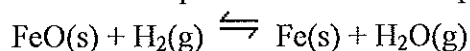


Now with Solutions!

15.1. Which of the following is not part of the equilibrium constant expression, K_c ?

- A) Solids B) Liquids C) Dissolved species D) A and B E) B and C

15.2. Which is the correct equilibrium constant expression for the following reaction?



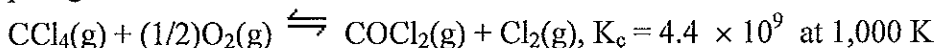
- A) $K_c = [\text{H}_2\text{O}] / [\text{H}_2]$ D) $K_c = [\text{Fe}][\text{H}_2\text{O}] / [\text{Fe}_2\text{O}_3][\text{H}_2]$
 B) $K_c = [\text{Fe}][\text{H}_2\text{O}] / [\text{Fe}_2\text{O}_3]$ E) $K_c = [\text{H}_2] / [\text{H}_2\text{O}]$
 C) $K_c = [\text{Fe}_2\text{O}_3][\text{H}_2] / [\text{Fe}][\text{H}_2\text{O}]$

15.3. The equilibrium constant expression for the reaction



- A) $K_c = [\text{Br}_2][\text{Cl}_2] / [\text{BrCl}_3]$ D) $K_c = [\text{BrCl}_3]^2 / [\text{Br}_2][\text{Cl}_2]^3$
 B) $K_c = [\text{Br}_2][\text{Cl}_2]^5 / [\text{BrCl}_3]^2$ E) $K_c = 2[\text{BrCl}_3]^2 / ([\text{Br}_2] \times 3[\text{Cl}_2]^3)$
 C) $K_c = [\text{Br}_2][\text{Cl}_2]^3 / [\text{BrCl}_3]^2$

15.4. Carbon tetrachloride reacts at high temperatures with oxygen to produce two toxic gases, phosgene and chlorine.



Calculate K_c for the reaction $2\text{CCl}_4\text{(g)} + \text{O}_2\text{(g)} \rightleftharpoons 2\text{COCl}_2\text{(g)} + 2\text{Cl}_2\text{(g)}$.

- A) 4.4×10^9 B) 8.8×10^9 C) 1.9×10^{10} D) 1.9×10^{19} E) 2.3×10^{-10}

15.5. 1.75 moles of H_2O_2 were placed in a 2.50 L reaction chamber at 307°C . After equilibrium was reached, 1.20 moles of H_2O_2 remained. Calculate the equilibrium constant, K_c , for the reaction $2\text{H}_2\text{O}_2\text{(g)} \rightleftharpoons 2\text{H}_2\text{O(g)} + \text{O}_2\text{(g)}$.

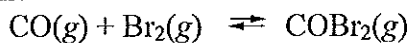
- A) 2.0×10^{-4} B) 2.3×10^{-2} C) 2.4×10^{-3} D) 5.5×10^{-3} E) 3.9×10^{-4}

15.6. Consider the reversible reaction: $2\text{NO}_2\text{(g)} \rightleftharpoons \text{N}_2\text{O}_4\text{(g)}$

If the concentrations of both NO_2 and N_2O_4 are 0.016 mol L^{-1} , what is the value of Q_c ?

- A) 0.016 B) 0.50 C) 1.0 D) 2.0 E) 63

15.7. A mixture 0.500 mole of carbon monoxide and 0.400 mole of bromine was placed into a rigid 1.00-L container and the system was allowed to come to equilibrium. The equilibrium concentration of COBr_2 was 0.233 M . What is the value of K_c for this reaction?



- A) 5.23 B) 1.22 C) 1.165 D) 0.858 E) 0.191

15.8. At 25°C , the equilibrium constant K_c for the reaction



is 0.035. A mixture of 8.00 moles of B and 12.00 moles of C in a 20.0 L container is allowed to come to equilibrium. What is the equilibrium concentration of A?

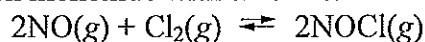
- A) $< 0.100 \text{ M}$ B) 0.339 M C) 0.678 M D) 6.78 M E) 13.56 M

15.9. Consider the equilibrium reaction: $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$

Which of the following correctly describes the relationship between K_c and K_p for the reaction?

