

**Strengthening Students' Math Fluency through
Calculator-Free Chemistry Calculations**

Appendix (42 pages)

Quantitative Problems Selected from
Calculator-Free Multiple-Choice Exams
in Second-Semester General Chemistry

with worked solutions showing pencil-and-paper calculation methods

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Quantitative Problems Selected From Calculator-Free Multiple-Choice Exams in Second-Semester General Chemistry

I. Chemical Equilibrium

(Here, we use K to mean the equilibrium constant expressed in terms of concentrations.)

Problem

- # 1, 2 Ratios of changes from initial to equilibrium concentrations
- # 3, 4 Given K and all but one equilibrium concentration, solve for the unknown one
- # 5, 6 Calculate K for a given reaction, given K values for related reactions
- # 7 Comparing Q (reaction quotient) to K to determine direction of spontaneity
- # 8 Convert K to K_p (the equilibrium constant expressed in terms of partial pressures)
- # 9 Calculate K given the initial concentrations and one equilibrium concentration
- # 10, 11 Calculate the equilibrium concentrations, given K and the initial concentrations
- # 12, 13 Calculate the equilibrium partial pressures, given K_p and the initial partial pressures
- # 14 Use the van't Hoff equation to calculate ΔH° , given K_p values at two temperatures
- # 15 Given K_{sp} (solubility product constant), calculate the solubility of a slightly soluble salt
- # 16 Given the solubility of a slightly soluble salt, calculate its K_{sp} value
- # 17 Given K_{sp} , calculate the solubility of a slightly soluble salt in the presence of a solute with a common ion

II. Acid-Base Reactions, Buffers and Titrations

(Here, we assume aqueous solutions at room temperature, unless otherwise specified.)

Problem

- # 18, 19 Calculate the pH of a solution of a strong acid, given its concentration
- # 20 Calculate the pH of a solution of a strong base, given its concentration
- # 21, 22 Given the pH of a solution, calculate its OH^- concentration
- # 23 Calculate the pH and pOH of water at a different temperature, given K_w
- # 24, 25, 26 Calculate the pH of a solution of a weak acid, given its concentration and K_a
- # 27 Calculate the K_a of a weak acid, given its concentration and the pH of the solution
- # 28 Calculate the "percent dissociation" of a weak acid, given its concentration and the pH of the solution
- # 29 Calculate the pH of a solution of a weak base, given its concentration and the K_a of its conjugate weak acid
- # 30 Calculate the $\text{p}K_b$ of a weak base, given its concentration and the pH of the solution
- # 31 Buffers: calculate the pH of a solution with given numbers of moles of a weak acid and its conjugate weak base, given the K_a of the weak acid
- # 32 Buffers: calculate the pH of a solution given the concentrations of a weak acid and (a lower concentration of) NaOH, and the $\text{p}K_a$ of the weak acid
- # 33, # 34 Buffers: calculate the pH of a solution with a given number of moles of a weak acid, its conjugate weak base, and strong base, given the $\text{p}K_a$ of the weak acid.
- # 35, # 36 Titrations involving strong acids and strong bases: calculate the pH of the solution after a given amount of the strong base (or strong acid) has been added
- # 37, # 38 Titration of a weak acid by a strong base: calculate the pH of the solution after a given amount of strong base has been added

Chem 1062 Equation Sheet

This is the equation sheet that will be provided with all of our exams this semester:

Ch. 13

$$\Delta T_f = i K_f m \quad \Delta T_b = i K_b m \quad \text{Molarity } (M) = \text{mol solute} / \text{L solution}$$

$$P_{\text{solvent}} = X_{\text{solvent}} P^{\circ}_{\text{solvent}} \quad S_{\text{gas}} = k_H P_{\text{gas}} \quad \text{molality } (m) = \text{mol solute} / \text{kg solvent}$$

Chap. 16

rate = k : $[A]_t = -kt + [A]_0$

rate = $k[A]$: $\ln[A]_t = -kt + \ln[A]_0$ $\ln ([A]_0/[A]_t) = kt$ $[A]_t = [A]_0 e^{-kt}$ $t_{1/2} = 0.693/k$

rate = $k[A]^2$: $1/[A]_t = kt + 1/[A]_0$

$k = Ae^{-E_a/(RT)}$

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

Ch. 17

$K_p = K(RT)^{\Delta n}$

$\ln(K_2/K_1) = (-\Delta H^{\circ}/R) ((1/T_2) - (1/T_1))$ $\ln \frac{K_2}{K_1} = \frac{\Delta H}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$

$x = (-b \pm (b^2 - 4ac)^{1/2}) / (2a)$

Ch. 19

$pH = pK_a + \log ([\text{base}] / [\text{acid}])$

Chap. 20

$\Delta S_{\text{sur}} = -\Delta H_{\text{sys}} / T$

$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$

$\Delta G^{\circ} = -RT \ln K = -2.303 RT \log K$

$\Delta G = \Delta G^{\circ} + RT \ln Q = RT \ln (Q/K) = 2.303 RT \log (Q/K)$

$\ln K = -\Delta H^{\circ}/RT + \Delta S^{\circ}/R$

Chap. 21

$\Delta G^{\circ} = -nFE^{\circ}_{\text{cell}}$

$\log K = n E^{\circ}_{\text{cell}} / 0.0592V$ (at 25°C)

$E_{\text{cell}} = E^{\circ}_{\text{cell}} - (0.0592V / n) \log Q$ (at 25°C)

$E_{\text{cell}} = -2.303 (RT/nF) \log (Q/K)$

Ch. 23

Spectrochemical series: $I^- < Cl^- < F^- < OH^- < H_2O < SCN^- < NH_3 \dots$
 $\dots < en$ (ethylenediamine) $< NO_2^-$ (N-bonded) $< CN^- < CO$

$R = 8.314 \text{ J}/(\text{mol}\cdot\text{K}) = 0.08206 \text{ (atm}\cdot\text{L)} / (\text{mol}\cdot\text{K})$

$N_A = 6.022 \times 10^{23} / \text{mol}$

$e = 1.602 \times 10^{-19} \text{ C}$ charge of an electron (or proton)

$F = 9.649 \times 10^4 \text{ C}/\text{mole}$

1. amu = $1.661 \times 10^{-27} \text{ kg}$

1. atm = 760 torr

$0^{\circ} \text{ C} = 273.15 \text{ K}; T(^{\circ}\text{C}) = (5/9) [T(^{\circ}\text{F}) - 32]$

1. $\text{cm}^3 = 1. \text{ mL}$ 1. $\text{\AA} = 1. \times 10^{-8} \text{ cm} = 1. \times 10^{-10} \text{ m}; 1. \text{ nm} = 1. \times 10^{-9} \text{ m}; 1. \text{ pm} = 1. \times 10^{-12} \text{ m}$

$\sqrt{2} \approx 1.4, \sqrt{3} \approx 1.7, \sqrt{5} \approx 2.2, \sqrt{6} \approx 2.4, \sqrt{7} \approx 2.6, \sqrt{8} \approx 2.8$ [logs: we use "ln" for base e and "log" for base 10.]

$\log(a \cdot b) = \log(a) + \log(b); \log(a/b) = \log(a) - \log(b); \log(a^n) = n \log(a)$ ← same three relations hold for \ln

$\log 1 = 0; \ln 1 = 0; \ln 2 \approx 0.693; \ln 10 \approx 2.30; \ln a \approx 2.30 \log a; e^a \approx 10^{a/2.30}; \log e = 1/(\ln 10) \approx 0.43; e \approx 2.7$

$\log 2 \approx 0.30; \log 3 \approx 0.48; \log 4 \approx 0.60; \log 5 \approx 0.70; \log 6 \approx 0.78; \log 7 \approx 0.85; \log 8 \approx 0.90; \log 9 \approx 0.95; \log 10 = 1.$

| | | | | | | |
|----------|--------------------|---------------------|---------------------|---------------------|---------------------|-------------------|
| 18 8A | 2 He 4.00260 | 10 Ne 20.1797 | 18 Ar 39.948 | 36 Kr 83.80 | 54 Xe 131.29 | 86 Rn (222) |
| 17 7A | 9 F 18.9984 | 17 Cl 35.4527 | 35 Br 79.904 | 53 I 126.904 | 85 At (210) | (222) |
| 16 6A | 8 O 15.9994 | 16 S 32.066 | 34 Se 78.96 | 52 Te 127.60 | 84 Po (209) | (222) |
| 15 5A | 7 N 14.0067 | 15 P 30.9738 | 33 As 74.9216 | 51 Sb 121.76 | 83 Bi 208.980 | (222) |
| 14 4A | 6 C 12.011 | 14 Si 28.0855 | 32 Ge 72.61 | 50 Sn 118.710 | 82 Pb 207.2 | (222) |
| 13 3A | 5 B 10.811 | 13 Al 26.9815 | 31 Ga 69.723 | 49 In 114.818 | 81 Tl 204.383 | (222) |
| 12 | | | | | | |
| 11 | | | | | | |
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I. Chemical Equilibrium (An equation sheet is provided on p. 4)

Note: for all problems in this section, we use K to mean K_c , the equilibrium constant expressed in terms of concentrations. We use K_p to represent the equilibrium constant expressed in terms of partial pressures.

1. Notes to instructor:

(F10 Exam 2 #4)

Given the initial concentrations of all of the species that take part in a reaction and one equilibrium concentration, calculate another species' equilibrium concentration.

Consider the reaction: $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2 \text{HI}(\text{g})$

A sealed container initially holds 0.040 M H_2 , 0.030 M I_2 and 0.060 M HI .

At equilibrium, the concentration of H_2 is 0.050 M.

What is the equilibrium concentration of **HI**?

- | | | | |
|----|---------|----|---------|
| A. | 0.10 M | F. | 0.050 M |
| B. | 0.090 M | G. | 0.040 M |
| C. | 0.080 M | H. | 0.030 M |
| D. | 0.070 M | I. | 0.020 M |
| E. | 0.060 M | J. | 0.010 M |

Answer: G. 0.040 M

The H_2 concentration increases by 0.010 M (that is, from 0.040 to 0.050 M).

Therefore, the HI concentration must have *decreased* by twice as much, or by 0.020 M.

So the equilibrium $[\text{HI}]$ is 0.060 M - 0.020 M = 0.040 M.

