(g)$ and $H_2O(l)$

2. In which temperature range will the following reaction be thermodynamically most favored:

$$O{=}O(g) + O(g) \rightarrow O{=}O{-}O(g)$$

a. at all temperatures b. at no temperatures c. at high temperatures ***d. at low temperatures***

The reaction involves forming a bond so it is enthalpy favored. It involves two moles of gas forming one mole of gas, so the reaction is entropy disfavored. Enthalpy favors reactions at low temperature, so the reaction is favored at low temperatures.

3. What thermodynamic term controls why oil and water do not mix?

a. enthalpy change for water is disfavored ***c. entropy change for water is disfavored***

b. enthalpy change for oil is disfavored d. entropy change for oil is disfavored

4. Consider the reaction: $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

The reaction does not occur at room temperature. What can be said about thermodynamic control of the reaction?

a. it is disfavored and enthalpy controlled

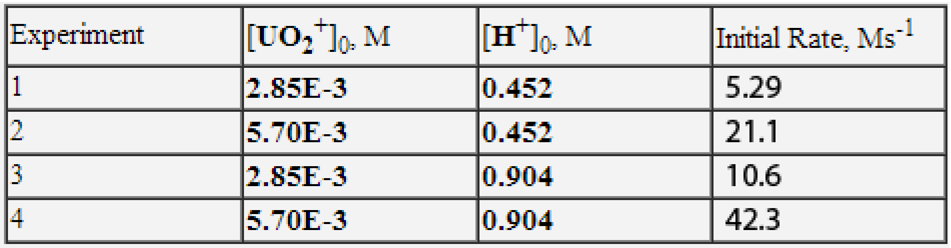
Since the reaction does not occur, it must be thermodynamically disfavored. It therefore must be disfavored by enthalpy, entropy, or both. The reaction is clearly entropy favored, so it must be enthalpy disfavored. Because it is overall disfavored, and that happens because it is enthalpy disfavored, it is controlled by enthalpy.

5. For a reaction to actually occur, it must be favored by:

d. both thermodynamics and kinetics

6. Initial rate data was found for the following reaction:

$2\ UO_2^+ + 4\ H^+ \longrightarrow U^{4+} + UO_2^{2+} + 2\ H_2O$



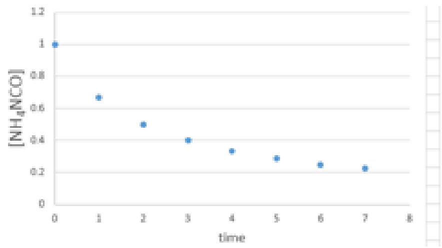
Experiment	$[UO_2^+]_0$, M	$[H^+]_0$, M	Initial Rate, Ms^{-1}
1	**2.85E-3**	**0.452**	5.29
2	**5.70E-3**	**0.452**	21.1
3	**2.85E-3**	**0.904**	10.6
4	**5.70E-3**	**0.904**	42.3

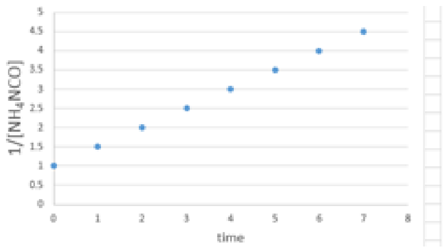
What is the rate law for the reaction?

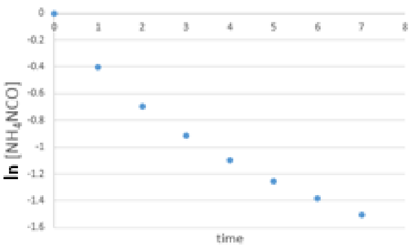
c. rate = k$[UO_2^+]^2[H^+]$

Using Experiments 1 and 2: the reaction rate quadruples when $[UO_2^+]$ doubles. The reaction is therefore second order in UO_2^+. Using experiments 1 and 3 (or 2 and 4), the reaction rate doubles when $[H^+]$ doubles. The reaction is therefore first order in H^+.

7. The reaction $NH_4NCO \rightarrow (NH_2)_2CO$ was performed and data obtained for the concentration of NH_4NCO over time. The following plots were made from the data.





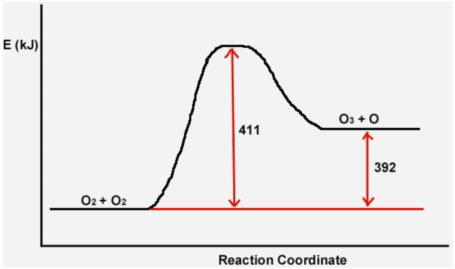


What is the order of the reaction with respect to NH_4NCO?

a. zero order b. first order ***c. second order*** d. cannot be determined from the plots alone

The 1/[concentration] plot is linear, so the reaction is second order.