- A) $K_p = K_c$
B) $K_p = RT \times K_c$
C) $K_p = (RT \times K_c)^{-1}$

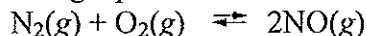
15.10. The equilibrium constant, K_p , has a value of 6.5×10^{-4} at 308 K for the reaction of nitrogen monoxide with chlorine.



What is the value of K_c ?

- A) 2.5×10^{-7}
B) 6.5×10^{-4}
C) 1.6×10^{-2}
D) 1.7
E) None of these choices is correct.

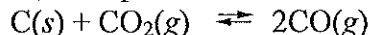
15.11. The reaction of nitrogen with oxygen to form nitrogen monoxide can be represented by the following equation.



At 2000°C, the equilibrium constant, K_c , has a value of 4.10×10^{-4} . What is the value of K_p ?

- A) 2.17×10^{-8}
B) 4.10×10^{-4}
C) 7.65×10^{-2}
D) 7.75
E) None of these choices is correct.

15.12. At 850°C, the equilibrium constant K_p for the reaction



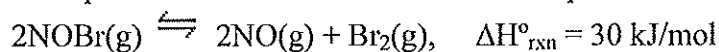
has a value of 10.7. If the total pressure in the system at equilibrium is 1.000 atm, what is the partial pressure of carbon monoxide?

- A) 0.362 atm B) 0.489 atm C) 0.667 atm D) 0.915 atm E) 0.921 atm

15.13. Hydrogen iodide decomposes according to the equation $2\text{HI}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \text{I}_2(\text{g})$, for which $K_c = 0.0156$ at 400°C . 0.550 mol HI was injected into a 2.00 L reaction vessel at 400°C . Calculate the concentration of HI at equilibrium.

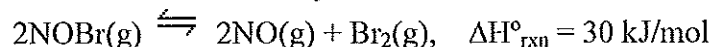
- A) 0.138 M B) 0.220 M C) 0.550 M D) 0.275 M E) 0.0275 M

15.14. For the following reaction at equilibrium, which choice gives a change that will shift the position of equilibrium to favor formation of more products?



- A) Increase the total pressure by decreasing the volume.
B) Add more NO.
C) Remove Br₂.
D) Lower the temperature.
E) Remove NOBr selectively.

15.15. For the following reaction at equilibrium, which one of the changes below would cause the equilibrium to shift to the *left*?



- A) Increase the container volume. D) Add more NOBr.
 B) Remove some NO. E) Decrease the temperature.
 C) Remove some Br₂.

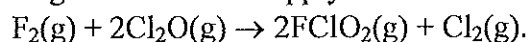
14.1 Butadiene, C₄H₆ (used to make synthetic rubber and latex paints) dimerizes to C₈H₁₂ with a rate law of rate = 0.014 L/(mol·s) [C₄H₆]². What will be the concentration of C₄H₆ after 3.0 hours if the initial concentration is 0.025 M?

- A) 0.0052 M B) 0.024 M C) 43 M D) 190 M E) 0.0000 M

14.2 What is the slope of a plot of ln k vs. 1/T for the Arrhenius equation $k = Ae^{-(E_a/RT)}$?

- A) A B) -k C) -E_a/R D) k E) E_a

14.3 The following initial rate data apply to the reaction



Expt. #	[F ₂] (M)	[Cl ₂ O] (M)	Initial rate (M/s)
1	0.05	0.010	5.0 × 10 ⁻⁴
2	0.05	0.040	2.0 × 10 ⁻³
3	0.10	0.010	1.0 × 10 ⁻³

Which of the following is the rate law (rate equation) for this reaction?

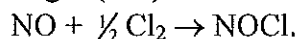
- A) rate = k[F₂]²[Cl₂O]⁴ D) rate = k[F₂][Cl₂O]²
 B) rate = k[F₂]²[Cl₂O] E) rate = k[F₂]²[Cl₂O]²
 C) rate = k[F₂][Cl₂O]

14.4 The thermal decomposition of acetaldehyde, CH₃CHO → CH₄ + CO, is a second-order reaction. The following data were obtained at 518°C.

time, s	Pressure CH ₃ CHO, mmHg
0	364
42	330
105	290
720	132

Calculate the rate constant for the decomposition of acetaldehyde from the above data.