One can also see this by drawing up an ICE table:

| | | | |
|-------------|----------------------------------------------------------------------------------------|---------|------------|
| | $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2 \text{HI}(\text{g})$ | | |
| initial (M) | 0.040 | 0.030 | 0.060 |
| change | x | x | -2x |
| equilibrium | 0.050 | 0.030+x | 0.060 - 2x |

So, from the data for H_2 , $x = 0.050 - 0.040 = 0.010 \text{ M}$

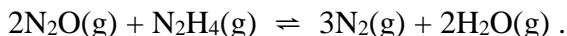
Then, at equilibrium $[\text{HI}] = 0.060 - 2x = 0.060 - 2(0.010) = 0.060 - 0.020 = 0.040 \text{ M}$

2. Note to instructor:

(S11 Exam 2 #6)

Given initial numbers of moles of all of the species taking part in a reaction and the equilibrium concentration of one of them, calculate that of another.

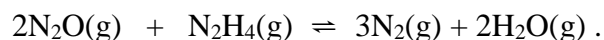
Consider the following reaction:



Initially there are 0.10 mole of $\text{N}_2\text{O}(\text{g})$ and 0.20 mole of $\text{N}_2\text{H}_4(\text{g})$, and no N_2 or H_2O , in a 1.0 liter container. If there is 0.04 mole of $\text{N}_2\text{O}(\text{g})$ at equilibrium, how much $\text{N}_2\text{H}_4(\text{g})$ is present at equilibrium?

- | | | | |
|----|-----------|----|-----------|
| A. | 0.02 mole | E. | 0.17 mole |
| B. | 0.03 mole | F. | 0.23 mole |
| C. | 0.08 mole | G. | 0.26 mole |
| D. | 0.14 mole | H. | 0.32 mole |

Answer: E. 0.17 mole



| | | |
|-------------|-------------------|-------------------|
| initial | 0.10 mole | 0.20 mole |
| change | <u>-0.06 mole</u> | <u>-0.03 mole</u> |
| equilibrium | 0.04 mole | <i>0.17 mole</i> |

In the ICE table above, the values given in the problem are shown in bold.

Since we start with 0.10 mole of $\text{N}_2\text{O}(\text{g})$ and there is only 0.04 mole left at equilibrium, the change in the amount of N_2O is -0.06 mole.

Since the stoichiometric ratio is 2 N_2O : 1 N_2H_4 , the change in the amount of N_2H_4 will be half as much as that of N_2O .

Since both species are reactants, their changes will have the same sign (i.e., the amount of N_2H_4 will also decrease at equilibrium).

So, the change in the amount of N_2H_4 will be half of 0.06 mole = 0.03 mole.

Adding this change to the initial amount gives:

$$0.20 - 0.03 \text{ mole} = 0.17 \text{ mole } \text{N}_2\text{H}_4(\text{g}) \text{ at equilibrium.}$$

3. Notes to instructor:

(S11 Exam 2 #3)

Given K and the equilibrium concentrations of all but one of the species that take part in a reaction, solve for the unknown concentration.

Consider the reaction: $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$

At a certain temperature, the equilibrium constant (K) is 50., and the equilibrium concentrations are 0.10 M for SO_2 , and 0.50 M for SO_3 . What is the equilibrium concentration of O_2 ?

- A. 1250 M
- B. 5.0 M
- C. 2.0 M
- D. 1.0 M
- E. 0.50 M
- F. 0.10 M
- G. 0.050 M
- H. 0.020 M

Answer: E. 0.50 M

$$K = \frac{[\text{SO}_3]^2}{([\text{SO}_2]^2 [\text{O}_2])}$$

$$\text{Rearranging, } [\text{O}_2] = \frac{[\text{SO}_3]^2}{([\text{SO}_2]^2 K)}$$

$$[\text{O}_2] = \frac{(0.5)^2}{(0.1^2 \times 50)} = \frac{(0.25 / 0.01)}{50} = 25 / 50 = 1 / 2 = 0.50 \text{ M}$$

Another way to do this:

$$[\text{O}_2] = \frac{(0.5)^2}{(0.1^2 \times 50)} = \frac{(0.5^2 / 0.1^2)}{50} = \frac{(0.5 / 0.1)^2}{50} = \frac{5^2}{50} = 25/50 = 1/2 = 0.50 \text{ M}$$

Can check the answer:

$$K = \frac{[\text{SO}_3]^2}{([\text{SO}_2]^2 [\text{O}_2])} = \frac{0.5^2}{(0.1^2 \cdot 0.5)} = 0.50 / 0.01 = 50 / 1 = 50 \text{ ok}$$

4. Notes to instructor:

(S12 Exam 2 #3)

Given K and the equilibrium concentrations of all but one of the species that take part in a reaction, solve for the unknown concentration.

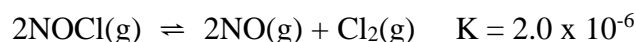
Requires multiplying and dividing numbers in scientific notation, including dividing by a

number with a negative exponent: $2 \times 10^{-6} / 1 \times 10^{-2} = 2 \times 10^{-6 - (-2)} = 2 \times 10^{-4} \text{ M}$

Also requires taking the square root of a number in scientific notation (with an even exponent):

$$(2 \times 10^{-4})^{1/2} = \sqrt{2} \times 10^{-4/2} = 1.4 \times 10^{-2}$$

At 35 °C, the equilibrium constant for the reaction below is:



An equilibrium mixture was found to have the following concentrations:

$$[\text{Cl}_2] = 4.0 \times 10^{-2} \text{ M}; \quad [\text{NOCl}] = 2.0 \text{ M.}$$

Calculate the concentration of **NO(g)** at equilibrium.

- | | | | |
|----|--------------------------------|----|--------------------------------|
| A. | $1.7 \times 10^{-1} \text{ M}$ | F. | $1.4 \times 10^{-4} \text{ M}$ |
| B. | $1.4 \times 10^{-2} \text{ M}$ | G. | $1.0 \times 10^{-4} \text{ M}$ |
| C. | $1.0 \times 10^{-2} \text{ M}$ | H. | $4.0 \times 10^{-6} \text{ M}$ |
| D. | $5.0 \times 10^{-3} \text{ M}$ | I. | $2.0 \times 10^{-6} \text{ M}$ |
| E. | $2.0 \times 10^{-4} \text{ M}$ | J. | $2.0 \times 10^{-8} \text{ M}$ |

Answer: B. $1.4 \times 10^{-2} \text{ M}$

$$K = [\text{NO}]^2 [\text{Cl}_2] / [\text{NOCl}]^2$$

$$[\text{NO}]^2 = K [\text{NOCl}]^2 / [\text{Cl}_2]$$

$$[\text{NO}]^2 = 2.0 \times 10^{-6} \times 2.0^2 / 4.0 \times 10^{-2} = 2 \times 10^{-6} \times 4 / 4 \times 10^{-2} = 2 \times 10^{-6} / 1 \times 10^{-2}$$

$$[\text{NO}]^2 = 2 \times 10^{-6 - (-2)} = 2 \times 10^{-4} \text{ M}$$

$$[\text{NO}] = \sqrt{2} \times 10^{-4/2} = 1.4 \times 10^{-2} \text{ M}$$

Can check the answer:

$$K = [\text{NO}]^2 [\text{Cl}_2] / [\text{NOCl}]^2 = (1.4 \times 10^{-2})^2 \times 4 \times 10^{-2} / 2^2 = (1.4)^2 \times (10^{-2})^2 \times 4 \times 10^{-2} / 4$$

$$K = 2 \times 10^{-4} \times 1 \times 10^{-2} = 2 \times 10^{-6} \quad \text{ok}$$

5. Notes to instructor:

(S11 Exam 2 #5)

Obtain K for a reaction, given K for the reverse reaction with different coefficients.

Requires estimating a square root and a reciprocal: $1 / \sqrt{50} \approx 1 / 7 \approx 0.14$

If the equilibrium constant (K) is 50. for the reaction $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$,
what is the equilibrium constant for the reaction $\text{SO}_3(\text{g}) \rightleftharpoons \text{SO}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g})$
at the same temperature?

- A. 4.0×10^{-4}
- B. 0.010
- C. 0.020
- D. 0.040
- E. 0.14
- F. 7.0
- G. 25
- H. 50

Answer: E. 0.14

Let's call K for the first reaction listed K_1 : $K_1 = [\text{SO}_3]^2 / ([\text{SO}_2]^2 [\text{O}_2])$

Let's call K for the second reaction listed K_2 : $K_2 = [\text{SO}_2] [\text{O}_2]^{1/2} / [\text{SO}_3]$

so, $K_2 = 1 / (K_1)^{1/2} = 1 / \sqrt{K_1}$

$K_2 = 1 / \sqrt{50} \approx 1 / 7 = 0.14$

6. Notes to instructor:

(F10 Exam 2 #5)

Combine equilibrium constants of two reactions to obtain that of a third.

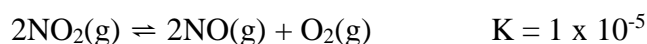
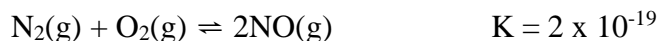
Requires taking the reciprocal of a number in scientific notation: $1/(2 \times 10^{-19}) = 0.5 \times 10^{19} = 5 \times 10^{18}$

Also requires multiplying two numbers in scientific notation: $(5 \times 10^{18})(1 \times 10^{-5}) = 5 \times 10^{13}$

A scientist studying atmospheric chemistry wants to find the equilibrium constant for the

reaction: $2 \text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2(\text{g}) + 2\text{O}_2(\text{g})$ $K = ?$

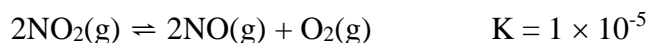
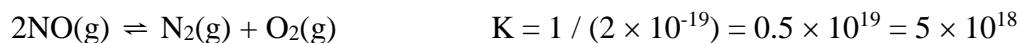
Use the following data (obtained at the same temperature) to find the unknown K:



- A. 2×10^{-24}
- B. 2×10^{-14}
- C. 1×10^{-5}
- D. 5×10^{-1}
- E. 1×10^5
- F. 2×10^9
- G. 5×10^{13}
- H. 5×10^{18}

Answer: G. 5×10^{13}

To add the two reactions together to get the overall reaction of interest, we need to reverse the first reaction. Its equilibrium constant will then be the inverse (reciprocal) of the value provided.





That is, when a reaction is the sum of two reactions, its equilibrium constant is the product of those two reactions' equilibrium constants.

7. Notes to instructor:

(S10 Exam 2 #4)

Comparison of the reaction quotient, Q , to the equilibrium constant (K , given) to determine the direction in which the reaction will shift as it approaches equilibrium.

