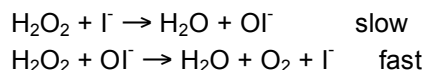


Use the following information to answer questions 1 through 3

A proposed mechanism for the decomposition of hydrogen peroxide by iodide ion is:



1. The rate law consistent with this mechanism is:

- (A)  $R = k[\text{H}_2\text{O}_2]^2$  (D)  $R = k[\text{H}_2\text{O}_2]^2[\text{I}^-]/[\text{H}_2\text{O}]$   
 (B)  $R = k[\text{H}_2\text{O}_2][\text{I}^-]$  (E)  $R = k[\text{H}_2\text{O}][\text{OI}^-]/[\text{H}_2\text{O}_2][\text{I}^-]$   
 (C)  $R = k[\text{H}_2\text{O}][\text{OI}^-]$

*The rate limiting step is the first reaction, in which one  $\text{H}_2\text{O}_2$  reacts with one  $\text{I}^-$ .*

2. A catalyst in this mechanism is:

- (A)  $\text{I}^-$  (C)  $\text{O}_2$  (E) there is none  
 (B)  $\text{OI}^-$  (D)  $\text{H}_2\text{O}$

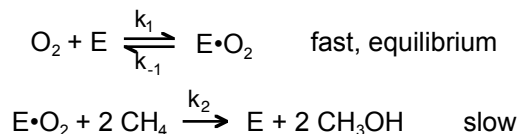
*$\text{I}^-$  is the catalyst. Overall, it is not produced or consumed, but it is added to the reaction and is involved in the rate-limiting step.*

3. An intermediate in this mechanism is:

- (A)  $\text{I}^-$  (C)  $\text{O}_2$  (E) there is none  
 (B)  $\text{OI}^-$  (D)  $\text{H}_2\text{O}$

*$\text{OI}^-$  is an intermediate. Overall, it's not produced or consumed, and it's not added to the reaction, but is produced by one reaction and consumed by another.*

4. Methanogens are a class of bacteria that metabolize methane. They have an enzyme that allows them to convert methane to methanol. A very simplified mechanism has two steps: First, oxygen binds to the enzyme (E) to produce an enzyme- $\text{O}_2$  complex ( $\text{E}\cdot\text{O}_2$ ), then methane reacts with the  $\text{E}\cdot\text{O}_2$  complex to produce methanol:



What is the rate law for this reaction ? (Note: k is a combination of  $k_1$ ,  $k_{-1}$  and  $k_2$ )

- (A)  $\text{Rate} = k[\text{O}_2][\text{CH}_4][\text{E}]$  (C)  $\text{Rate} = k[\text{O}_2][\text{E}]$  (E)  $\text{Rate} = k[\text{CH}_4]^2$   
 (B)  $\text{Rate} = k[\text{O}_2][\text{CH}_4]^2[\text{E}]$  (D)  $\text{Rate} = k[\text{E}][\text{CH}_4]^2$

*Rate law is determined by rate-limiting (slow) step, so*

$$\text{Rate} = k_2[\text{E}\cdot\text{O}_2][\text{CH}_4]^2$$

*However,  $\text{E}\cdot\text{O}_2$  is an intermediate, and it's best to write rate laws in terms of reactants (and products, if necessary), so express  $[\text{E}\cdot\text{O}_2]$  in terms of other concentrations. From reaction 1,  $k_1[\text{O}_2][\text{E}] = k_{-1}[\text{E}\cdot\text{O}_2]$ , so  $[\text{E}\cdot\text{O}_2] = (k_1/k_{-1}) [\text{O}_2][\text{E}]$*

Plug this in to the rate equation to get

$$\text{Rate} = k_2(k_1/k_{-1}) [\text{O}_2][\text{E}][\text{CH}_4]^2$$

5. A reaction with an activation energy of  $E_a = 100 \text{ kJ/mol}$  has a rate constant  $k = 10 \text{ s}^{-1}$  at a temperature of  $20^\circ\text{C}$ . What is the rate of this reaction (in  $\text{s}^{-1}$ ) at  $50^\circ\text{C}$ ?