- A) 2.2 × 10⁻³/s D) 6.7 × 10⁻⁶/mmHg·s
 B) 0.70 mmHg/s E) 5.2 × 10⁻⁵/mmHg·s
 C) 2.2 × 10⁻³/mmHg·s

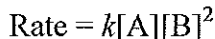
$$\text{NO} + \frac{1}{2} \text{Cl}_2 \rightarrow \text{NOCl}.$$


Expt. #	Rate (M/hr)	NO (M)	Cl ₂ (M)
---------	-------------	--------	---------------------

Expt. #	Rate (M/hr)	NO (M)	Cl ₂ (M)
1	1.19	0.50	0.50
2	4.79	1.00	0.50
3	9.59	1.00	1.00

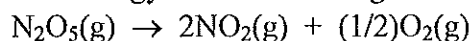
A) $\text{Rate} = k[\text{NO}]$ D) $\text{Rate} = k[\text{NO}]^2$

- A) Rate = $k[\text{NO}]$
 B) Rate = $k[\text{NO}][\text{Cl}_2]^{1/2}$
 C) Rate = $k[\text{NO}][\text{Cl}_2]$
 D) Rate = $k[\text{NO}]^2[\text{Cl}_2]$
 E) Rate = $k[\text{NO}]^2[\text{Cl}_2]^2$

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


A) 3.0 B) 6.0 C) 9.0 D) 18 E) 27

- A) 3.0 B) 6.0 C) 9.0 D) 18 E) 27

$$\text{N}_2\text{O}_5(\text{g}) \rightarrow 2\text{NO}_2(\text{g}) + (1/2)\text{O}_2(\text{g})$$


A) $8.2 \times 10^{-7} \text{ s}^{-1}$ D) $2.2 \times 10^{-2} \text{ s}^{-1}$

- A) $8.2 \times 10^{-7} \text{ s}^{-1}$
 B) $1.9 \times 10^{-5} \text{ s}^{-1}$
 C) $4.2 \times 10^{-5} \text{ s}^{-1}$
 D) $2.2 \times 10^{-2} \text{ s}^{-1}$
 E) None of these

a. Would you expect the rate constant for the back reaction to be smaller

- a. Would you expect the rate constant for the back reaction to be smaller or larger than that for the forward reaction? Explain, briefly.
- b. Draw a fully-labeled reaction energy diagram for this reaction, showing the locations of the reactants, products and transition state.

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- | | | | |
|--------|--------|--------|-------------|
| 15.1. | Ans: D | 15.13. | Ans: B |
| 15.2. | Ans: A | 15.14. | Ans: C |
| 15.3. | Ans: C | 15.15. | Ans: E |
| 15.4. | Ans: D | | |
| 15.5. | Ans: B | 14.1. | Ans: A |
| 15.6. | Ans: E | 14.2. | Ans: C |
| 15.7. | Ans: A | 14.3. | Ans: C |
| 15.8. | Ans: C | 14.4. | Ans: D |
| 15.9. | Ans: B | 14.5. | Ans: D |
| 15.10. | Ans: C | 14.6. | Ans: E |
| 15.11. | Ans: B | 14.7. | Ans: A |
| 15.12. | Ans: E | 14.8. | On your own |

15-1 SOLIDS + LIQUIDS CONCENTRATIONS ARE CONSTANT
SO BECOME PART OF K "D"

15-2 LEAVE OUT SOLIDS, CHOOSE "A"

15-3 RAISE CONCENTRATIONS TO THE POWER OF
STOICHIOMETRY ie $3\text{Cl}_2(\text{g})$ is $[\text{Cl}_2]^3$
CHOOSE "C"