Requires multiplying 2 numbers less than 1 ($0.20 \times 0.20 = 0.04$) and simplifying a ratio:

$$2.00 / 0.040 \text{ M} = 200 / 4.0 = 50$$

For the reaction: $\text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons \text{PCl}_5(\text{g})$, $K = 30 \text{ M}^{-1}$ at a certain temperature.

A system is initially prepared with $[\text{PCl}_3] = 0.20 \text{ M}$, $[\text{Cl}_2] = 0.20 \text{ M}$, and $[\text{PCl}_5] = 2.00 \text{ M}$.

Which species will increase in concentration as the system approaches equilibrium?

- A. PCl_3 and Cl_2
- B. PCl_5 (only)
- C. PCl_3 (only)
- D. Cl_2 (only)
- E. The system is already at equilibrium, so the concentrations will not change.

Answer: A. PCl_3 and Cl_2

$$Q = [\text{PCl}_5] / ([\text{PCl}_3] [\text{Cl}_2]) = 2.00 \text{ M} / (0.20 \text{ M} \times 0.20 \text{ M}) = 2.00 / 0.040 \text{ M} = 200 / 4.0 = 50 \text{ M}^{-1}$$

$Q > K$ (since $Q = 50 \text{ M}^{-1}$ and $K = 30 \text{ M}^{-1}$) so the system will shift to the left, i.e., there will be a net reaction of PCl_5 to form more PCl_3 and Cl_2 .

8. Notes to instructor:

(S10 Exam 2 #6)

Convert K to K_p .

Requires estimating RT : $0.08206 \times 300 \approx 0.08 \times 300 = 8 \cdot 3 = 24$

Consider the reaction: $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$

If $K = 8 \times 10^{25} \text{ M}^{-1}$ at about 300 Kelvin, what is the value of the equilibrium constant expressed in terms of pressures, K_p (in atm^{-1}) ?

- A. 3×10^{22}
- B. 1×10^{23}
- C. 3×10^{24}
- D. 2×10^{25}
- E. 3×10^{26}
- F. 2×10^{27}
- G. 1×10^{28}
- H. 2×10^{29}

Answer: C. 3×10^{24}

$K_p = K(\text{RT})^{\Delta n}$ where $\Delta n = \text{moles of products minus moles of reactants}$

$\Delta n = 2 - 3 = -1$ so $K_p = K(\text{RT})^{-1}$

$K_p = K / (\text{RT}) = 8 \times 10^{25} \text{ M}^{-1} / (0.08206 \text{ L} \cdot \text{atm} / \text{K} \cdot \text{mol} \times 300 \text{ K})$

where $0.08206 \text{ L} \cdot \text{atm} / \text{K} \cdot \text{mol} \cdot 300 \text{ K} \approx 0.08 \times 300 = 8 \times 3 = 24 \text{ L} \cdot \text{atm} / \text{mol}$

$8 \times 10^{25} \text{ L} / \text{mol} / (24 \text{ L} \cdot \text{atm} / \text{mol}) = (8 / 24) \times 10^{25} \text{ atm}^{-1} = (1/3) \times 10^{25} \text{ atm}^{-1} = 3 \times 10^{24} \text{ atm}^{-1}$

9. Notes to instructor:

(S10 Exam 2 #7)

Calculate K, given the initial concentrations and one equilibrium concentration.

Requires dividing by a number less than one: $4 / 0.5 = 8$

Consider the following reaction: $2 \text{CO}(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{CO}_2(\text{g})$

At a certain temperature, when 3.0 moles of $\text{CO}_2(\text{g})$ (and no CO or O_2) are placed in a 1.0-L container and allowed to come to equilibrium, the concentration of $\text{CO}(\text{g})$ is 1.0 M.

The equilibrium constant, K, for this reaction at this temperature is:

- A. 8.0
- B. 6.0
- C. 4.0
- D. 3.0
- E. 2.0
- F. 1.0
- G. 0.5
- H. 0.2

Answer: A. 8.0

| | | | |
|-------------|-----------------------------------------------------------------------------------------|----------|--------------|
| | $2\text{CO}(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{CO}_2(\text{g})$ | | |
| initial | 0 | 0 | 3.0 M |
| change | +2x | + x | -2x |
| equilibrium | 2x | x | 3.0 - 2x |
| | 1.0 M | 0.50 M | 2.0 M |

The problem tells us that $[\text{CO}]$ is 1.0 M at equilibrium, so $2x = 1.0 \text{ M}$, so x must be 0.5 M.

Therefore, $[\text{CO}_2] = 3.0 - 2(0.5) = 2.0 \text{ M}$ and $[\text{O}_2] = x = 0.5 \text{ M}$ at equilibrium.

$$K = [\text{CO}_2]^2 / ([\text{CO}]^2 [\text{O}_2]) = 2.0^2 / (1.0^2 \times 0.5) = 4.0 / 0.5 = 8.0 \text{ M}$$

10. Notes to instructor:

(S12 Exam 2 #6)

Given K and the initial concentrations, calculate an equilibrium concentration

Requires taking the square roots of both sides of an equation, and rearranging an equation to solve for an unknown.

Consider the reaction: $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$,

for which $K = 4.0$ at a certain temperature. Starting with initial concentrations of

0.20 M for N_2 and 0.20 M for O_2 (and no NO present initially),

what is the equilibrium concentration of **NO** at this temperature?

- | | | | |
|----|----------|----|--------|
| A. | 0.0050 M | F. | 0.20 M |
| B. | 0.010 M | G. | 0.40 M |
| C. | 0.020 M | H. | 0.80 M |
| D. | 0.050 M | I. | 1.0 M |
| E. | 0.10 M | J. | 2.0 M |

Answer: F. 0.20 M

| | | | | | |
|-------------|--------------|---|--------------|----------------------|---------------|
| | N_2 | + | O_2 | \rightleftharpoons | 2NO |
| initial | 0.20 | | 0.20 | | 0 |
| change | -x | | -x | | +2x |
| equilibrium | 0.20-x | | 0.20-x | | 2x |

$$K = 4.0 = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]} = \frac{(2x)^2}{(0.20-x)^2}$$

Short cut: *take square roots of both sides.*

$$4.0^{1/2} = 2.0 = 2x / (0.20 - x)$$

$$2x = 2.0 (0.20 - x) = 0.40 - 2.0 x$$

$$4x = 0.40$$

$$x = 0.40 / 4 = 0.10 \text{ M}$$

$$[\text{NO}] = 2x = 0.20 \text{ M}$$

Can check the answer: $[\text{NO}]^2 / [\text{N}_2][\text{O}_2] = (0.2)^2 / (0.2 - 0.1)^2 = 0.04 / 0.01 = 4$ ok

11. Notes to instructor:

(F10 Exam 2 #7)

Given K and the initial concentrations, calculate an equilibrium concentration

Requires taking the square root of a number in scientific notation (with an even exponent):

$$(9.0 \times 10^{-6})^{1/2} = 3.0 \times 10^{-3}$$

Consider the following equilibrium: $2\text{NOCl}(g) \rightleftharpoons 2\text{NO}(g) + \text{Cl}_2(g)$ with $K = 9.0 \times 10^{-6}$.

2.00 moles of pure NOCl and 1.00 mole of pure Cl₂ are placed in a 1.00-L container.

Calculate the equilibrium concentration of NO(g).

- A. $6.0 \times 10^{-3} \text{ M}$
- B. $3.0 \times 10^{-3} \text{ M}$
- C. $4.2 \times 10^{-4} \text{ M}$
- D. $2.1 \times 10^{-4} \text{ M}$
- E. $3.6 \times 10^{-5} \text{ M}$
- F. $1.8 \times 10^{-5} \text{ M}$
- G. $9.0 \times 10^{-6} \text{ M}$
- H. $3.0 \times 10^{-6} \text{ M}$

Answer: A. $6.0 \times 10^{-3} \text{ M}$



| | | | |
|-------------|---------|----|----------|
| initial | 2.00 | 0 | 1.00 M |
| change | -2x | 2x | x |
| equilibrium | 2.00-2x | 2x | 1.00 + x |

$$K = 9.0 \times 10^{-6} = \frac{[\text{NO}]^2[\text{Cl}_2]}{[\text{NOCl}]^2} = \frac{(2x)^2(1.00 + x)}{(2.00 - 2x)^2}$$

Since K is small, approximate $1.00 + x \approx 1.00$; $2.00 - 2x \approx 2.00$, giving:

$$9.0 \times 10^{-6} \approx 4x^2 / 4 = x^2$$

$$x = (9.0 \times 10^{-6})^{1/2} = 3.0 \times 10^{-3} \text{ M}$$

$$[\text{NO}] = 2x = \mathbf{6.0 \times 10^{-3} \text{ M}}$$

Can check the answer:

$$[\text{NO}]^2[\text{Cl}_2] / [\text{NOCl}]^2 = (6.0 \times 10^{-3})^2 (1.00) / (2.00)^2 = 36 \times 10^{-6} / 4 = 9 \times 10^{-6} \text{ ok}$$

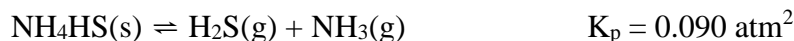
12. Notes to instructor:

(F10 Exam 2 #6)

Given K_p and the initial partial pressures (zero), calculate an equilibrium partial pressure.

Requires taking the square root of a number less than one: $\sqrt{(0.090)} = 0.30$

Ammonium hydrogen sulfide decomposes according to the following reaction,
for which $K_p = 0.090 \text{ atm}^2$ at a particular temperature:



If 2.0 moles of $\text{NH}_4\text{HS}(s)$ are initially placed in a sealed 1.0 L container, what is the partial pressure of ammonia (NH_3) at equilibrium (in atmospheres)?

- A. 0.60
- B. 0.30
- C. 0.15
- D. 0.090
- E. 0.045
- F. 0.015
- G. 0.0081
- H. 0.0015

Answer: B. 0.30



Also, $P_{\text{H}_2\text{O}} = P_{\text{NH}_3}$ since they are produced in a 1:1 ratio as the $\text{NH}_4\text{HS}(s)$ decomposes.

So, $K_p = 0.090 = P_{\text{NH}_3}^2$

$$P_{\text{NH}_3} = \sqrt{(0.090 \text{ atm}^2)} = 0.30 \text{ atm}$$

(To solve for the square root of 0.09 without a calculator, can convert to exponential notation:

$$0.09 = 9 \times 10^{-2} \text{ so } (9 \times 10^{-2})^{1/2} = 9^{1/2} \times 10^{-2 \cdot 1/2} = 3 \times 10^{-1} = 0.3$$

where the exponent of $1/2$ means the square root)

(Similar to Silberberg & Amateis problem 17.48 (8th Ed.), but here the value of K_p was changed from 0.11 to 0.09 to make it easier to take the square root without a calculator.)