8. Using the reaction coordinate diagram below, determine the activation energy and type of enthalpy change for the reaction.



a. E_a = 392 kJ, endothermic ***c. E_a = 411 kJ, endothermic***

b. E_a = 392 kJ, exothermic d. E_a = 411 kJ, exothermic

The activation energy is the energy change from the reactants to the activated complex. This reaction is endothermic because the energy of the products is higher than that of the reactants.

9. The reaction $2\ HI \rightarrow H_2 + I_2$ is second order in [HI]. If the initial concentration of HI is 0.200 M and drops to 0.168 M in 125 seconds, what is the rate constant?

a. 0.00760 s^{-1} b. 0.95 s^{-1} c. 1.05 s^{-1} d. 83.4 s^{-1}

$$\frac{1}{0.168} = \frac{1}{0.200} - k(125s)$$ *Solve this for k.*

10. Two mechanisms are proposed for the reaction,

$(CH_3)C{=}CH_2 + H_2O \rightarrow (CH_3)_3COH$

Mechanism A: Step 1. $(CH_3)C{=}CH_2 + H_2O \rightarrow (CH_3)_3COH$

Mechanism B: Step 1. $(CH_3)C{=}CH_2 + H^+ \rightarrow (CH_3)_3C^+$ (slow)

Step 2. $(CH_3)_3C^+ + H_2O \rightarrow (CH_3)_3COH$ (fast)

The experimentally determined rate law is: Rate = $k[(CH_3)C{=}CH_2][H^+]$

Which mechanism is supported by the experimental evidence?

a. Mechanism A ***b. Mechanism B*** c. neither mechanism d. both mechanisms

The presence of $[H^+]$ *in the rate law includes Mechanism B as possible and excludes Mechanism A.*

11. What is the standard entropy change for the following reaction?

$4\ HCl(g) + O_2(g) \longrightarrow 2\ H_2O(g) + 2\ Cl_2(g)$

a. +129 J/K ***b. -129 J/K*** c. +20 d. -20 J/K

S°:
HCl: 186 J/K
O_2: 205 J/K
H_2O:189 J/K
Cl_2: 223 J/K

12. Use the following reaction and the data given to calculate ΔG° at 228 °C.

$2\ H_2S(g) + 3\ O_2(g) \rightarrow 2\ H_2O(l) + 2\ SO_2(g)$ $\Delta H^o = -1120$ kJ $\Delta S^o = -391$ J/K

a. -1030 kJ ***b. -924 kJ*** c. +88000 kJ d. +195000 kJ

$\Delta G = \Delta H - T\Delta S$; $\Delta G = -1120\text{ kJ} - (228+273)(-0.391\text{ kJ/K}) = -924\text{ kJ}$

13. Cesium-137 is radioactive, with a half-life of 30 years. If 500 g of Cs-137 was emitted during Chernobyl nuclear disaster in the year 1986, what mass of Cs-137 will remain in the year 2046?

a. 67 g ***b. 125 g*** c. 250 g d. 375 g

No calculation needed. 2046 – 1986 = 60 years = 2 half-lives. So, 500 g → 250 g → 125 g

Fill-in Questions

14. The following reaction is 2nd–order in NO_2 in and zero–order in CO. Write the rate law for the reaction.

$NO_2 + CO \longrightarrow NO + CO_2$ *Rate =* $k[NO_2]^2$

15. The following mechanism is proposed for a reaction:

Step 1: $NO_2Cl \rightarrow NO_2 + Cl$

Step 2: $Cl + NO_2Cl \rightarrow NO_2 + Cl_2$

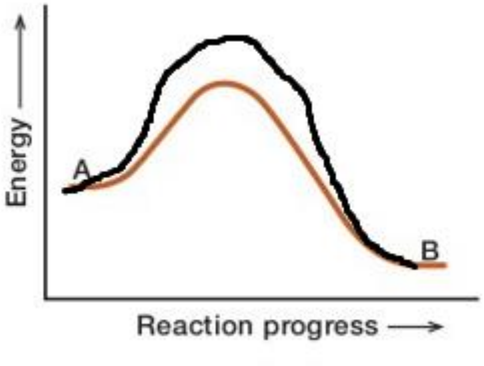
Write the overall reaction: $2\ NO_2Cl \rightarrow 2\ NO_2 + Cl_2$

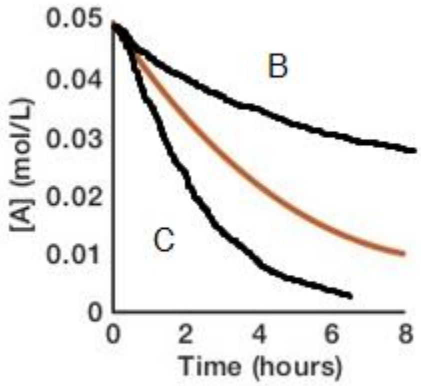
What is the molecularity of Step 2: bimolecular

Give formulas of intermediates (if none, enter “none): Cl

Give formulas of catalysts (if none, enter “none): none

16. The reaction coordinate diagram for a reaction and its concentration-time curve are shown for the reaction run at 25 °C.