(A) 7.1

(B) 10.0

(C) 14.0

(D) 450

(E) 3300

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

$T_1$  is  $20^\circ\text{C} = 293 \text{ K}$ , and  $T_2$  is  $50^\circ\text{C} = 323 \text{ K}$ .

$$\ln\left(\frac{k_2}{10 \text{ s}^{-1}}\right) = -\frac{100 \text{ kJ/mol}}{8.314 \times 10^{-3} \text{ kJ/(molK)}}\left(\frac{1}{323 \text{ K}} - \frac{1}{293 \text{ K}}\right)$$

$$\ln\left(\frac{k_2}{10 \text{ s}^{-1}}\right) = -1.203 \times 10^4 \text{ K} \left(0.003095975 \frac{1}{\text{K}} - 0.00341297 \frac{1}{\text{K}}\right)$$

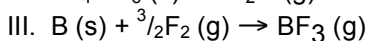
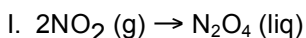
$$\ln\left(\frac{k_2}{10 \text{ s}^{-1}}\right) = -1.203 \times 10^4 \text{ K} \left(-0.00031699 \frac{1}{\text{K}}\right)$$

$$\ln\left(\frac{k_2}{10 \text{ s}^{-1}}\right) = 3.8134$$

$$\frac{k_2}{10 \text{ s}^{-1}} = e^{3.8134} = 45.3$$

$$k_2 = (10 \text{ s}^{-1})(45.3) = 453 \text{ s}^{-1}$$

6. Predict the sign of  $\Delta S^\circ_{\text{rxn}}$  for the three reactions below:



	I	II	III
(A)	+	+	+
(B)	-	+	-
(C)	+	+	-

	I	II	III
(D)	-	-	+
(E)	+	-	+

A reaction that produces more moles of gas than it consumes is entropy favored ( $\Delta S > 0$ ), so reactions I and III have  $\Delta S < 0$ , reaction II has  $\Delta S > 0$

7. Under what circumstances will  $\Delta G$  for a chemical reaction always be positive?

(A) An endothermic reaction that generates fewer moles of gaseous products than gaseous reactants.

(B) An exothermic reaction that generates solids from liquid reactants.

(C) An exothermic reaction that generates fewer moles of gaseous products than gaseous reactants.

(D) An endothermic reaction that generates more moles of gaseous products than gaseous

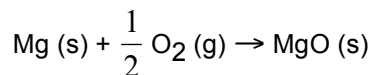
reactant.

(E) both (B) and (C) above.

$$\Delta G = \Delta H - T\Delta S$$

For  $\Delta G$  to be positive (at all temperatures),  $\Delta H$  must be positive (endothermic reaction) and  $-T\Delta S$  must be positive, so  $\Delta S$  must be negative (entropy disfavored: generate fewer moles of gas in products than in reactants)

For questions 8 and 9 use the thermodynamic data at 298 K given below and the following reaction.



	$\Delta H^\circ_f$ (kJ/mol)	$\Delta G^\circ_f$ (kJ/mol)	$S^\circ$ (J/mol K)
Mg (s)	0	0	33
O <sub>2</sub> (g)	0	0	205
MgO (s)	-602	-569	27

8. What is  $\Delta S^\circ_{\text{rxn}}$  in J/mol K?

- (A) -175                      (C) -27                      (E) -108  
(B) 27                        (D) 108

$$\Delta S^\circ = \sum S^\circ(\text{products}) - \sum S^\circ(\text{reactants})$$

$$\Delta S^\circ_{\text{rxn}} = 27 - 33 - \left(\frac{1}{2}\right)(205) = -108.5 \text{ J/(mol K)}$$

Note that  $\Delta S^\circ_{\text{rxn}}$  is negative, as reaction is entropy disfavored (consume  $\frac{1}{2}$  mol gas, produce 0 moles gas)

9. If magnesium metal is ignited in oxygen atmosphere in an isolated system at 300 K:

- (A) no reaction will take place because  $\Delta S^\circ_{\text{rxn}}$  is negative.  
(B) no reaction will take place because  $\Delta S_{\text{surroundings}} = 0$ .  
(C) a reaction will take place because  $\Delta S_{\text{universe}}$  is positive.  
(D) no reaction will take place because  $\Delta G^\circ_{\text{reaction}}$  is positive.  
(E) a reaction will take place because  $\Delta S_{\text{surroundings}}$  is negative.