13. Note to Instructor:

(S11 Exam 2 # 7)

For a gas phase reaction, given K_p and the initial partial pressures, calculate one of the equilibrium partial pressures.

Requires taking the cube root of a number in scientific notation, by dividing the exponent (which is a multiple of 3) by 3: $(1.00 \times 10^{-12})^{1/3} = 1.00 \times 10^{-4}$

Consider the decomposition of nitrogen dioxide, $2\text{NO}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g}) + \text{O}_2(\text{g})$, for which $K_p = 1.00 \times 10^{-12}$ atm at a certain temperature. A pressure of 2.00 atm of NO_2 is introduced into a container (with no NO or O_2 initially present) and allowed to come to equilibrium. What is the equilibrium partial pressure of $\text{O}_2(\text{g})$, in atmospheres?

- A. 2.8×10^6
- B. 1.0×10^4
- C. 2.0×10^4
- D. 1.4×10^{-3}
- E. 2.0×10^{-4}
- F. 1.0×10^{-4}
- G. 8.0×10^{-5}
- H. 2.8×10^{-6}

Answer: F. 1.0×10^{-4}

| | | | | | |
|-------------|--------------------------|----------------------|------------------------|---|------------------------|
| | $2\text{NO}_2(\text{g})$ | \rightleftharpoons | $2\text{NO}(\text{g})$ | + | $\text{O}_2(\text{g})$ |
| Initial | 2.00 | | 0 | | 0 |
| Change | - 2x | | 2x | | x |
| Equilibrium | $2.00 - 2x$ | | 2x | | x |

$$K_p = (\text{P}_{\text{NO}})^2 (\text{P}_{\text{O}_2}) / (\text{P}_{\text{NO}_2})^2 = (2x)^2 (x) / (2.00-2x)^2 = 1.00 \times 10^{-12}$$

Since K_p is so small, we can approximate the equilibrium partial pressure of NO_2 as 2.00 atm.

$$1.00 \times 10^{-12} = 4x^3 / (2.00)^2$$

$$x^3 = (1.00 \times 10^{-12} \times 4.00 / 4) = 1.00 \times 10^{-12}$$

$$x = (1.00 \times 10^{-12})^{1/3} = 1.00 \times 10^{-4} \text{ atm} = \text{P}_{\text{O}_2}$$

Can check answer: $(\text{P}_{\text{NO}})^2 (\text{P}_{\text{O}_2}) / (\text{P}_{\text{NO}_2})^2 = K_p = (2.00 \times 10^{-4})^2 (1.00 \times 10^{-4}) / (2.00)^2 = 1 \times 10^{-12}$ ok
(This problem is similar to 17.51 in Silberberg & Amateis, 8th Ed.)

14. Notes to instructor:

(S10 Exam 2 #8)

Use of the van't Hoff equation to calculate ΔH° , given the values of K_p at two temperatures.

Requires calculating the natural log from the common log:

$$\log(1.0 \times 10^{15}) = 15.00, \quad \ln(1.0 \times 10^{15}) = 2.3(15) \approx 35$$

Given: $\text{NH}_4\text{Cl}(s) \rightleftharpoons \text{NH}_3(g) + \text{HCl}(g)$

If the equilibrium constant for this reaction is

$1.0 \times 10^{-16} \text{ atm}^2$ at 25°C , and it is 0.10 atm^2 at 325°C ,

then the value of ΔH° (in kJ/mol) is (choose the closest answer):

- | | | | |
|----|------|----|------|
| A. | -290 | E. | 0.50 |
| B. | -170 | F. | 2.0 |
| C. | -75 | G. | 75 |
| D. | -2.0 | H. | 170 |
| | | I. | 290 |

Answer: H. 170

$$\ln \frac{K_2}{K_1} = \frac{\Delta H}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

(This form for the term in parentheses is easier to calculate than $1/T_2 - 1/T_1$.)

We can approximate $T_1 = 25^\circ\text{C} + 273 \approx 300\text{ K}$, $T_2 = 325^\circ\text{C} + 273 \approx 600\text{ K}$

Since the equilibrium constant increases with increasing temperature, we know that the reaction is endothermic, so ΔH° is positive.

$$\left(\frac{T_2 - T_1}{T_1 T_2} \right) = \left(\frac{600 - 300}{600(300)} \right) = \left(\frac{300}{180,000} \right) = \left(\frac{3}{1,800} \right) = \left(\frac{1}{600} \right)$$

$$K_2 / K_1 = 0.10 / (1.0 \times 10^{-16}) = 1.0 \times 10^{-1} / (1.0 \times 10^{-16}) = 1.0 \times 10^{15}$$

$$\log(K_2 / K_1) = \log(1.0 \times 10^{15}) = 15.00$$

$$\ln(K_2 / K_1) = 2.3 \log(K_2 / K_1) = 2.3(15) \approx 35$$

Rearranging and approximating R as $8 \text{ J/(K}\cdot\text{mol)}$:

$$\Delta H = \frac{R \ln \frac{K_2}{K_1}}{\left(\frac{T_2 - T_1}{T_1 T_2} \right)} = \frac{8(35)}{\left(\frac{1}{600} \right)} = 8(35)(600) = 168,000 \approx 170,000 \text{ J} = 170 \text{ kJ}$$

15. Notes to instructor:

(F10 Exam 2 #8)

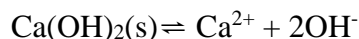
Given K_{sp} (solubility product constant), calculate the solubility of a slightly soluble salt.

Requires taking the cube root of a number in scientific notation (having an exponent which is a multiple of 3): $(8.0 \times 10^{-6})^{1/3} = 8.0^{1/3} \times 10^{-6 \cdot 1/3} = 2.0 \times 10^{-2}$

Calculate the solubility (in moles/L) of Ca(OH)_2 at a temperature at which $K_{sp} = 3.2 \times 10^{-5} \text{ M}^3$.

- A. 1.6×10^{-4}
- B. 9.6×10^{-4}
- C. 2.0×10^{-3}
- D. 4.0×10^{-3}
- E. 6.4×10^{-3}
- F. 2.0×10^{-2}
- G. 4.0×10^{-2}
- H. 6.4×10^{-2}

Answer: F. 2.0×10^{-2}



$$K_{sp} = [\text{Ca}^{2+}][\text{OH}^-]^2 = 3.2 \times 10^{-5} \text{ M}^3$$

At equilibrium, $[\text{Ca}^{2+}] = s$ and $[\text{OH}^-] = 2s$, where s is the molar solubility of Ca(OH)_2

$$3.2 \times 10^{-5} = (s)(2s)^2 = 4s^3$$

$$s^3 = 3.2 \times 10^{-5} / 4 = (3.2 / 4) \times 10^{-5} = 0.80 \times 10^{-5} = 8.0 \times 10^{-6}$$

$$s = (8.0 \times 10^{-6})^{1/3} = 8.0^{1/3} \times 10^{-6 \times 1/3} = 2.0 \times 10^{-2} \text{ M}$$

Can check answer: $4s^3 = 4(2 \times 10^{-2})^3 = 4(2 \times 10^{-2})(2 \times 10^{-2})(2 \times 10^{-2}) = 32 \times 10^{-6} = 3.2 \times 10^{-5}$ ok

16. Notes to instructor:

(S10 Exam 3 #4)

Given the solubility of a slightly soluble salt, calculate its K_{sp} value.

Requires cubing a number:

$$(0.03)^3 = 0.03 \times 0.03 \times 0.03 = (3 \times 10^{-2})^3 = 3^3 \times (10^{-2})^3 = 27 \times 10^{-2 \times 3} = 27 \times 10^{-6} = 2.7 \times 10^{-5}$$

If the solubility of silver carbonate (Ag_2CO_3) at a certain temperature is 0.03 M, what is its K_{sp} value?

- A. 4×10^{-7}
- B. 9×10^{-7}
- C. 3×10^{-5}
- D. 5×10^{-5}
- E. 1×10^{-4}
- F. 9×10^{-4}
- G. 4×10^{-3}
- H. 3×10^{-2}

Answer: E. 1×10^{-4}

The reaction for which K_{sp} is the equilibrium constant is:



$$K_{sp} = [\text{Ag}^+]^2 [\text{CO}_3^{2-}] = (2s)^2 (s) = 4s^3 \quad \text{where } s \text{ is the solubility}$$

We have set $[\text{CO}_3^{2-}]$ at equilibrium equal to the solubility, s , because one mole of salt dissolves to produce one mole of CO_3^{2-} (and twice as much Ag^+).

$$K_{sp} = 4s^3 = 4(0.03)^3 = 4 \cdot 2.7 \times 10^{-5} = 10.8 \times 10^{-5} = \mathbf{1 \times 10^{-4}} \quad (\text{to 1 sig fig}); \text{ units are } \text{M}^3$$

$$\text{note: } (0.03)^3 = 0.03 \times 0.03 \times 0.03 = (3 \times 10^{-2})^3 = 3^3 \times (10^{-2})^3 = 27 \times 10^{-2 \cdot 3} = 27 \times 10^{-6} = 2.7 \times 10^{-5}$$

17. Notes to instructor:

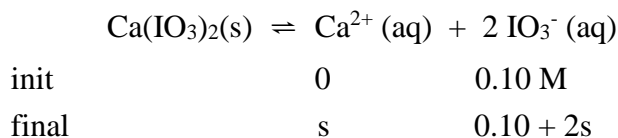
(S11 Exam 2 #20)

Calculate the solubility of a slightly soluble ionic compound in the presence of a common ion, given the K_{sp} value (solubility product constant).

Calculate the molar solubility of $\text{Ca}(\text{IO}_3)_2$ ($K_{sp} = 7 \times 10^{-7}$) in 0.10 M NaIO_3 .

- A. 7×10^{-11}
- B. 7×10^{-10}
- C. 7×10^{-9}
- D. 7×10^{-8}
- E. 7×10^{-7}
- F. 7×10^{-6}
- G. 7×10^{-5}
- H. 7×10^{-4}

Answer: G. 7×10^{-5}



$$7 \times 10^{-7} = K_{sp} = s(0.10 + 2s)^2 \approx s(0.10)^2 = 0.010 s$$

(where we have used the "small s" approximation since K_{sp} is small)

$$s = 7 \times 10^{-7} \text{ M}^3 / 0.01 \text{ M}^2 = 7 \times 10^{-7} \times 100 = 7 \times 10^{-5} \text{ M} = \text{molar solubility of } \text{Ca}(\text{IO}_3)_2$$

(This is similar to Silberberg & Amateis 19.77, 8th Ed.)

