

Chemical Kinetics Practice Items

1. Which of the following describes a first order reaction?

- I. The reaction rate is directly proportional to the concentration of a single reagent.
- II. Reagent concentration decreases with a half life that is independent of the initial reagent concentration.
- III. A linear decrease of reagent concentration with time is observed.

- A. I only
- B. I and II
- C. II and III
- D. I, II, and III

2. Which of the following is a homogeneous reaction?

- A. $4\text{NH}_3(\text{g}) + 5\text{O}_2(\text{g}) \longrightarrow 4\text{NO}(\text{g}) + 6\text{H}_2\text{O}(\text{g})$
- B. $\text{H}_2\text{O}(\text{g}) \longrightarrow \text{H}_2\text{O}(\text{l})$
- C. $\text{Ca}(\text{l}) + \text{H}_2(\text{g}) \longrightarrow \text{CaH}_2(\text{s})$
- D. $\text{C}(\text{s}) + \text{H}_2\text{O}(\text{g}) \longrightarrow \text{CO}(\text{g}) + \text{H}_2(\text{g})$

3. If the reaction rate is quadrupled by doubling the concentration of a reactant, the order of the reaction with respect to that reactant is

- A. 1
- B. 2
- C. 4
- D. cannot be determined except by experiment

4. In the presence of a catalyst

- I. Effective collisions among reactant molecules become more likely to occur.
- II. Chemical equilibrium will shift toward the products.
- III. The activation energy for the reaction is lowered.

- A. I only
- B. I and III
- C. II and III
- D. I, II, and III

5. Choose the correct rate expression for the reaction below



- A. $\text{rate} = k [\text{MgO}] [\text{Si}]$
- B. $\text{rate} = k [\text{MgO}]^2 [\text{Si}]$
- C. $\text{rate} = 2k [\text{MgO}][\text{Si}]$
- D. can't determine from given information

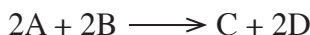
6. In general the rate constant is **not** a function of

- A. the activation energy of the reaction.
- B. reaction temperature.
- C. concentration of reactants.
- D. the probability of collision.

7. H_2 and O_2 can be kept together at standard conditions for many years without appreciable reaction to form water. The reaction doesn't occur because

- A. equilibrium favors the reagents.
- B. the standard free energy change for the reaction is positive.
- C. pressure in the reaction vessel is too low.
- D. the mixture of gases is kinetically stable.

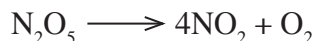
8. The table below contains experimental data for the reaction



Trial #	Initial [A]	Initial [B]	Initial Formation Rate of C
1	$2.0 \times 10^{-4} M$	$1.0 \times 10^{-2} M$	$8.0 \times 10^{-5} M \text{ sec}^{-1}$
2	$4.0 \times 10^{-4} M$	$2.0 \times 10^{-2} M$	$6.4 \times 10^{-4} M \text{ sec}^{-1}$
3	$2.0 \times 10^{-4} M$	$3.0 \times 10^{-2} M$	$2.4 \times 10^{-4} M \text{ sec}^{-1}$

Which of the following is the correct rate equation for the reaction?

- A. rate = $k [A]^2 [B]^2$
 B. rate = $k [A][B]$
 C. rate = $k [A]^2 [B]$
 D. rate = $k [A]^2 [B]^3$
9. The decomposition of N_2O_5 in carbon tetrachloride can be represented



The reaction rate equation was found to be

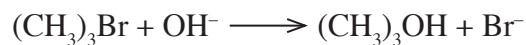
$$\text{rate} = (6.9 \times 10^{-4} \text{ s}^{-1}) [N_2O_5]$$

If we begin with 30 g of N_2O_5 in solution, approximately how much time elapses before only 1 g remains?

- A. $5.0 \times 10^3 \text{ s}$
 B. $1.4 \times 10^4 \text{ s}$
 C. $2.0 \times 10^4 \text{ s}$
 D. $4.0 \times 10^4 \text{ s}$

The following passage pertains to questions 10-12.