A reaction is spontaneous if  $\Delta S_{\text{universe}}$  is positive (or equivalently, if  $\Delta G^\circ_{\text{reaction}}$  is negative).

Recall that  $\Delta S_{\text{universe}} = \Delta S_{\text{reaction}} + \Delta S_{\text{surroundings}}$  and

$$\Delta S_{\text{surroundings}} = -\frac{\Delta H_{\text{rxn}}}{T}$$

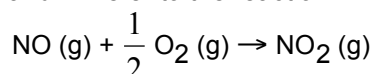
$$\Delta H_{\text{rxn}} = -602 - (0) - \left(\frac{1}{2}\right)(0) = -602 \text{ kJ/mol}$$

$$\Delta S_{\text{surroundings}} = -(-602 \text{ kJ/mol})/300 \text{ K} = 2.007 \text{ kJ/(mol K)} = 2007 \text{ J/(mol K)}$$

$$\text{So, } \Delta S_{\text{universe}} = -108 \text{ J/(mol K)} + 2007 \text{ J/(mol K)} = 1899 \text{ J/(mol K)}$$

The reaction is so exothermic that  $\Delta S_{\text{surroundings}}$  is very large and positive, completely overwhelming (small, negative)  $\Delta S_{\text{universe}}$

Questions 10 and 11 refer to the reaction



for which  $\Delta H_{\text{rxn}} = -57 \text{ kJ/mol}$  and  $\Delta S_{\text{rxn}} = -73 \text{ J/(mol K)}$  at 298 K.

10. What is  $\Delta G_{\text{rxn}}$  in kJ/mol at 25 °C for this reaction?

- (A) -35 (B) -79 (C) -22 (D) 68 (E) 85

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G = -57 \text{ kJ/mol} - (298 \text{ K}) (-73 \times 10^{-3} \text{ kJ/(mol K)})$$

$$\Delta G = -35 \text{ kJ/mol}$$

11. What is the temperature in °C above/below which this reaction would have  $K_p$  greater than one?

- (A) below 508 °C (D) above 128 °C  
(B) above 508 °C (E) There is none.  
(C) below 128 °C

$K_p = 1$  if  $\Delta G = 0$ , and  $K_p > 1$  when  $\Delta G$  is negative. Find  $T$  for which  $\Delta G = 0$ :

$$\Delta G = \Delta H - T\Delta S = 0$$

$$-57 \text{ kJ/mol} - T(-73 \times 10^{-3} \text{ kJ/(mol K)}) = 0$$

$$(0.073 \text{ kJ/mol K}) T = 57 \text{ kJ/mol}$$

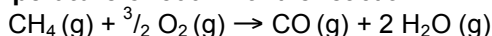
$$T = (57 \text{ kJ/mol}) / (0.073 \text{ kJ/mol K}) = 781 \text{ K, or } 508 \text{ °C}$$

If  $T$  is below 508 °C, then  $\Delta G$  is negative (see #10), and  $K_p > 1$ .

Thermodynamic values for Problems 12 and 13:

Species	$\Delta H_f^\circ(298\text{ K})$ kJ/mol	$S^\circ(298\text{ K})$ J/(K mol)	$\Delta G_f^\circ(298\text{ K})$ kJ/mol
C(s, graphite)	0	5.6	0
CH <sub>4</sub> (g)	-74.87	186.26	-50.8
C <sub>2</sub> H <sub>4</sub> (g)	52.47	219.36	68.35
C <sub>2</sub> H <sub>6</sub> (g)	-83.85	229.2	-31.89
CO(g)	-110.53	197.67	-137.17
CO <sub>2</sub> (g)	-393.51	213.74	-394.36
H <sub>2</sub> (g)	0	130.7	0
H <sub>2</sub> O(g)	-241.83	188.84	-228.59
H <sub>2</sub> O(l)	-285.83	69.95	-237.15
NO(g)	90.29	210.76	86.58
NO <sub>2</sub> (g)	33.1	240.04	51.23
O <sub>2</sub> (g)	0	205.07	0