II. Acid-Base Equilibria, Buffer Solutions, Titrations

(An equation sheet is provided on p. 4)

Note: All problems in this section refer to aqueous solutions at room temperature, unless otherwise stated.

18. Notes to instructor:

(S11 Exam 2 #11)

Calculate the pH of a solution of a strong acid.

What is the pH of a 0.0010 M aqueous solution of nitric acid (HNO₃) ?

- A. 1.00
- B. 2.00
- C. 3.00
- D. 5.00
- E. 7.00
- F. 9.00
- G. 11.00
- H. 12.00
- I. 13.00

Answer: C. 3.00

$$\text{pH} = -\log (\text{H}_3\text{O}^+) = -\log (1.0 \times 10^{-3}) = -(-3.00) = 3.00$$

19. Notes to instructor:

(S10 Exam 2 #12)

Calculate the pH of a solution of a strong acid.

Requires use of: $\log(ab) = \log a + \log b$

Here, $\log(5 \times 10^{-2}) = \log 5 + \log(1 \times 10^{-2}) = 0.7 - 2.0 = -1.3$

What is the pH of a 5×10^{-2} M HClO₄ (perchloric acid) solution?

- | | | | |
|----|------|----|------|
| A. | -2.0 | E. | 1.5 |
| B. | -1.5 | F. | 2.0 |
| C. | -1.3 | G. | 7.0 |
| D. | 1.3 | H. | 10.0 |

Answer: D. 1.3

HClO₄ (perchloric acid) is a strong acid, so [H₃O⁺] will also be 5×10^{-2} M

because the reaction with water will go to completion: $\text{HClO}_4 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{ClO}_4^-$

$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(5 \times 10^{-2}) = -(\log 5 + \log(1 \times 10^{-2})) = -(0.7 - 2.0) = -(-1.3) = 1.3$

(Here we have used $\log(ab) = \log a + \log b$)

20. Notes to instructor:

(F10 Exam 2 #15)

Calculate the pH of a solution of a strong base, given the concentration.

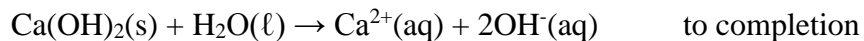
Requires taking the log of a power of ten:

$$\log(0.01) = -2.0 \quad \log(1 \times 10^{-12}) = -12.0$$

What is the pH of a 0.005 M aqueous solution of $\text{Ca}(\text{OH})_2$?

- A. 1.7
- B. 2.0
- C. 2.3
- D. 7.0
- E. 10.0
- F. 11.3
- G. 11.7
- H. 12.0
- I. 12.3
- J. 12.7

Answer: H. 12.0



So a 0.005 M solution of $\text{Ca}(\text{OH})_2$ has an OH^{-} concentration of 0.01 M.

$$\text{pOH} = -\log(0.01) = -2.0$$

$$\text{pH} = 14.0 - 2.0 = 12.0$$

Another way to do it:

$$[\text{H}_3\text{O}^{+}] = K_w / [\text{OH}^{-}] = 1 \times 10^{-14} / (1 \times 10^{-2}) = 1 \times 10^{-14-(-2)} = 1 \times 10^{-12} \text{ M}$$

$$\text{pH} = -\log(1 \times 10^{-12}) = 12.0$$

21. Notes to instructor:

(F10 Exam 2 #14)

Given the pH, solve for the OH^- concentration.

Requires obtaining a value in scientific notation from the log (given as an integer):

$$10^{-3.0} = 1 \times 10^{-3}$$

$$10^{-11.0} = 1 \times 10^{-11}$$

What is the OH^- concentration, in mol/L, in a pH = 3.0 solution of HF ?

- A. 11
- B. 3
- C. 3×10^{-3}
- D. 1×10^{-3}
- E. 1×10^{-5}
- F. 1×10^{-7}
- G. 1×10^{-11}
- H. 1×10^{-14}
- I. 1×10^{-17}

Answer: G. 1×10^{-11}

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-3.0} = 1 \times 10^{-3}$$

$$[\text{OH}^-] = 1 \times 10^{-14} / (1 \times 10^{-3}) = 1 \times 10^{-14 - (-3)} = 1 \times 10^{-11} \text{ M}$$

Another way to do it:

$$\text{pOH} = 14.0 - 3.0 = 11.0$$

$$[\text{OH}^-] = 10^{-\text{pOH}} = 10^{-11.0} = 1 \times 10^{-11}$$

22. Notes to instructor:

(S10 Exam 2 #13)

Calculate $[\text{OH}^-]$, given the pH of the solution.

Requires converting 10^a (where a is not an integer) into scientific notation:

$$10^{-10.7} = 10^{(-11+0.3)} = 10^{-11} \times 10^{0.3} = 10^{-11} \times 2 = 2 \times 10^{-11}$$

Also requires dividing numbers with negative exponents:

$$1 \times 10^{-14} / (2 \times 10^{-11}) = 0.5 \times 10^{-14 - (-11)} = 0.5 \times 10^{-3} = 5 \times 10^{-4}$$

$\text{Ca}(\text{OH})_2$ is dissolved in water at room temperature until the pH of the solution is 10.7 .

What is the hydroxide ion concentration $[\text{OH}^-]$ of the solution ?

- | | | | |
|----|-------------------------------|----|------------------------------|
| A. | $2 \times 10^{-11} \text{ M}$ | E. | $1 \times 10^{-3} \text{ M}$ |
| B. | $7 \times 10^{-10} \text{ M}$ | F. | $3 \times 10^{-3} \text{ M}$ |
| C. | $3 \times 10^{-4} \text{ M}$ | G. | $2 \times 10^{-2} \text{ M}$ |
| D. | $5 \times 10^{-4} \text{ M}$ | H. | $5 \times 10^{-2} \text{ M}$ |

Answer: D. $5 \times 10^{-4} \text{ M}$

If the pH is 10.7, then the pOH is $14.0 - 10.7 = 3.3 = -\log [\text{OH}^-]$

$$[\text{OH}^-] = 10^{-\text{pOH}} = 10^{-3.3} = 10^{(0.7 - 4.0)} = 10^{0.7} \times 10^{-4.0} = 5 \times 10^{-4}$$

(where we have used $10^a \times 10^b = 10^{a+b}$ and $\log 5 = 0.7$ so $10^{0.7} = 5$)

Another approach is to first use the pH to calculate $[\text{H}_3\text{O}^+]$:

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-10.7} = 10^{(0.3 - 11)} = 10^{0.3} \times 10^{-11} = 2 \times 10^{-11}$$

$$[\text{OH}^-] [\text{H}_3\text{O}^+] = K_w$$

$$[\text{OH}^-] = K_w / [\text{H}_3\text{O}^+] = 1 \times 10^{-14} / (2 \times 10^{-11}) = 0.5 \times 10^{-14 - (-11)} = 0.5 \times 10^{-3} = 5 \times 10^{-4}$$

Note: it is not necessary to know that the source of the OH^- is $\text{Ca}(\text{OH})_2$ to solve this problem.

23. Notes to instructor:

(S12 Exam 2 #12)

Calculate the pH and pOH of pure water at a different temperature, given K_w .

Requires taking the square root of a number in scientific notation, with an even exponent:

$$(4.0 \times 10^{-14})^{1/2} = 4.0^{1/2} \times 10^{-14 \times 1/2} = 2.0 \times 10^{-7}$$

Also requires taking the log of a number in scientific notation:

$$\text{pH} = -\log(2.0 \times 10^{-7}) = -(\log 2 + \log 1 \times 10^{-7}) = -(0.3 - 7.0) = -(-6.7) = 6.7$$

At a certain temperature, K_w for water is $4.0 \times 10^{-14} \text{ M}^2$. What are the pH and the pOH of pure water at this temperature?

- A. pH = 6.2, pOH = 6.2
- B. pH = 6.2, pOH = 7.8
- C. pH = 6.7, pOH = 6.7
- D. pH = 6.7, pOH = 7.3
- E. pH = 7.0, pOH = 7.0
- F. pH = 7.3, pOH = 6.7
- G. pH = 7.8, pOH = 6.2
- H. pH = 7.8, pOH = 7.8
- I. pH = 13.4, pOH = 0.6
- J. pH = 13.4, pOH = 13.4

Answer: C. pH = 6.7, pOH = 6.7

$K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$ and $[\text{H}_3\text{O}^+] = [\text{OH}^-]$ since the reaction is $2 \text{H}_2\text{O}(\ell) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{OH}^-(\text{aq})$

Substituting, $K_w = [\text{H}_3\text{O}^+]^2 = 4.0 \times 10^{-14}$

$$[\text{H}_3\text{O}^+] = (4.0 \times 10^{-14})^{1/2} = 4.0^{1/2} \times 10^{-14 \times 1/2} = 2.0 \times 10^{-7}$$

$$\text{pH} = -\log(2.0 \times 10^{-7}) = -(\log 2 + \log 1 \times 10^{-7}) = -(0.3 - 7.0) = -(-6.7) = 6.7$$

$[\text{OH}^-]$ is the same, 2.0×10^{-7} , so the pOH is also 6.7.

At this temperature, $\text{pH} + \text{pOH} = 13.4$ (which is the pK_a when K_w is 4.0×10^{-14}).

24. Notes to instructor:

(S11 Exam 2 #12)

Calculate the pH of a solution of a weak acid, given its K_a value and concentration.

Requires taking the square root of a number (with an even exponent):

$$(4.0 \times 10^{-6})^{1/2} = 4.0^{1/2} \times 10^{(-6 \cdot 1/2)} = 2.0 \times 10^{-3}$$

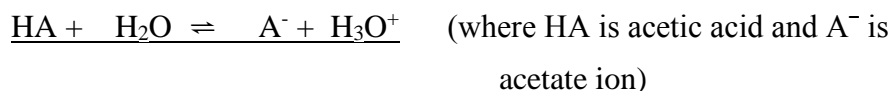
Also requires taking the log of a number that is not exactly a power of ten:

$$\log(2 \times 10^{-3}) = \log 2 + \log(1 \times 10^{-3}) = 0.3 - 3.0 = -2.7$$

What is the pH of a 0.20 M solution of acetic acid, assuming that $K_a = 2.0 \times 10^{-5}$?