15-4 HERE WE DOUBLED EVERYTHING SO $K'_c = K_c^2 = (4.4 \times 10^9)^2$ FIRST REACTION
BECAUSE $\frac{[\text{Cl}_2]^2 [\text{COCl}_2]^2}{[\text{CO}]^2 [\text{O}_2]}$ IS $\left(\frac{[\text{Cl}_2] [\text{COCl}_2]}{[\text{CO}] [\text{O}_2]^{1/2}} \right)^2$ DOUBLED RXN = 1.9×10^{19} "D"

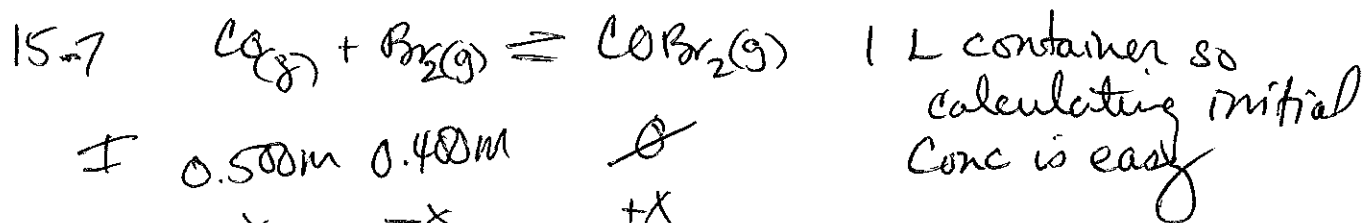
15-5 $2\text{H}_2\text{O}_2(\text{g}) \rightleftharpoons 2\text{H}_2\text{O}(\text{g}) + \text{O}_2(\text{g})$ $K_c = \frac{[\text{H}_2\text{O}]^2 [\text{O}_2]}{[\text{H}_2\text{O}_2]^2}$ CAREFUL!
1.75 mol / 2.5 L ← CALCULATE $[\text{H}_2\text{O}_2]$ THESE ARE CONCENTRATIONS
1.20 mol / 2.5 L = 0.48 M @ EQUIL. for H_2O_2

	0.700 M	0	0
I			
C	-2x	+2x	+x
E	0.48 M	+2x	+x

Find x
 $0.700 - 2x = 0.48$
 $-2x = -0.22$
 $x = 0.11$

$[\text{H}_2\text{O}] = 2x = 0.22$
 $[\text{O}_2] = x = 0.11$
 $K_c = \frac{(0.22)^2 (0.11)}{(0.48)^2}$
 $K_c = 2.31 \times 10^{-2}$ "B"

15-6 $Q_c = \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2} = \frac{(0.016)}{(0.016)^2} = 62.5$ "E"

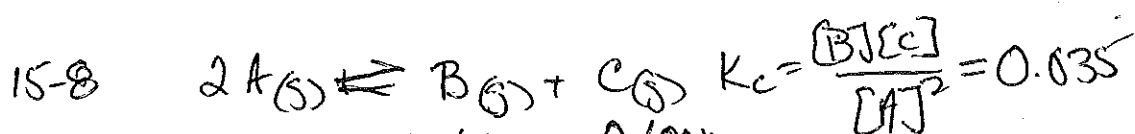


I	0.500M	0.400M	0
C	-x	-x	+x
E	0.500-x	0.400-x	0.233

$$\begin{aligned} 0.500 - 0.233 &= 0.267 \\ 0.400 - 0.233 &= 0.167 \end{aligned}$$

note $x = 0.233$

$$K_c = \frac{[\text{COBr}_2]}{[\text{CO}][\text{Br}_2]} = \frac{0.233}{(0.267)(0.167)} = 5.23 \quad \text{"A"}$$



I	0	0.400M	0.600M
C	+2x	-x	-x
E	2x	0.4-x	0.6-x

Plug into K_c expression

$$0.035 = \frac{[\text{B}][\text{C}]}{[\text{A}]^2} = \frac{(0.4-x)(0.6-x)}{(2x)^2}$$

Now make your quadratic: $4x^2 \cdot 0.035 = 0.24 - 1x + x^2$

$$\frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$[\text{A}] = 2x = 2 \times 0.339$$

$$= 0.678 \quad \text{"C"}$$

$$\begin{aligned} 0.14x^2 &= 0.24 - x + x^2 \\ 0 &= 0.24 - x + 0.86x^2 \end{aligned}$$