12. Use the thermodynamic values above to calculate  $\Delta G_{\text{rxn}}$  in kJ/mol  
at a temperature of 500 K for the reaction



- (A) -275      (B) -280      (C) -479      (D) -544      (E) -560

$\Delta G = \Delta H - T\Delta S$ , so calculate  $\Delta H$  and  $\Delta S$  for the reaction using the table, then calculate  $\Delta G$ . Note that the  $\Delta G$  values given in the table are at 298 K, so you can't just use them (as  $\Delta G$  depends on temperature !)

$$\Delta H = -110.53 + 2(-241.83) - [-74.87 + (3/2)(0)] = -519.32 \text{ kJ/mol}$$

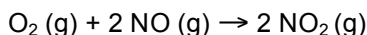
$$\Delta S = 197.67 + 2(188.84) - [186.26 + (3/2)(205.07)] = 81.49 \text{ J/mol K}$$

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G = -519.32 \text{ kJ/mol} - (500 \text{ K})(81.49 \times 10^{-3} \text{ kJ/mol K})$$

$$\Delta G = -560.1 \text{ kJ/mol}$$

13. Use the thermodynamic values at the top of this page to calculate the equilibrium constant  $K_p$  at 298 K for the reaction



- (A)  $4.0 \times 10^{-13}$       (B)  $6.4 \times 10^{-7}$       (C)  $4.8 \times 10^{-4}$       (D)  $1.6 \times 10^6$       (E)  $2.5 \times 10^{12}$

First calculate  $\Delta G$  for the reaction. Since you want a value at 298 K, can use  $\Delta G_f^\circ(298\text{ K})$  values directly:

$$\Delta G_{\text{rxn}}^\circ = \sum G_f^\circ(\text{products}) - \sum G_f^\circ(\text{reactants})$$

$$\Delta G_{\text{rxn}}^\circ = 2(51.23) - [0 + 2(86.58)] = -70.7 \text{ kJ/mol}$$

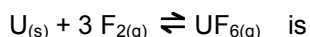
$$K_p = e^{-\Delta G/RT}$$

$$-\Delta G/RT = -(-70.7 \text{ kJ/mol})/[(8.314 \times 10^{-3} \text{ kJ/mol})(298 \text{ K})] = 28.54$$

$$\text{So, } K_p = e^{28.54} = 2.5 \times 10^{12}$$

Recall that  $\Delta G$  is negative, so  $K_p > 1$ .

14. The equilibrium constant  $K_c$  for the reaction



$$(A) \quad K_c = \frac{[\text{UF}_6]}{[\text{U}][\text{F}_2]}$$

$$(D) \quad K_c = \frac{[\text{UF}_6]}{[\text{F}_2]}$$

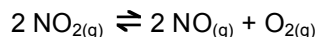
$$(B) K_c = \frac{[UF_6]}{[U][3F_2]} \quad (E) K_c = \frac{[UF_6]}{[F_2]^3}$$

$$(C) K_c = \frac{[UF_6]}{[U][F_2]^3}$$

Don't include U, as it's a solid, so the answer is (E)

15. At a particular temperature, an equilibrium mixture contains the following concentrations of gases:

$[NO_2] = 0.32 \text{ M}$ ,  $[NO] = 10^{-4} \text{ M}$ ,  $[O_2] = 0.045 \text{ M}$ . What is the equilibrium constant  $K_c$  for the reaction

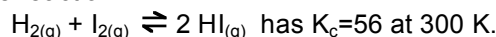


- (A)  $4.5 \times 10^{-10}$  (D)  $1.4 \times 10^{-5}$   
 (B)  $1.4 \times 10^{-9}$  (E)  $4.5 \times 10^{-5}$   
 (C)  $4.4 \times 10^{-9}$

$$K_c = \frac{[NO]^2[O_2]}{[NO_2]^2}$$

$$K_c = (10^{-4})^2 (0.045) / (0.32)^2 = 4.4 \times 10^{-9}$$

16. The reaction



A 1 liter flask is filled with 0.2 moles of  $H_2$ , 0.2 moles of  $I_2$  and 0.4 moles of HI.