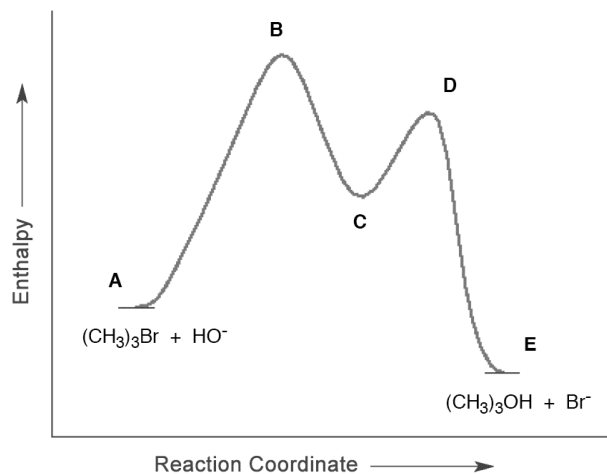
Reaction of an alkyl halide with base can proceed by either a substitution or an elimination pathway. The substitution that tert-butyl bromide would undergo with base is represented by the reaction below.



It has been found that the rate of the substitution reaction by which tert-butyl bromide is converted to tert-butyl alcohol varies directly with the concentration of alkyl halide but does not depend upon the concentration of base. The rate equation for the reaction is as follows:

$$\text{rate} = k [(CH_3)_3Br]$$

Below is the energy diagram representing the reaction mechanism. The energy of the stages from A (reactants) to E (products) is shown.



10. Which of the following best describes the reaction of tert-butyl bromide to form tert-butyl alcohol?
- A. endothermic unimolecular
 B. exothermic unimolecular
 C. endothermic bimolecular
 D. exothermic bimolecular

11. The vertical difference on the graph between stages A and B represents

- A. the enthalpy change of the reaction.
- B. the activation energy of the reaction.
- C. the enthalpy of the intermediate.
- D. the enthalpy difference between the reagents and the reaction intermediate.

12. Which of the following is the rate determining step in the reaction of tert-butyl bromide to form tert-butyl alcohol?

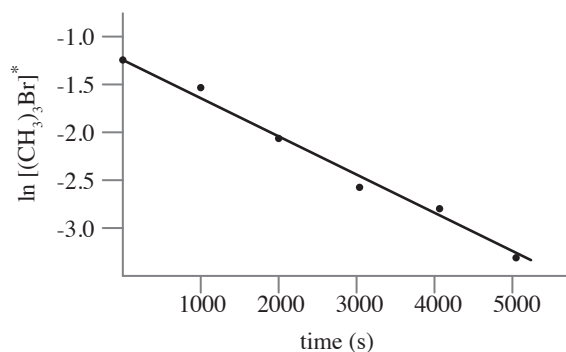
- A. formation of the carbocation intermediate.
- B. capture of the carbocation intermediate by hydroxide ion.
- C. backside displacement of bromide by hydroxide ion.
- D. direct displacement of bromide by hydroxide ion.

13. The concentration of trimethylbromide changes with time during the reaction described in the passage according to the following equation.

$$\ln [(\text{CH}_3)_3\text{Br}] = \ln [(\text{CH}_3)_3\text{Br}]_0 - kt$$

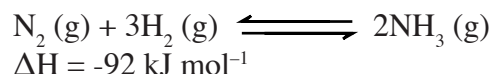
Experimental data was plotted on the graph below. What is the approximate rate constant for the reaction?

- A. $4.0 \times 10^{-4} \text{ s}^{-1}$
- B. $1.3 \times 10^{-3} \text{ s}^{-1}$
- C. $3.9 \times 10^{-3} \text{ s}^{-1}$
- D. $2.0 \times 10^{-2} \text{ s}^{-1}$

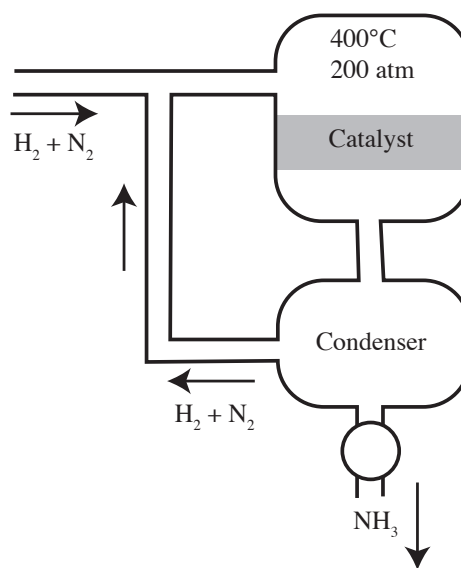


The following passage pertains to questions 14-17.