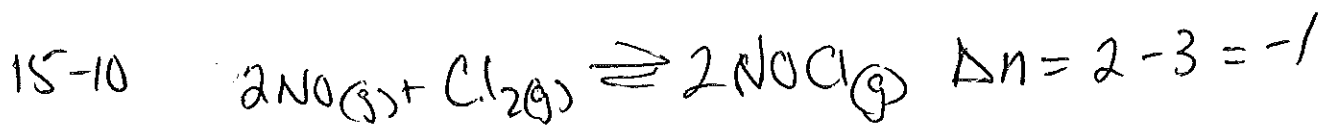
$$x = 0.82x \text{ or } 0.339$$

Larger than starting $[\text{B}]$ or $[\text{C}]$

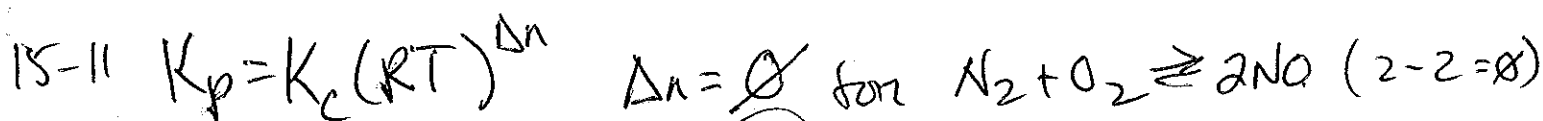
20.0 L container
 $\frac{8 \text{ mol B}}{20.0 \text{ L}} = 0.400 \text{ M}$
 $\frac{12.00 \text{ mol C}}{20 \text{ L}} = 0.600 \text{ M}$

$$15-9 \quad K_p = K_c(RT)^{\Delta n} \quad 1 \text{ N}_2\text{O}_4 \rightleftharpoons 2 \text{NO}_2$$

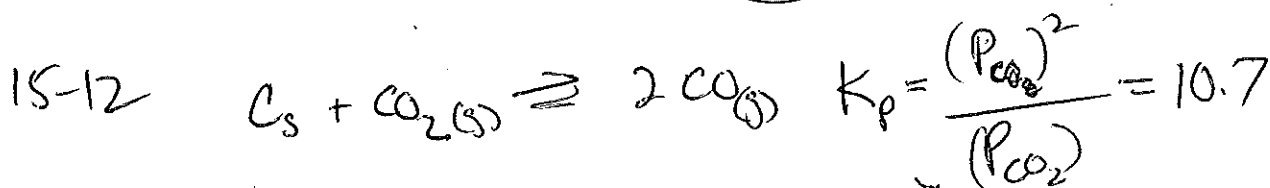
$$K_p = K_c RT \quad \text{"B"} \quad \Delta n = 2 - 1 = 1$$



$$K_p = K_c(RT)^{-1} \text{ so } K_c = K_p RT = 6.5 \times 10^4 \times 0.08206 \times 308 = 1.6 \times 10^8 \quad \text{"C"}$$



$$\text{so } K_p = K_c = 4.1 \times 10^4 \quad \text{"B"}$$



$$P_T = 1 \text{ atm} = P_{\text{CO}} + P_{\text{CO}_2} \quad \text{substitute} \rightarrow \frac{(P_{\text{CO}})^2}{(1 - P_{\text{CO}})} = 10.7$$

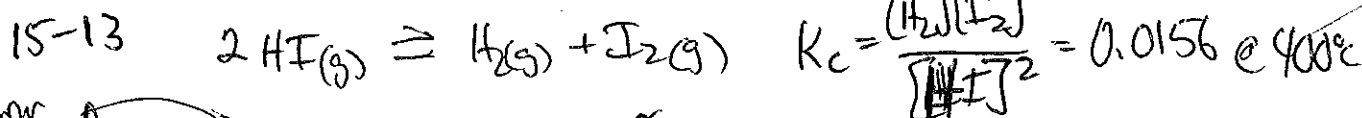
$$P_{\text{CO}_2} = 1 - P_{\text{CO}}$$

$$P_{\text{CO}}^2 = 10.7 - 10.7 P_{\text{CO}}$$

$$P_{\text{CO}}^2 + 10.7 P_{\text{CO}} - 10.7 = 0$$

$$\text{Quadratic for } P_{\text{CO}} \quad P_{\text{CO}} = 0.921$$

CHOOSE "E"



