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.

$$rate = k\,[\mathrm{A}]$$

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.

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

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.

$$k = A\mathrm{e}^{\frac{-E_A}{RT}}$$

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:

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

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 mount of time for the concentration to decrease to $1/30$ of its original value. Because $1/30$ is approximately $1/32$, 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

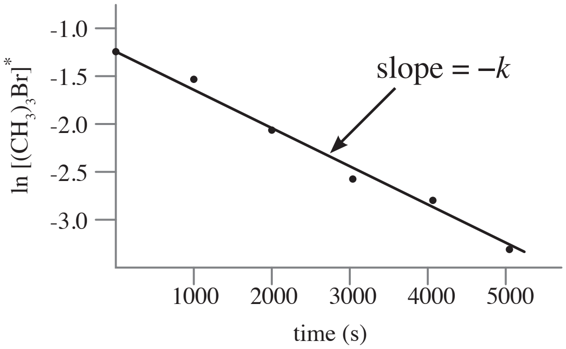
Stage 'B' represents the transition state on the way to the intermediate 'C' (the carbocation formed after the departure of the leaving group). The energy barrier to achieve the highest energy transition state in a reaction is the activation energy of the reaction. This is the rate determining step of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

$$-k = \textit{slope} = \frac{\text{rise}}{\text{run}} = \frac{(-3.25 - -1.25)}{(5000\text{s} - 0\text{s})}$$

$$= 4.0 \times 10^{-4}\,\text{s}^{-1}$$

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 NH_3 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 fraction 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.