Will any reaction occur? If so, is HI produced or consumed?

- (A) No reaction will occur  
 (B) A reaction will occur; HI will be produced  
 (C) A reaction will occur; HI will be consumed

$$Q = \frac{[HI]^2}{[H_2][I_2]}$$

$$Q = (0.4)^2 / [(0.2)(0.2)] = 4$$

$Q < K_c$ , so as the reaction proceeds, Q will become larger (eventually reaching  $K_c$  at equilibrium), for Q to increase, need to make more HI product, less  $H_2$  and  $I_2$  reactant

17. 2 moles of  $NH_4Cl_{(s)}$  are put into an evacuated 1 liter container at 550 K, and the following reaction occurs:



At equilibrium,  $[NH_{3(g)}] = 2.2 \times 10^{-3} \text{ M}$ . What is  $K_c$  for the reaction?

- (A)  $2.2 \times 10^{-3}$  (B)  $2.4 \times 10^{-6}$  (C)  $4.8 \times 10^{-6}$  (D)  $9.6 \times 10^{-6}$  (E)  $1.9 \times 10^{-5}$

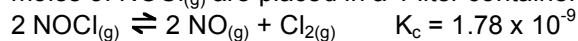
$K_c = [NH_3][HCl]$  (note that  $NH_4Cl$  isn't in  $K_c$ , as it's a solid).

	$NH_4Cl$	$NH_3$	$HCl$
Initial	2	0	0
Change	-x	x	x
Equil.	2-x	x	x

So, if  $[NH_3] = 2.2 \times 10^{-3} \text{ M}$  at equilibrium,  $x = [HCl] = 2.2 \times 10^{-3} \text{ M}$

$$K_c = (2.2 \times 10^{-3})(2.2 \times 10^{-3}) = 4.84 \times 10^{-6}$$

18. 0.1 moles of  $\text{NOCl}_{(g)}$  are placed in a 1 liter container at 372 K. The following reaction occurs:



What is the  $\text{Cl}_2$  concentration at equilibrium?

(Hint:  $K_c$  is so small that very little of the  $\text{NOCl}$  decomposes)

- (A)  $6.67 \times 10^{-6}$  (D)  $1.64 \times 10^{-4}$   
 (B)  $1.33 \times 10^{-5}$  (E)  $3.28 \times 10^{-4}$   
 (C)  $2.66 \times 10^{-5}$

	$\text{NOCl}$	$\text{NO}$	$\text{Cl}_2$
Initial	0.1	0	0
Change	-2x	2x	x
Equil.	0.1-2x	2x	x

$$K_c = \frac{[\text{NO}]^2 [\text{Cl}_2]}{[\text{NOCl}]^2}$$

$$K_c = \frac{(2x)^2 (x)}{(0.1-2x)^2} = 1.78 \times 10^{-9}$$

Because  $K_c$  is so small, it's probably a good approximation to assume that  $x$  is small (note that that's what the hint says). If  $x$  is small, then

$0.1 - 2x$  is approximately 0.1, so

$$\frac{(2x)^2 (x)}{(0.1)^2} = 1.78 \times 10^{-9}$$

$$4x^3 / 0.01 = 1.78 \times 10^{-9}$$

$$4x^3 = 1.78 \times 10^{-11}$$

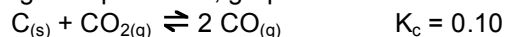
$$x^3 = 4.45 \times 10^{-12}$$

$$x = 1.64 \times 10^{-4}$$

Note that this is much less than 0.1, so our approximation is good.

Since  $[\text{Cl}_2] = x$ ,  $[\text{Cl}_2] = 1.64 \times 10^{-4} \text{ M}$

19. At high temperatures, graphite reacts with  $\text{CO}_2$  to produce  $\text{CO}$ :



If 0.07 moles of  $\text{CO}_2$  are placed in a 1 liter container, what is the  $\text{CO}$  concentration at equilibrium?

