

## Equations and Constant

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

$$t_{1/2} = \frac{[A]_0}{2k}$$

$$\Delta S_{\text{phase change}} = \frac{\Delta H_{\text{phase change}}}{T_{\text{phase change}}}$$

$$\ln \frac{[A]_t}{[A]_0} = -kt$$

$$t_{1/2} = \frac{0.693}{k}$$

$$\Delta H_{\text{rxn}}^{\circ} = \Sigma \Delta H_f^{\circ}(\text{products}) - \Sigma \Delta H_f^{\circ}(\text{reactants})$$

$$\Delta S_{\text{rxn}}^{\circ} = \Sigma S^{\circ}(\text{products}) - \Sigma S^{\circ}(\text{reactants})$$

$$[A]_t = [A]_0 e^{-kt}$$

$$\frac{1}{[A]_t} = \frac{1}{[A]_0} + kt$$

$$t_{1/2} = \frac{1}{k[A]_0}$$

$$\Delta G^{\circ} = \Sigma \Delta G_f^{\circ}(\text{products}) - \Sigma \Delta G_f^{\circ}(\text{reactants})$$

$$\Delta G_{\text{rxn}}^{\circ} = \Delta H_{\text{rxn}}^{\circ} - T \Delta S_{\text{rxn}}^{\circ}$$

$$\ln \frac{k_2}{k_1} = \frac{-E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \frac{-\Delta H_{\text{rxn}}}{T}$$

$$k = A e^{-E_a/RT}$$

$$R = 8.314 \text{ J/K}\cdot\text{mol}$$

1. For each pair, choose the species with the greater entropy:

NO(g) or NO<sub>2</sub>(g)

H<sub>2</sub>O(g) or H<sub>2</sub>O(l)

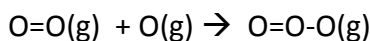
a. NO and H<sub>2</sub>O(g)

b. NO and H<sub>2</sub>O(l)

c. NO<sub>2</sub>(g) and H<sub>2</sub>O(g)

d. NO<sub>2</sub>(g) and H<sub>2</sub>O(l)

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



a. at all temperatures

b. at no temperatures

c. at high temperatures

d. 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:  $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$

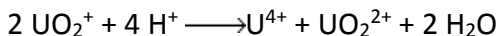
The reaction does not occur at room temperature. What can be said about thermodynamic control of the reaction?

- a. it is disfavored and enthalpy controlled
- b. it is disfavored and entropy controlled
- c. it is favored and enthalpy controlled
- d. it is favored and entropy controlled

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

- a. thermodynamics
- b. kinetics
- c. either thermodynamics or kinetics
- d. both thermodynamics and kinetics

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

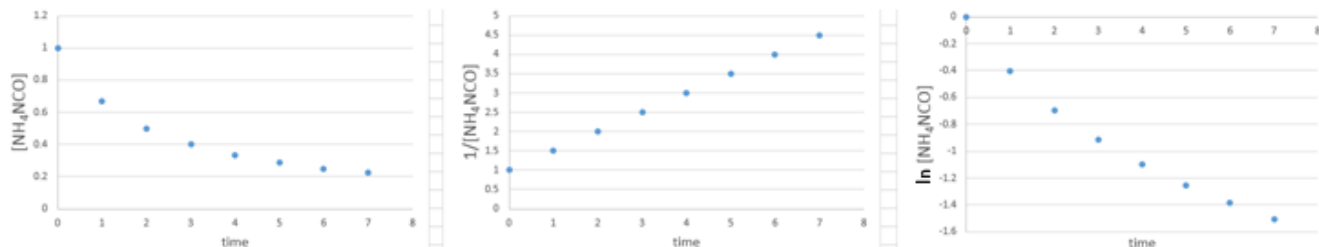


Experiment	$[\text{UO}_2^+]_0, \text{M}$	$[\text{H}^+]_0, \text{M}$	Initial Rate, $\text{Ms}^{-1}$
1	2.85E-3	0.452	5.29
2	5.70E-3	0.452	21.1
3	2.85E-3	0.904	10.6
4	5.70E-3	0.904	42.3

What is the rate law for the reaction?

- a. rate =  $k[\text{UO}_2^+][\text{H}^+]$
- b. rate =  $k[\text{UO}_2^+]^2[\text{H}^+]^4$
- c. rate =  $k[\text{UO}_2^+]^2[\text{H}^+]$
- d. rate =  $k[\text{UO}_2^+][\text{H}^+]/[\text{U}^{4+}][\text{UO}_2^{2+}]$

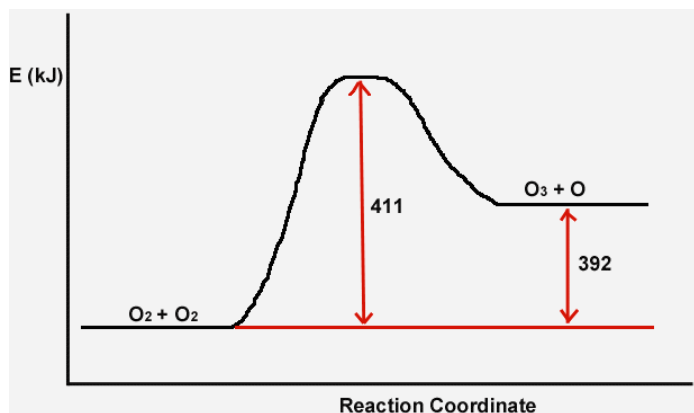
7. The reaction  $\text{NH}_4\text{NCO} \rightarrow (\text{NH}_2)_2\text{CO}$  was performed and data obtained for the concentration of  $\text{NH}_4\text{NCO}$  over time. The following plots were made from the data.