- A. 1.5
- B. 2.3
- C. 2.7
- D. 3.3
- E. 4.7
- F. 5.4
- G. 6.6
- H. 10.7

Answer: C. 2.7



| | | | |
|-------------|---------|---|-------------|
| initial | 0.20 M | 0 | ≈ 0 |
| change | -x | x | x |
| equilibrium | 0.20 -x | x | x |

$$K_a = [\text{A}^-][\text{H}_3\text{O}^+] / [\text{HA}] \quad \text{Since } K_a \text{ is small, } [\text{HA}] \approx [\text{HA}]_0$$

$$2.0 \times 10^{-5} = x^2 / 0.20$$

$$x^2 = 2.0 \times 10^{-5} (0.20) = 0.40 \times 10^{-5} = 4.0 \times 10^{-6}$$

$$x = (4.0 \times 10^{-6})^{1/2} = 4.0^{1/2} \times 10^{(-6 \cdot 1/2)} = 2.0 \times 10^{-3} = [\text{H}_3\text{O}^+]$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log(2.0 \times 10^{-3}) = -(\log 2 + \log 10^{-3}) = -(0.3 - 3.0) = -(-2.7) = 2.7$$

25. Notes to instructor:

(S10 Exam 2 #14)

Calculate the pH of a solution of a weak acid, given its K_a value and concentration.

Requires estimating a square root of a number in scientific notation:

$$(15 \times 10^{-12})^{1/2} = 15^{1/2} \times (10^{-12})^{1/2} = 15^{1/2} \times 10^{-12 \times 1/2} \approx 4 \times 10^{-6} \text{ M}$$

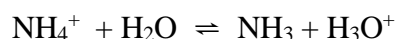
Also requires taking the log of a number in scientific notation:

$$\log(4 \times 10^{-6}) = \log 4 + \log(1 \times 10^{-6}) = 0.6 - 6.0 = -5.4$$

What is the pH of a 0.03 M solution of NH_4Cl ? (For NH_4^+ , $K_a \approx 5 \times 10^{-10}$)

- | | | | |
|----|------|----|-----|
| A. | 10.8 | E. | 4.7 |
| B. | 7.2 | F. | 4.1 |
| C. | 6.9 | G. | 3.2 |
| D. | 5.4 | H. | 2.6 |

Answer: D. 5.4



This is the reaction that defines K_a of NH_4^+

| | | | |
|-------------|----------|---|-------------|
| initial | 0.03 M | 0 | ≈ 0 |
| change | -x | x | x |
| equilibrium | 0.03 - x | x | x |

$$K_a = 5 \times 10^{-10} = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]} \approx \frac{x^2}{0.03}$$

where we are using the "small x" approximation for $[\text{NH}_4^+]$ at equilibrium.

$$x^2 = 0.03 \times 5 \times 10^{-10} = (3 \times 10^{-2}) \times (5 \times 10^{-10}) = 15 \times 10^{-10+(-2)} = 15 \times 10^{-12}$$

$$x = (15 \times 10^{-12})^{1/2} = 15^{1/2} \times (10^{-12})^{1/2} = 15^{1/2} \times 10^{-12 \times 1/2} \approx 4 \times 10^{-6} \text{ M} = [\text{H}_3\text{O}^+]$$

Here we estimate the square root of 15 to be close to the square root of 16, which is 4.

Raising a number to an exponent of 1/2 means taking its square root.

We also use $(10^a)^b = 10^{a \cdot b}$.

$$\text{pH} = -\log(4 \times 10^{-6}) = -(\log 4 + \log(1 \times 10^{-6})) = -(0.6 - 6.0) = -(-5.4) = 5.4$$

Here we use (from the equation sheet): $\log 4 = 0.6$

26. Notes to instructor:

(S12 Exam 2 #13)

Calculate the pH of a solution of a weak acid, given its concentration and K_a value.

Requires taking the square root of a number in scientific notation by converting to one with an even exponent (and estimating the square root of the coefficient).

$$(1.8 \times 10^{-5})^{1/2} = (18 \times 10^{-6})^{1/2} \approx 4 \times 10^{-3} \quad (\text{since } \sqrt{16} = 4, \text{ and } 18 \text{ is close to } 16)$$

Calculate the pH of a 0.3 M solution of benzoic acid (C_6H_5COOH), assuming a K_a value of 6×10^{-5} .

- A. 1.4
- B. 1.9
- C. 2.4
- D. 3.1
- E. 3.6
- F. 4.2
- G. 4.7
- H. 5.3
- I. 10.4
- J. 11.8

Answer: C. 2.4

The reaction is: $C_6H_5COOH + H_2O \rightleftharpoons C_6H_5COO^- + H_3O^+$

| | | | |
|---------|--------|---|----|
| initial | 0.3 M | 0 | ~0 |
| change | -x | x | x |
| equilib | 0.3 -x | x | x |

$$K_a = 6 \times 10^{-5} \approx x^2 / 0.3 \quad (\text{since } K_a \text{ is small})$$

$$x^2 = (6 \times 10^{-5})(0.3) = 1.8 \times 10^{-5}$$

$$x = [H_3O^+] = (1.8 \times 10^{-5})^{1/2} = (18 \times 10^{-6})^{1/2} \approx 4 \times 10^{-3} \text{ M} \quad (\text{since } \sqrt{16} = 4, \text{ and } 18 \text{ is close to } 16)$$

$$\text{pH} = -\log [H_3O^+] = -\log (4 \times 10^{-3}) = -(\log 4 - 3.0) = -(0.6 - 3.0) = -(-2.4) = 2.4$$

(here we have used $\log 4 = 0.6$ from the last line of the equation sheet)

27. Notes to instructor:

(S10 Exam 2 #15)

Calculate the K_a value of a weak acid, given the pH of a solution with a given concentration.

Requires obtaining a number, given its log (an integer):

$$10^{-5.0} = 1 \times 10^{-5}$$

... and squaring a number in scientific notation:

$$(1 \times 10^{-5})^2 = 1^2 \times 10^{-5 \times 2} = 1 \times 10^{-10}$$

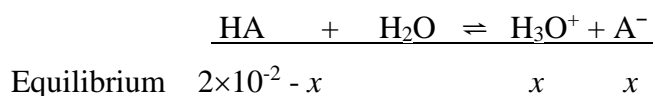
... and evaluating a ratio, in which the denominator has a negative exponent:

$$1 \times 10^{-10} / (2 \times 10^{-2}) = (1/2) \times 10^{-10 - (-2)} = 0.5 \times 10^{-10 + 2} = 0.5 \times 10^{-8} = 5 \times 10^{-9}$$

Given that the pH of a 0.02 M solution of a weak monoprotic acid is 5.0, estimate the acid dissociation constant (K_a) for this acid.

- A. 5×10^{-4}
- B. 1×10^{-5}
- C. 5×10^{-7}
- D. 5×10^{-8}
- E. 5×10^{-9}
- F. 5×10^{-10}
- G. 4×10^{-11}
- H. 2×10^{-12}

Answer: E. 5×10^{-9}



$$x = [\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-5.0} = 1 \times 10^{-5}$$

Here we can use the "small- x approximation", since $2 \times 10^{-2} - x = 2 \times 10^{-2} - 1 \times 10^{-5} = 2 \times 10^{-2}$:
(so the change is negligible, to one significant figure).

$$K_a = x^2 / 0.02 = (1 \times 10^{-5})^2 / (2 \times 10^{-2}) = (1 \times 10^{-10}) / (2 \times 10^{-2}) = 0.5 \times 10^{-8} = 5 \times 10^{-9}$$

28. Notes to instructor:

(S12 Exam #14)

Given the pH of a solution of a weak acid and its concentration, calculate the percent dissociation.

Requires obtaining a number from its log, where the log is not an integer:

$$10^{-\text{pH}} = 10^{-2.7} = 10^{-3.0+0.3} = 10^{0.3} \times 10^{-3} = 2 \times 10^{-3} \text{ M}$$

Also requires multiplying by 100 to obtain a percentage.

The pH of a **0.5 M** solution of a weak acid is **2.7**. What is the *percent dissociation* of this weak acid in this solution?

- A. 0.001 %
- B. 0.002 %
- C. 0.004 %
- D. 0.1 %
- E. 0.2 %
- F. 0.4 %
- G. 1%
- H. 2 %
- I. 4 %
- J. 40 %

Answer: F. 0.4 %

The reaction is:

| | | | |
|-------------|---------------------------------------------------------------------------------------|---|----|
| | $\text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{A}^- + \text{H}_3\text{O}^+$ | | |
| initial | 0.5 M | 0 | ~0 |
| change | -x | x | x |
| equilibrium | 0.5 - x | x | x |

At equilibrium, $[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-2.7} = 10^{0.3-3.0} = 10^{0.3} \times 10^{-3} = 2 \times 10^{-3} \text{ M}$,

since $\log 2 = 0.3$ (last line of equation sheet)

This is also the concentration of the conjugate base of the weak acid, and the amount of the weak acid that has reacted with water.

The equilibrium concentration of the weak acid is approximately 0.5 M (ignoring the small amount that has reacted).

Percent dissociation is then: $(2 \times 10^{-3} \text{ M} / 0.5 \text{ M}) \times 100 = 4 \times 10^{-3} \times 100 = 0.4 \%$

29. Notes to instructor:

(F10 Exam 2 #17)

Calculate the pH of a solution of a weak base, given the concentration and the K_a of its conjugate weak acid.

Requires dividing by a number with a negative exponent, $1 \times 10^{-14} / 1 \times 10^{-3} = 1 \times 10^{-14-(-3)} = 1 \times 10^{-11}$

and obtaining the square root of a number in scientific notation (with an even exponent):

$$(4 \times 10^{-12})^{1/2} = 4^{1/2} \times 10^{-12 \cdot 1/2} = 2 \times 10^{-6}$$

and calculating the log of a number that is not exactly a (negative) power of ten:

$$-\log(2 \times 10^{-6}) = -(\log 2 + \log(1 \times 10^{-6})) = -(0.3 - 6.0) = -(-5.7) = 5.7$$

What is the pH of a 0.4 M aqueous solution of sodium fluoride (NaF) ?

Assume that K_a of HF is approximately 1×10^{-3} .