The Haber Process combines nitrogen from the air with hydrogen derived from methane to form ammonia. The reaction is reversible. The production of ammonia is exothermic.



This conversion is typically conducted at 150–250 atm and between 300–550 °C, as the gases are passed over four beds of an iron wool catalyst, with cooling between each pass. The reaction mechanism involving the catalyst involves a number of steps of which the adsorption and cleavage of nitrogen is the rate determining step. Iron is predominantly in the zero oxidation state in the catalyst. Importantly, the rate-limiting step of the catalytic process is N₂ chemisorption and N-N bond cleavage to give surface-bound nitrides (N³⁻), which react with H₂ to form the N-H bonds in NH₃. On each pass only about 15% conversion occurs, but any unreacted gases are recycled, and eventually an overall conversion of 97% is achieved.



Gaseous ammonia is not removed from the reactor itself, since the temperature is too high. It is removed from the equilibrium mixture of gases leaving the

reaction vessel. The hot gases are cooled enough, whilst maintaining a high pressure, for the ammonia to condense and be removed as liquid. Unreacted hydrogen and nitrogen gases are then returned to the reaction vessel to undergo further reaction.

14. Which of the following could we expect to increase the concentration of ammonia in the equilibrium mixture of gases exiting the reaction chamber?

- I. Increasing pressure in the reactor.
- II. Changes to the catalyst that lower the activation energy for the N_2 adsorption and cleavage steps.
- III. Redesigning the reactor to accommodate a reaction temperature of $650\text{ }^\circ\text{C}$.

- A. I only
- B. I and III
- C. II and III
- D. I, II, and III

15. The reaction is carried out at high temperatures in order to

- A. decrease the equilibrium constant.
- B. increase the equilibrium constant.
- C. increase the rate constant.
- D. decrease the activation energy.

16. Why does the design call for the iron catalyst to be utilized in the form iron wool?

- A. increased surface area
- B. increased effective concentration
- C. increased molar density
- D. decreased heat capacity

17. It is believed that three iron atoms in the catalyst cooperate to break the N-N triple bond through a six-electron reduction of the N_2 . After the mechanism is complete and the ammonia is released, the iron will be

- A. in the Fe_2N form of ferrous nitride.
- B. in the Fe_3N_4 form of ferrous nitride.
- C. in the zero oxidation state of pure iron.
- D. in the +3 ferric oxidation state.



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Chemical Kinetics

Answers and Explanations

1. B

Choice 'I' is correct. The reaction rate is directly proportional to the concentration of a single reagent in a first order reaction.

$$\text{rate} = k [A]$$

Choice 'II' is correct. A first order reaction will have a half-life that is independent of the initial reagent concentration. The half-life is a function of the rate constant. The higher the rate constant the shorter the half-life.

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.69}{k}$$

Choice 'III' is incorrect. With a first order reaction, there is not a linear decrease of reagent concentration with time but an exponential decrease.

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

2. A

Homogeneous reactions are chemical reactions in which the reactants and products are in the same phase, while heterogeneous reactions have reactants in two or more phases. Reactions that take place on the surface of a catalyst of a different phase are also heterogeneous.

3. B

If the reaction rate quadruples in an experiment when the concentration of a reagent is doubled, the exponent for that reagent in the rate expression will be 2. The reaction is second order for that reagent.

4. B

Choices 'I' and 'III' are true. 'II' is not true. A catalyst speeds up both the forward and reverse reactions. A catalyst does not change the thermodynamics of the reaction, ie. the free energy change between products and reagents. A catalyst affects the kinetics.

5. D

The stoichiometry of a reaction will not reveal the rate expression. The stoichiometry does not reveal which species are present in the rate determine step of the reaction. You can determine a rate expression only by analyzing experimental data or if you know specific mechanistic details.

6. C

A rate constant relates changes in the concentration of reagents to changes in reaction rate. The rate constant is a function of a variety of determinants of reaction rate such as temperature and activation energy. The factors underlying the rate constant for a reaction appear in the Arrhenius equation.

$$k = Ae^{\frac{-E_a}{RT}}$$

T is the absolute temperature (in kelvins). E_a is the activation energy for the reaction. A is the pre-exponential factor, a constant for each chemical reaction. A depends on how often molecules collide when all concentrations are 1 mol/L and on whether the molecules are properly oriented when they collide.