What is the order of the reaction with respect to  $\text{NH}_4\text{NCO}$ ?

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

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

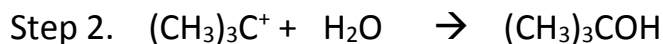
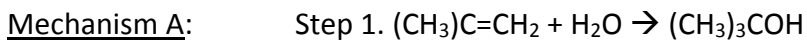
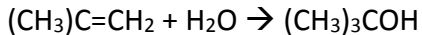


- a.  $E_a = 392$  kJ, endothermic      c.  $E_a = 411$  kJ, endothermic  
 b.  $E_a = 392$  kJ, exothermic      d.  $E_a = 411$  kJ, endothermic

9. The reaction  $2 \text{HI} \rightarrow \text{H}_2 + \text{I}_2$  is second order in  $[\text{HI}]$ . If the initial concentration of  $\text{HI}$  is  $0.200 \text{ M}$  and drops to  $0.168 \text{ M}$  in  $125$  seconds, what is the rate constant?

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

10. Two mechanisms are proposed for the reaction,

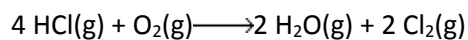


The experimentally determined rate law is:  $\text{Rate} = k[(\text{CH}_3)\text{C}=\text{CH}_2][\text{H}^+]$

Which mechanism is supported by the experimental evidence?

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

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



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

12. Use the following reaction and the data given to calculate  $\Delta G^\circ$  at 228 °C.



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

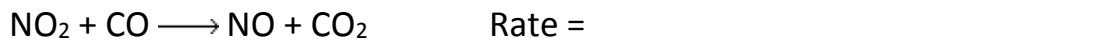
13. Cesium-137 is radioactive, with a half-life of 30 years. If 500 g of Cs-137 was emitted during Chernobyl nuclear disaster in the year 1986, what mass of Cs-137 will remain in the year 2046?

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

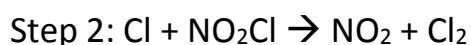
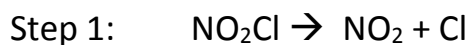
- |    |   |   |   |   |     |   |   |   |   |
|----|---|---|---|---|-----|---|---|---|---|
| 1. | a | b | c | d | 7.  | a | b | c | d |
| 2. | a | b | c | d | 8.  | a | b | c | d |
| 3. | a | b | c | d | 9.  | a | b | c | d |
| 4. | a | b | c | d | 10. | a | b | c | d |
| 5. | a | b | c | d | 11. | a | b | c | d |
| 6. | a | b | c | d | 12. | a | b | c | d |
|    |   |   |   |   | 13. | a | b | c | d |

Fill-in Questions

14. The following reaction is 2<sup>nd</sup>-order in NO<sub>2</sub> in and zero-order in CO. Write the rate law for the reaction.



15. The following mechanism is proposed for a reaction:



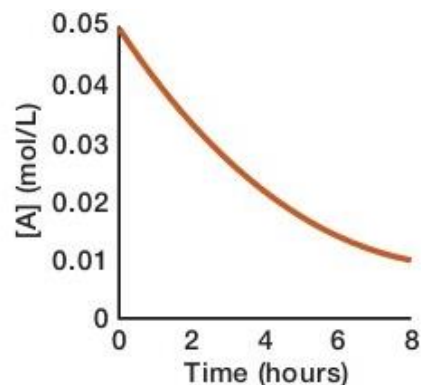
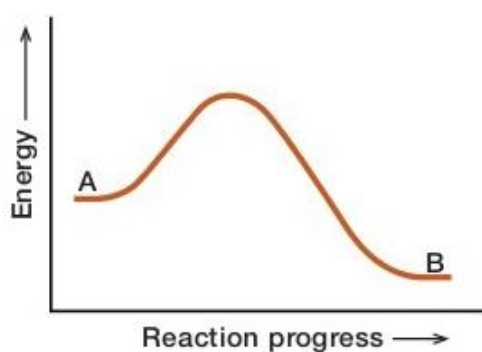
Write the overall reaction:

What is the molecularity of Step 2: \_\_\_\_\_

Give formulas of intermediates (if none, enter "none"): \_\_\_\_\_

Give formulas of catalysts (if none, enter "none"): \_\_\_\_\_

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



- draw a curve on the left plot that has a higher activation energy.
- draw a curve on the right plot for the reaction run if the activation energy were higher. Label it **B**.
- draw a curve on the right plot for the reaction run at higher temperature. Label it **C**.
- If the energy of the products were lower, the reaction rate would be:

faster    slower    the same

Long Answer Question:

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

What is the activation energy?

$k = 12.0 \text{ s}^{-1}$  at 270 K  
 $k = 44.0 \text{ s}^{-1}$  at 300 K

$E_a = \underline{\hspace{2cm}} \text{ kJ}$