from 0.550 mol in 2.0 L

I	0.275 M	0	0
C	-2x	+x	+x
E	0.275 - 2x	x	x

$$\frac{0.275 - 2(0.0275)}{0.22 \text{ M}} \quad \text{"B"}$$

$$\sqrt{0.0156} = \frac{x \cdot x}{(0.275 - 2x)^2} \Rightarrow \frac{x^2}{(0.275 - 2x)^2} = 0.125$$

$$0.125 = \frac{x}{0.275 - 2x} \quad x = 0.0275$$

15-14 To make more prds, Add reactants (Q becomes less than K)

Remove prds (Q becomes less than K)

Increase pressure, Rxn Responds by going to side w/ fewer moles

for endothermic Rxns, need to add heat to force Rxn towards prds

So choose "C"

15-15 A - increase Vol, Lower P Room for more molecules
Rxn would go right

B - remove NO; Q less than K; goes right

C Remove Br₂ same as B

D Add NOBr Q less than K

Yes! → E Decrease Temp favors Reactants for endothermic Rxns

14-1 2nd order $\left(\frac{1}{[A]_t}\right)^{-1} = \left(k t + \frac{1}{[A]_0}\right)^{-1}$ $k = 0.014 \text{ M}^{-1}\text{s}^{-1}$
 $t = 10800 \text{ s (3 hrs)}$

$$[A]_t = \left(0.014 \cdot 10800 + \frac{1}{0.025}\right)^{-1}$$

$[A]_0 = 0.025 \text{ M}$

$$= (151.2 + 40)^{-1}$$

$$[A]_t = (191.2)^{-1} = \boxed{0.0052 \text{ M}} \quad \text{"B"}$$

14-2 $\ln(k) = \ln(A e^{-E_a/RT})$

$\ln k = \frac{-E_a}{R} \times \frac{1}{T} + \ln A$
 \nwarrow slope "C"

14-3 Rate for F_2 use 1+3 Rate doubles w/ conc double
 first order
 or if you wish $\text{Rate} \propto [F_2]^x$

for Cl_2 use 1+2

conc x4 Rate x4

first order again

"C"

$2 = 2^x$
 $\ln 2 = x \ln 2$
 $1 = \frac{\ln 2}{\ln 2} = x$

14-4 use $\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$ I used $t=0$ & $t=105$

$A = 364 \text{ mmHg}$ $A = 290 \text{ mmHg}$

$\frac{1}{290} = k(105) + \frac{1}{364}$

(Just use 2 points)

$\frac{7.0 \times 10^{-4}}{6.68 \times 10^{-6}} = k$

"D"

14-5 for NO use 1+2 conc doubles Rate x4 Rate $\propto []^x$
 \nwarrow 2nd order $4 = 2^x$ $x=2$

for Cl_2 2+3 conc doubles Rate doubles

first order "D"

$$14-6 \quad \frac{\text{Rate}(2)}{\text{Rate}(1)} = \frac{k(0.3)(0.3)^2}{k(0.1)(0.1)^2} = 27 \quad \text{"E"}$$

k is constant
so cancels

14-7

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad \ln \frac{k_1}{1.35 \times 10^{-4}} = \frac{102000 \text{ J/mol}}{8.314 \text{ J/mol K}} \left(\frac{1}{308} - \frac{1}{273} \right)$$

$$k_2 = 1.35 \times 10^{-4} \text{ s}^{-1} \quad T_2 = 308 \text{ K}$$

$$k_1 = ? \quad T_1 = 273 \text{ K} \quad \left(\frac{k_1}{1.35 \times 10^{-4}} \right) = (-5.10) e$$

$$\frac{k_1}{1.35 \times 10^{-4}} = 0.00606$$

$$k_1 = 8.17 \times 10^{-7} \quad \text{"A"}$$

14-8