7. D

This is an example of a reaction which, though spontaneous, does not occur at an appreciable rate without a catalyst under standard conditions because the activation energy is very high. Though not *thermodynamically stable*, hydrogen and oxygen gas comprise a mixture which is *kinetically stable*. some form of the following:

$$\text{rate} = k [A]^x [B]^y$$

We need to determine what the order of the reaction is with respect to the concentrations of each reagent. Notice that in between trials #1 and #3 (through which $[A]$ is constant), the reaction rate triples when $[B]$ is tripled. Therefore the reaction is first order with regard to $[B]$. Between trials #1 and #2, the concentrations of both species are doubled. We know now that doubling $[B]$, doubles the rate. The actual rate, though, is eight times greater, ie. four times greater

than the effect of doubling [B], so the reaction rate is second order with regard to [A], quadrupling when [A] is doubled.

$$\text{rate} = k [A]^2 [B]$$

9. A

With first order reactions, we can express the time for the concentration of reactant to be halved.

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.69}{k}$$

$$t_{1/2} = \frac{6.9 \times 10^{-1}}{6.9 \times 10^{-4} \text{ s}^{-1}} = 1.0 \times 10^3 \text{ s}$$

The half-life is 1.0×10^3 s. This gives us what we need to determine the approximate amount of time for the concentration to decrease to $\frac{1}{30}$ of its original value. Because $\frac{1}{30}$ is approximately $\frac{1}{32}$, the time required will be approximately five half lives for that amount of reagent to be remaining or 5.0×10^3 s.

10. B

On the reaction coordinate we can see that the enthalpy of the products 'E' is lower than the enthalpy of the reagents 'A'. The enthalpy decreased. Heat flowed out. The reaction is exothermic.

Additionally, because the rate of the reaction only depends on the concentration of alkyl halide, the rate determining step is 'unimolecular'.

11. B

Stage 'B' represents the transition state on the way to the intermediate 'C' (the carbocation formed after the departure of the leaving group). The energy barrier to achieve the highest energy transition state in a reaction is the activation energy of the reaction. This is the rate determining step of the reaction.

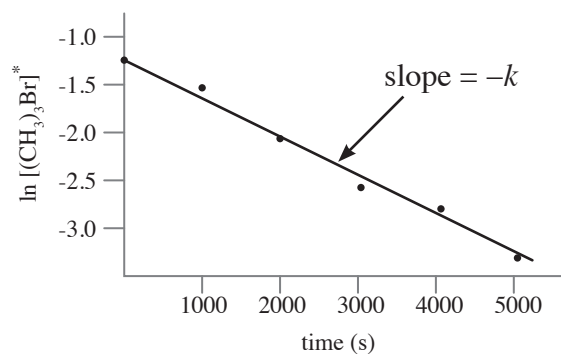
12. A

The reaction described in the passage is SN1 substitution. The rate determining step is the departure of the leaving group, in this case, bromide, to form

a carbocation. The carbocation will be subsequently captured by the nucleophilic hydroxide.

13. A

An important skill for the exam to be able to associate a formula in a linear form with a linear plot. First order kinetics represents a classic of this genre. In the given equation in slope-intercept form, the slope is $-k$.



We need to choose two points on the line to graphically determine the slope. The points (0, -1.25) and (5000, -3.25) look convenient.

$$\begin{aligned} -k = \text{slope} &= \frac{\text{rise}}{\text{run}} = \frac{(-3.25 - -1.25)}{(5000\text{s} - 0\text{s})} \\ &= 4.0 \times 10^{-4} \text{ s}^{-1} \end{aligned}$$

14. A

'I' is correct. There are four moles of gas on the reagent side of the reaction and only two moles on the product side. Le Chatelier's principle teaches us that increasing the pressure for such a reaction at equilibrium will shift the equilibrium to favor the side of the reaction with a lower volume, ie. fewer moles of gas.