- | | | | |
|----|-----|----|------|
| A. | 2.6 | F. | 8.7 |
| B. | 4.3 | G. | 9.2 |
| C. | 5.3 | H. | 9.7 |
| D. | 5.7 | I. | 10.5 |
| E. | 8.3 | J. | 11.4 |

Answer: E. 8.3

K_b is the equilibrium constant for the following reaction, where F^- , the conjugate base of HF, is produced by the dissolution of NaF in water to form $Na^+(aq) + F^-(aq)$.

| | | | | | |
|-------------|---------|----------|----------------------|------|----------|
| | F^- | $+ H_2O$ | \rightleftharpoons | HF | $+ OH^-$ |
| initial | 0.4 M | | | 0 | ~0 |
| change | -x | | | x | x |
| equilibrium | 0.4 - x | | | x | x |

$$K_b = [HF][OH^-] / [F^-]$$

We can obtain K_b of F^- from K_a of HF: $K_a K_b = K_w$ so

$$K_b = K_w / K_a = 1 \times 10^{-14} / 1 \times 10^{-3} = 1 \times 10^{-14-(-3)} = 1 \times 10^{-11}$$

since K_b is small, the F^- concentration at equilibrium is approximately the initial F^- concentration.

$$1 \times 10^{-11} \approx x^2 / 0.4$$

$$x^2 = 1 \times 10^{-11} (0.4) = 0.4 \times 10^{-11} = 4 \times 10^{-12}$$

$$x = (4 \times 10^{-12})^{1/2} = 4^{1/2} \times 10^{-12 \cdot 1/2} = 2 \times 10^{-6} = [H_3O^+]$$

$$pH = -\log [H_3O^+] = -\log(2 \times 10^{-6}) = -(\log 2 + \log(1 \times 10^{-6})) = -(0.3 - 6) = -(-5.7) = 5.7$$

$$pOH = 14.0 - 5.7 = 8.3$$

30. Notes to instructor:

(S11 Exam 2 #13)

Calculate the pK_b of a weak base, given the pH of a solution with a given concentration.

Requires squaring a number in scientific notation and dividing by a number less than one:

$$(1 \times 10^{-3})^2 / (0.1) = 1 \times 10^{-6} / 0.1 = 1 \times 10^{-6} \times 10 = 1 \times 10^{-5}$$

Also requires calculating the log of a power of ten: $-\log(1 \times 10^{-5}) = 5.0$

A 0.1 M aqueous solution of putrescine [$\text{NH}_2(\text{CH}_2)_4\text{NH}_2$] has a pH of about 11.0.

What is the pK_b of putrescine?

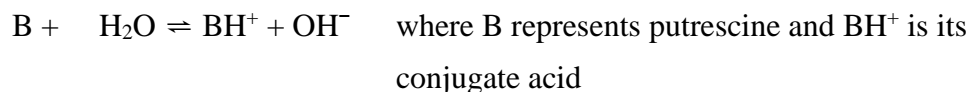
- | | | | |
|----|-----|----|------|
| A. | 3.0 | F. | 8.0 |
| B. | 4.0 | G. | 9.0 |
| C. | 5.0 | H. | 10.0 |
| D. | 6.0 | I. | 11.0 |
| E. | 7.0 | J. | 12.0 |

Answer: C. 5.0

Putrescine is a derivative of ammonia (NH_3), and both are weak bases.

We can also deduce that putrescine is a weak base from the high pH value given in the problem.

K_b is the equilibrium constant for the reaction of the weak base, putrescine, with water:



| | | | |
|-------------|----------|---|-------------|
| initial | 0.10 M | 0 | ≈ 0 |
| change | - x | x | x |
| equilibrium | 0.10 - x | x | x |

$$K_b = [\text{BH}^+][\text{OH}^-] / [\text{B}] = x^2 / (0.10 - x)$$

Since the pH is given as 11.0, the pOH is $14.0 - 11.0 = 3.0$, so $[\text{OH}^-] = 1 \times 10^{-3}$ (this is x).

Using the "small x approximation" with the equilibrium putrescine concentration as 0.10 M:

$$K_b = (1 \times 10^{-3})^2 / (0.1) = 1 \times 10^{-6} / 0.1 = 1 \times 10^{-6} \times 10 = 1 \times 10^{-5}$$

so the pK_b is $-\log(1 \times 10^{-5}) = 5.0$

Note that the "small x approximation" is justified here, since the initial concentration of putrescine is 0.1 M and x, the amount that reacts with water, is only 0.001 M.

(This question is similar to Silberberg & Amateis 18.178, 8th Ed.)

31. Notes to instructor:

(S10 Exam 2 #19)

Buffer problem: calculate the pH of a solution with a given amount of a weak acid and its conjugate weak base; can use the Henderson-Hasselbalch equation.

Requires taking the log of a number that is not exactly a (negative) power of 10:

$$\log(2 \times 10^{-4}) = \log 2 + \log(1 \times 10^{-4}) = 0.3 - 4.0 = -3.7$$

Also requires taking the log of a ratio:

$$\log(0.6 / 0.3) = \log 2 = 0.3$$

Calculate the pH of a 5 L solution containing 0.3 mol of cyanic acid (HCNO, $K_a = 2 \times 10^{-4}$) and 0.6 mol of sodium cyanate (NaCNO).

- | | | | |
|----|-----|----|-----|
| A. | 2.1 | E. | 4.0 |
| B. | 3.4 | F. | 4.2 |
| C. | 3.7 | G. | 5.2 |
| D. | 3.9 | H. | 5.7 |

Answer: E. 4.0

This is a buffer solution, so we can use the Henderson-Hasselbalch equation:

$$\text{pH} \approx \text{p}K_a + \log([\text{base}]_o / [\text{acid}]_o)$$

(where $[\text{acid}]_o$ and $[\text{base}]_o$ are the initial concentrations of the weak acid, HCNO, and its conjugate weak base, CNO^- , prior to their reactions with water)

$$\text{p}K_a = -\log(2 \times 10^{-4}) = -(\log 2 + \log(1 \times 10^{-4})) = -(0.3 - 4.0) = -(-3.7) = 3.7$$

$$\text{pH} = 3.7 + \log(0.6 / 0.3) = 3.7 + \log 2 = 3.7 + 0.3 = 4.0$$

(Since the HH equation involves a ratio of concentrations of the base to acid in the same volume of solution, the volumes cancel, so we can use the ratio of moles.)

32. Notes to Instructor:

(S12 Exam 2 #18)

Calculate the pH of a buffer solution prepared by reacting a weak acid with (fewer moles of) a strong base, given the concentrations and the pK_a of the weak acid.

Can use the Henderson-Hasselbalch equation.

Requires simplifying a ratio

$$0.025/0.075 = 1/3$$

and taking the log of a fraction:

$$\log(1/3) = -\log 3 = -0.5$$

If 0.025 mole of NaOH is added to 500. mL of a 0.200 M solution of HCN (hydrocyanic acid, $pK_a = 9.2$), what is the pH of the resulting solution?

- | | | | |
|----|-----|----|------|
| A. | 7.7 | F. | 9.2 |
| B. | 8.2 | G. | 9.5 |
| C. | 8.4 | H. | 9.7 |
| D. | 8.7 | I. | 10.1 |
| E. | 8.9 | J. | 12.7 |

Answer: D. 8.7

Amount of HCN present initially: $(0.50 \text{ L})(0.20 \text{ m/L}) = 0.10 \text{ mole}$

The reaction of OH^- (from the dissolution of NaOH) with the acid will go to completion:

| | | | | | | | |
|---------|---------------|---|------------|---------------|----------------------|---|-----------------------------|
| | OH^- | + | HCN | \rightarrow | H_2O | + | CN^- (cyanide ion) |
| initial | 0.025 mole | | 0.100 mole | | | | 0 |
| change | -0.025 | | -0.025 | | | | +0.025 |
| final | ≈ 0 | | 0.075 | | | | 0.025 |

This makes a buffer solution (similar amounts of a weak acid and its conjugate weak base), so we can use the Henderson-Hasselbalch equation:

$$\text{pH} = \text{p}K_a + \log([\text{base}]/[\text{acid}])$$

$$\text{pH} = 9.2 + \log(0.025/0.075) = 9.2 + \log(1/3) = 9.2 - \log 3 = 9.2 - 0.5 = 8.7$$

33. Notes to instructor:

(S10 Exam 2 #20)

Calculate the pH of a buffer solution after a strong base (NaOH) has been added, given the numbers of moles of the weak acid, conjugate weak base, and the NaOH, and the pK_a of the acid. Can use the Henderson-Hasselbalch equation.

Requires using the log of 1:

$$\log (0.6 / 0.6) = \log 1 = 0$$

A buffer is prepared by mixing 0.4 mole of NaNO_2 and 0.8 mole of HNO_2 ($pK_a = 3.35$) in 1.00 L of water. After the addition of 0.2 mole of KOH, what is the pH of this solution?

- A. 13.30
- B. 4.05
- C. 3.85
- D. 3.65
- E. 3.35
- F. 3.05
- G. 2.65
- H. 0.70

Answer: E. 3.35

| | | | |
|-----------------|-------------------------------------------------------------------------------------------|-------------|-------------|
| | $\text{OH}^- + \text{HNO}_2 \rightarrow \text{H}_2\text{O} + \text{NO}_2^-$ to completion | | |
| initial (moles) | 0.2 | 0.8 | 0.4 |
| change | <u>-0.2</u> | <u>-0.2</u> | <u>+0.2</u> |
| final | 0.0 | 0.6 | 0.6 |

$$\text{pH} \approx \text{p}K_a + \log ([\text{base}]_o / [\text{acid}]_o)$$

here we use the "final" values, *after* the reaction of the weak acid, HNO_2 , with the strong base, OH^- (from NaOH), has gone to completion

$$\text{pH} = 3.35 + \log (0.6 / 0.6) = 3.35 + \log (1) = 3.35 \quad \text{since } \log 1 = 0$$

(Since the HH equation involves the ratio of the concentrations of the weak base to the weak acid in the same volume, the volumes cancel, so we can use the ratio of moles.)

34. Notes to instructor:

(F10 Exam 2 #19)

Calculate the pH of a buffer solution after a strong base (NaOH) has been added, given the numbers of moles of the weak acid, conjugate weak base, and the NaOH, and the pK_a of the acid. Can use the Henderson Hasselbalch equation.

Requires using the log of an integer:

$$\log(0.030/0.010) = \log 3 = 0.48 \text{ (from the equation sheet)}$$

What is the pH of a 1.00 L buffer solution initially containing 0.020 mole of ammonia (NH_3) and 0.020 mole of ammonium chloride (NH_4Cl), after the addition of 0.010 mole of NaOH?