a. draw a curve on the left plot that has a higher activation energy. *Curve reaches a higher energy at the transition state, but the energy of A and B are unchanged.*

b. draw a curve on the right plot for the reaction run if the activation energy were higher. Label it **B**. *Reaction will go slower.*

c. draw a curve on the right plot for the reaction run at higher temperature. Label it **C**. *The reaction will go faster at higher temperature.*

d. If the energy of the products were lower, the reaction rate would be:

faster slower ***the same***

Long Answer Question:

k = 12.0 s^{-1} at 270 K

k = 44.0 s^{-1} at 300 K

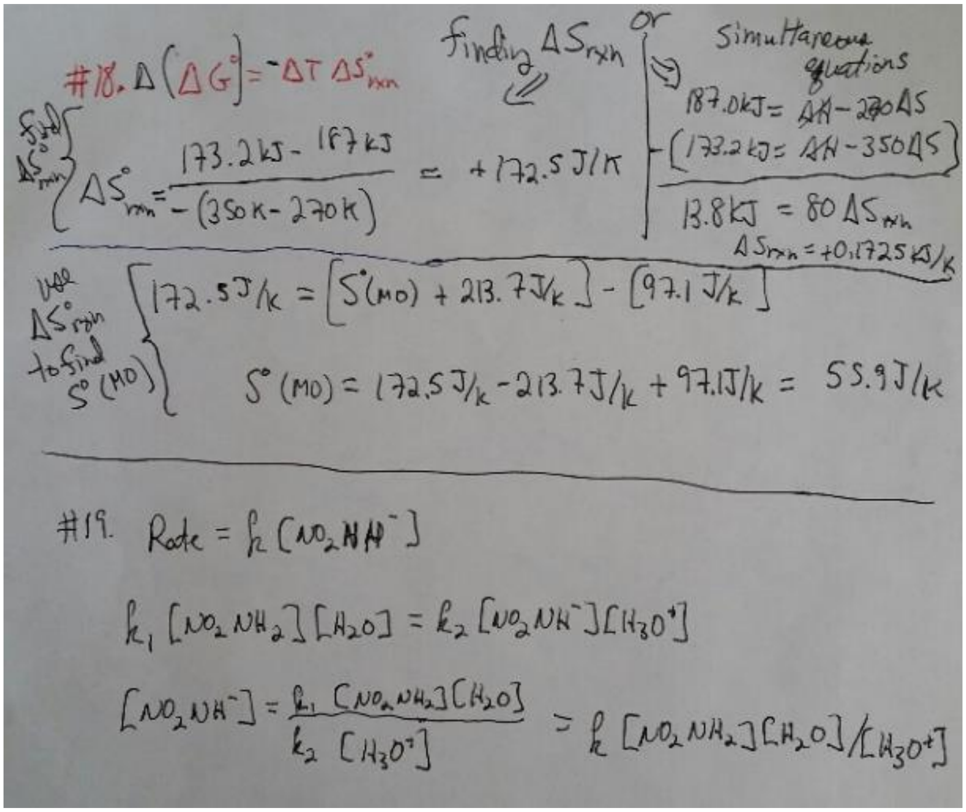
17. A reaction has the following measured rate constants at two temperatures.

What is the activation energy?

$$\ln\frac{44.0}{12.0} = \frac{-Ea}{8.314J/K}\left[\frac{1}{(300+273)\text{K}} - \frac{1}{(270+273)K}\right]$$

Solve for Ea and convert to kJ. E_a = 29.1 kJ

#18: First determine ΔS^o_{rxn} and then use that to solve for S^o(MO). I show two methods for determining ΔS^o_{rxn}.



#18. $\Delta(\Delta G^\circ) = -\Delta T \Delta S^\circ_{rxn}$

finding ΔS_{rxn} or Simultaneous equations

find ΔS°_{rxn}

$$\Delta S^\circ_{rxn} = \frac{173.2\text{kJ} - 187\text{kJ}}{-(350\text{K} - 270\text{K})} = +172.5\text{ J/K}$$

$$187.0\text{kJ} = \Delta H - 270\Delta S$$
$$-(173.2\text{kJ} = \Delta H - 350\Delta S)$$
$$13.8\text{kJ} = 80\Delta S_{rxn}$$
$$\Delta S_{rxn} = +0.1725\text{ kJ/K}$$

use ΔS°_{rxn} to find S°(MO)

$$172.5\text{J/K} = [S^\circ(\text{MO}) + 213.7\text{J/K}] - [97.1\text{ J/K}]$$

$$S^\circ(\text{MO}) = 172.5\text{ J/K} - 213.7\text{J/K} + 97.1\text{J/K} = 55.9\text{J/K}$$

#19. $\text{Rate} = k[NO_2NH^-]$

$$k_1[NO_2NH_2][H_2O] = k_2[NO_2NH^-][H_3O^+]$$

$$[NO_2NH^-] = \frac{k_1[NO_2NH_2][H_2O]}{k_2[H_3O^+]} = k[NO_2NH_2][H_2O]/[H_3O^+]$$