'II' is incorrect. Although improvements in the performance of the catalyst could definitely increase the *practical yield* of the reaction, the question is specific to the *equilibrium yield* of NH₃ in the gases leaving the reaction vessel as described in the passage. Across the entire span of general science, one of the most generative themes for the MCAT writers is the

distinction between reasoning based on principles is of chemical thermodynamics and reasoning based on principles of chemical kinetics. One of the most common questions, often in the context of enzyme activity, turns on the understanding that a catalyst does not change the equilibrium constant of a reaction. The equilibrium constant depends on the standard free energy change of the reaction.

$$K = e^{\frac{-\Delta G^\circ}{RT}}$$

This is thermodynamics reasoning. It's about state functions. Free energy is a state function. Free energy is built out of the state functions of the system whose change affects the entropy of the whole universe. If the entropy of the universe increases, a process is spontaneous. Things are changing. Events move forward and the change to the universe isn't reversible. Everyone knows the formula $G = H - TS$. Free energy is a state function built out of the enthalpy, temperature and entropy of the system.

While we're on the topic, it's worthwhile to ask how does the free energy keep track of the entropy of the whole universe? These state functions of the system change, the enthalpy and entropy of the system, and this tells us something about the whole universe? How does that work? The universe is basically what we're calling the system plus everything else that's not the system. This other part of the universe that's not the system we refer to as *the surroundings*.

Free energy keeps track of the entropy of the universe. We're keeping track of the entropy of the system plus the entropy of the surroundings. The entropy of the system is ΔS . The change in the entropy of the surroundings is $-\Delta H \div T$. The entropy of the surroundings is affected by the heat flow that occurs in the reaction. If the reaction moving in some direction increases the entropy of the universe through those two combined effects, the reaction will be moving towards some definite state that is different than the state it's currently in. It will move towards some equilibrium state. Free energy gives us a way to keep track of just how the movement towards equilibrium in a chemical reaction is increasing the entropy of the universe. That's the free energy change. That's

how it works as a state function. Free energy is a state function of the system that when it changes means the entropy of the universe is changing.

That's thermodynamic thinking. It's about state functions. A change in a state function is *path independent*. The free energy change doesn't depend on the path between two states of the system. The two pillars of understanding that help you understand all chemical change are chemical thermodynamics and chemical kinetics. Chemical thermodynamics doesn't depend on the path while the kinetics of a reaction are path dependent.

In summary, why doesn't a catalyst affect the state of equilibrium? A catalyst doesn't affect the chemical thermodynamics. It only changes the path of the reaction. It affects the kinetics. The presence of a catalyst changes neither the initial nor the final state of a reaction process. *A catalyst gives a reaction a different path from reactants to products and vice versa*. It doesn't change the free energy comparison of any state of the system with any other state, nor does it have anything to do with what the equilibrium state of the reaction is. That's determined by the standard free energy change of the reaction which is independent of the activation energy of any particular reaction path. That's why choice 'II' is incorrect.

Choice 'III' is incorrect as well. The forward direction of the reaction is exothermic. ΔH is negative. Increasing the temperature shifts the position of equilibrium in favor of the endothermic direction of the reaction. This would decrease the equilibrium yield of the NH_3 in the gases leaving the reaction vessel.

15. C

The effect of temperature change on a rate constant can be seen in the Arrhenius equation.

$$k = Ae^{\frac{-E_A}{RT}}$$

Increasing temperature increases the rate constant (leading to a smaller negative exponent in the equation). To see it more directly, think of the Maxwell-Boltzmann distribution of the reactant-product mixture. Increasing temperature increases the frac-

tion in the vessel with sufficient energy to cross the activation energy barrier. The increase in the rate constant is reflected in an exponential increase in reaction rate with Kelvin temperature.

Regarding choice 'A'. Increasing temperature will lower the equilibrium constant. The choice is true in isolation, but to decrease the equilibrium constant is obviously not the reason the reaction is carried out at high temperature. That would lower the equilibrium yield. The reason for high temperature is to promote the kinetics and increase the practical yield of our reactor.

16. A

A reaction takes place on the surface of the solid iron catalyst and the nitrogen. Formation of the intermediate gives a path for the reaction. The surface area of a solid catalyst has a strong influence on the number of available active sites for catalyst-reagent intermediate to form. In industrial practice, solid catalysts are often porous to maximize surface area.

17. C

At the end of the reaction process, the catalyst must have returned to its initial state. Otherwise, it wouldn't be a catalyst. It would be a reagent appearing in the stoichiometry.