The pK_a of NH_4^+ is 9.24.

- A. 2.00
- B. 8.76
- C. 8.94
- D. 9.24
- E. 9.54
- F. 9.72
- G. 12.00
- H. 12.24

Answer: F. 9.72

| | | | | | | |
|---------|--------------------------|----------------------------|---------------------------------|--------------------------|----------------------------|-----------------------------------------------|
| | <u>OH^-</u> | <u>NH_4^+</u> | <u>\rightarrow</u> | <u>NH_3</u> | <u>$+ H_2O$</u> | to completion because OH^- is a strong base |
| initial | 0.010 | 0.020 | | 0.020 | | |
| change | -0.010 | -0.010 | | +0.010 | | |
| final | ~0 | 0.010 | | 0.030 | | |

Since we are left with similar amounts of the weak base, NH_3 , and its conjugate weak acid, NH_4^+ , and there is no excess OH^- , we can use the Henderson Hasselbalch equation:

$$pH = pK_a + \log(\text{base/acid}) = 9.24 + \log(0.030/0.010) = 9.24 + \log 3 = 9.24 + 0.48 = 9.72$$

35. Notes to instructor:

(S11 Exam 2 #16)

Titration: Calculate the pH of the solution in the titration of a strong acid by a strong base (with excess acid).

Requires simplifying a ratio:

$$0.020 \text{ mol} / 0.400 \text{ L} = 2 / 40 = 1 / 20 = 0.05 \text{ M}$$

Also requires taking the log of a number that is not exactly a power of 10:

$$\log (5 \times 10^{-2}) = \log 5 + \log (1 \times 10^{-2}) = 0.7 - 2.0 = -1.3$$

Calculate the pH during the titration of 300. mL of a 0.10 M solution of the strong acid HNO₃, after 100. mL of 0.10 M NaOH have been added.

- A. 1.1
- B. 1.3
- C. 1.5
- D. 1.7
- E. 2.3
- F. 2.7
- G. 3.5
- H. 11.3

Answer: B. 1.3

HNO₃ (nitric acid) is a strong acid that will react completely with water to give H₃O⁺.

The reaction with OH⁻ (from the NaOH) then proceeds to completion: H₃O⁺ + OH⁻ → 2 H₂O .

Before this reaction, moles H₃O⁺ = (0.10 M)(0.300 L) = 0.030 mol

moles OH⁻ (0.10 M)(0.100 L) = 0.010 mol (limiting reagent)



| | | |
|-----------------|---------------|---------------|
| initial (moles) | 0.030 | 0.010 |
| change | <u>-0.010</u> | <u>-0.010</u> |
| final | 0.020 | ≈ 0 |

After this reaction, there will be 0.020 mol excess H₃O⁺ and a total volume of 0.400 L so

$$[\text{H}_3\text{O}^+] = 0.020 \text{ mol} / 0.400 \text{ L} = 2 / 40 = 1 / 20 = 0.05 \text{ M}$$

$$\text{pH} = -\log (5 \times 10^{-2}) = -(\log 5 + \log 10^{-2}) = -(0.7 - 2.0) = -(-1.3) = 1.3$$

36. Notes to instructor:

(S12 Exam 2 #19)

Calculate the pH of the solution in the titration of a strong acid by a strong base (with excess base).

Requires obtaining the log of a number less than one:

$$\text{pOH} = -\log(0.50) = \log 2.0 = 0.30$$

As an example of a titration of a strong base by a strong acid, 50. mL of a 1.0 M NaOH solution is titrated with 2.0 M HNO₃ (nitric acid).

What will be the pH of the solution in the titration flask after **10. mL** of the nitric acid solution has been added?

- | | | | |
|----|------|----|------|
| A. | 14.0 | F. | 11.8 |
| B. | 13.7 | G. | 11.3 |
| C. | 13.0 | H. | 7.0 |
| D. | 12.7 | I. | 0.3 |
| E. | 12.2 | J. | 0.2 |

Answer: B. 13.7

NaOH will dissolve to give OH⁻ in solution

$$\text{moles OH}^- = 0.050 \text{ L} \times 1.0 \text{ mol/L} = \mathbf{0.050 \text{ mol}}$$

HNO₃ will protonate water to give 2.00 M H₃O⁺.

$$\text{moles H}_3\text{O}^+ = 0.010 \text{ L} \times 2.0 \text{ mol/L} = \mathbf{0.020 \text{ mol}}$$

So, H₃O⁺ is the limiting reagent.

Reaction in the titration flask is:

| | | | | | |
|---------|-----------------|---|-------------------------------|---|------------------------------------|
| | OH ⁻ | + | H ₃ O ⁺ | → | 2 H ₂ O (to completion) |
| initial | 0.050 mol | | 0.020 mol | | |
| change | <u>-0.020</u> | | <u>-0.020</u> | | |
| final | 0.030 mol | | 0.00 mol | | |

Thus, have 0.030 mol of OH⁻ in excess, and the total volume is 60 mL (0.060 L).

$$[\text{OH}^-] = 0.030 \text{ mol} / 0.060 \text{ L} = 0.50 \text{ M}$$

$$\text{pOH} = -\log 0.50 = \log 2.0 = 0.30$$

$$\text{pH} = 14.00 - 0.30 = \mathbf{13.70}$$

37. Notes to instructor:

(S11 Exam 2 #17)

Calculate the pH in the titration of a weak acid by a strong base (in the buffer region prior to the equivalence point). Can use the Henderson-Hasselbalch equation.

Requires obtaining the log of a fraction:

$$\log(1/2) = -\log 2 = -0.3$$

300 mL of a 0.10 M solution of a weak acid ($K_a = 1 \times 10^{-6}$) is being titrated with 0.10 M NaOH. What is the pH of the solution in the titration flask after 100 mL of NaOH have been added?

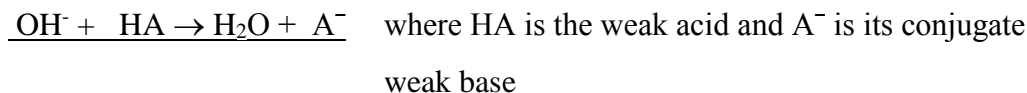
- | | | | |
|----|-----|----|------|
| A. | 5.0 | F. | 6.5 |
| B. | 5.5 | G. | 7.0 |
| C. | 5.7 | H. | 9.3 |
| D. | 6.0 | I. | 10.6 |
| E. | 6.3 | J. | 12.4 |

Answer: C. 5.7

moles acid initially: $(0.300 \text{ L})(0.10 \text{ m/L}) = 0.030 \text{ mole}$

moles OH^- added: $(0.100 \text{ L})(0.10 \text{ m/L}) = 0.010 \text{ mole}$

The following reaction will go to completion, until the OH^- from the NaOH has been consumed:



| | | | |
|-----------------|---------------|---------------|---------------|
| initial (moles) | 0.010 | 0.030 | 0 |
| change | <u>-0.010</u> | <u>-0.010</u> | <u>+0.010</u> |
| final | ≈ 0 | 0.020 | 0.010 |

After this reaction has occurred, the solution contains similar amounts of the weak acid, HA, its conjugate base, A^- , and no excess OH^- .

So, it is a buffer solution and we can use the HH equation to solve for the pH.

The $\text{p}K_a$ of the weak acid is 6.0 (since we are given that its K_a value is 1×10^{-6}).

$$\text{pH} \approx \text{p}K_a + \log(\text{base}_o / \text{acid}_o)$$

$$\text{pH} \approx 6.0 + \log(0.010 / 0.020) = 6.0 + \log(1/2) = 6.0 - \log 2 = 6.0 - 0.3 = 5.7$$

Here we have used the number of moles in the HH equation instead of converting to concentrations, since the volume will cancel, so the ratio of moles is the same as the ratio of concentrations.

38. Notes to instructor:

(S10 Exam 3 #2)

Calculate the pH in the titration of a weak acid by a strong base, in the buffer region prior to reaching the equivalence point (can use the Henderson-Hasselbalch equation).

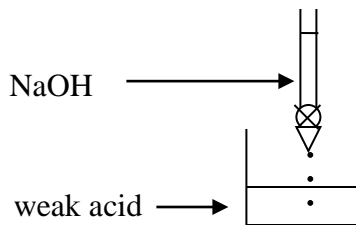
Requires simplifying a fraction and taking the log of a number less than one:

$$\log(0.005 / 0.015) = \log(1/3) = -\log(3) = -0.5$$

 200 mL of a 0.100 M solution of a weak acid ($K_a = 1 \times 10^{-9}$) is titrated with NaOH.

What is the pH of the solution in the titration flask after 50 mL of the 0.100 M NaOH solution have been added?

- A. 12.3
- B. 9.5
- C. 9.3
- D. 9.0
- E. 8.7
- F. 8.5
- G. 7.0
- H. 5.1



Answer: F. 8.5

moles acid initially present: $(0.100 \text{ M})(0.200 \text{ L}) = 0.020 \text{ mol}$

moles OH^- added: $(0.100 \text{ M})(0.050 \text{ L}) = 0.005 \text{ mol}$

Reaction taking place in solution (where HA is the weak acid):

$\text{OH}^-(\text{aq}) + \text{HA} \rightarrow \text{H}_2\text{O} + \text{A}^-(\text{aq})$ goes to completion because OH^- is a strong base

| | | | |
|---------|------------|------------|------------|
| initial | 0.005 mol | 0.020 mol | ~0 |
| change | -0.005 mol | -0.005 mol | +0.005 mol |
| final | | | |
| ~ 0 | 0.015 mol | 0.005 mol | |

Since we have similar amounts of a weak acid and its conjugate weak base in solution after the reaction with OH^- has gone to completion, we can use the Henderson-Hasselbalch equation.

$$\text{pH} = \text{p}K_a + \log(\text{A}^- / \text{HA})$$

Since $\log K_a = \log(1 \times 10^{-9}) = -9.0$, the $\text{p}K_a$ of the weak acid is 9.0.

$$\text{pH} = 9.0 + \log(0.005 / 0.015)$$

note $\log(0.005 / 0.015) = \log(1/3) = -\log(3)$

since $\log(1/a) = \log 1 - \log a = 0 - \log a = -\log a$

$\log 3 = 0.5$ (from log table on equation sheet), so $-\log 3 = -0.5$

$$\text{pH} = 9.0 - 0.5 = 8.5$$

Notice that we can tell that the pH has to be *below* 9.0, because we have not yet added enough OH^- to get to the midpoint of the titration (which would require 0.020 mol), at which the pH would be 9.0.