(Note:  $K_c$  is fairly large, so a significant amount of the  $\text{CO}_2$  reacts)

- (A) 0.022 M (D) 0.062 M  
 (B) 0.031 M (E) 0.13 M  
 (C) 0.043 M

	$\text{CO}_2$	$\text{CO}$
Initial	0.07	0
Change	-x	2x
Equil.	0.07-x	2x

$$K_c = \frac{[\text{CO}]^2}{[\text{CO}_2]} \text{ (note that C is a solid, so it's not in } K_c)$$

$$K_c = \frac{(2x)^2}{(0.07 - x)} = 0.10$$

Could assume that  $x$  is small, but this turns out to be a poor assumption (note that  $K_c$  is not very small; also, the hint says that a significant amount of  $\text{CO}_2$  reacts, so  $x$  isn't small).

So, solve the quadratic equation without approximations:

$$4x^2 = 0.10 (0.07 - x)$$

$$4x^2 + 0.1x - 0.007 = 0$$

$$Ax^2 + Bx + C = 0$$

$$x = \frac{-B \pm \sqrt{B^2 - 4AC}}{2A}$$

$$x = \frac{-0.1 \pm \sqrt{(0.1)^2 - 4(4)(-0.007)}}{2(4)}$$

$$x = \frac{-0.1 \pm \sqrt{0.122}}{8}$$

$$x = -0.056, 0.0312$$

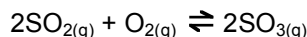
The negative root is unphysical, so  $x = 0.0312 \text{ M}$

$$[\text{CO}] = 2x = 0.0624 \text{ M}$$

(I gave partial credit for (B))

Questions 20 through 22 refer to the following gas phase equilibrium for which  $K_c = 12$  at 1100K and

$$\Delta H^\circ = -198 \text{ kJ/mol.}$$



20. Increasing the concentration (the pressure) on an equilibrium mixture by decreasing the volume at constant temperature would cause:

- (A) K to decrease and the amount of  $\text{O}_{2(g)}$  to increase.
- (B) K to decrease and the amount of  $\text{O}_{2(g)}$  to decrease.
- (C) K to increase and the amount of  $\text{O}_{2(g)}$  to decrease.
- (D) no change in K but an increase in the amount of  $\text{O}_{2(g)}$ .
- (E) no change in K but a decrease in the amount of  $\text{O}_{2(g)}$ .

Don't change temperature, so don't change K.

Increase pressure, so reaction proceeds in a direction that decreases pressure, reacting to make fewer moles of gas, so make more  $\text{SO}_3$  (consuming  $\text{SO}_2$  and  $\text{O}_2$ )

21. Addition of  $\text{SO}_3(g)$  to an equilibrium mixture of the three gases at constant volume and temperature would cause:

- (A) K to decrease and the amount of  $\text{O}_2(g)$  to increase.
- (B) K to decrease and the amount of  $\text{O}_2(g)$  to decrease.
- (C) K to increase and the amount of  $\text{O}_2(g)$  to decrease.
- (D) no change in K but an increase in the amount of  $\text{O}_{2(g)}$ .
- (E) no change in K but a decrease in the amount of  $\text{O}_2(g)$ .

Don't change temperature, so don't change K.

Add product, so reaction proceeds in a direction that consumes product ( $\text{SO}_3$ ), forming more  $\text{O}_2$  and  $\text{SO}_2$

22. An equilibrium mixture of the three gases is initially at 1100K. The temperature is increased to 1300K, at constant volume. This would cause:

- (A) K to decrease and the amount of  $\text{O}_2(g)$  to increase.
- (B) K to decrease and the amount of  $\text{O}_2(g)$  to decrease.
- (C) K to increase and the amount of  $\text{O}_2(g)$  to decrease.
- (D) no change in K but an increase in the amount of  $\text{O}_{2(g)}$ .
- (E) no change in K but a decrease in the amount of  $\text{O}_2(g)$ .

Change temperature, so change K.

Increase temperature, so reaction proceeds in a direction that uses heat (in the endothermic direction). Production of  $\text{SO}_3$  is exothermic, so consume  $\text{SO}_3$ , producing  $\text{SO}_2$  and  $\text{O}_2$ . Make less product, more reactant, so K decreases.