Calculations In Chemistry

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Module 35: Solubility Equilibrium
And
Module 36: Thermodynamics

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Module 35 — Solubility Equilibrium

Prerequisites: Before this module, complete Lessons 7B and 7C on ionic compounds, Lesson 12B on the *REC* steps, and Lessons 28C, D, and F on equilibrium calculations.

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Lesson 35A: Slightly Soluble Ionic Compounds

Pretest: If you think you know this topic, try the last two problems on both problem sets. If you can do those problems, skip the lesson.

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Slightly Soluble Salts

When any ionic compound (salt) is mixed with water, it dissolves to at least a *slight* extent.

In Module 13, our solubility scheme divided ionic compounds into *soluble* and *insoluble*, based on whether 0.10 moles of a compound dissolved per liter of aqueous solution at 25°C. For many problems, this general division is all we need to make useful predictions about chemical behavior.

However, the ionic compounds labeled *insoluble* in solubility schemes are more accurately described as **slightly soluble.** The extent of their solubility, even if it is quite small, can be important in many chemical processes.

When a salt with low solubility is mixed with water, some formula units leave the surface and form separated ions that move about freely in the solution. As these ions accumulate, the reverse reaction occurs as well: dissolved ions return to the solid, combining to form neutral formula units on the surface of the ionic crystal.

Over time, the rate at which the ions return to the solid becomes equal to the rate at which they dissolve. Though both reactions continue, there is no *net* change. As long as some solid is present and the temperature remains constant, the mixture will remain in this equilibrium condition.

At equilibrium, the *solution* above the solid is said to be **saturated**: the dissolved ion concentrations are theoretically as high as they can be in an aqueous solution at that temperature (exceptions occur that we will discuss later).

An example of this equilibrium is the slight solubility of lead chloride. In solubility schemes, the combination of Pb^{2+} and Cl^- ions is predicted to be insoluble, but the solid lead chloride does dissolve *slightly* in water. This reaction can be represented as

$$PbCl_2 \textit{(solid)} \leftarrow \leftarrow \rightarrow Pb^{2+}\textit{(aqueous)} + 2\,Cl^-\textit{(aq)} \qquad \text{(goes slightly)}$$
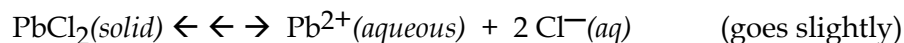
With mixing, the reaction reaches equilibrium. Thereafter, as long as the temperature remains constant, no further net change in the solid-solution mixture takes place.

For reactions that go to equilibrium, an equilibrium constant expression can be written. Write the *K* expression for the reaction above, then check your answer below.

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$$K \; = \; \frac{[Pb^{2+}]\,[Cl^{-}]^2}{1} \; = \; [Pb^{2+}]\,[Cl^{-}]^2 \; = \; K_{sp}$$

As with all equilibrium constants,

- the general form is "product of the concentrations of the products over product of the concentrations of the reactants."

- The lowest-whole-number *coefficients* of the balanced equation become *exponents* in the K expression.

- The concentration of a solid is assigned a value of 1 in K expressions because solids have a constant concentration. The concentrations of the ions are included in the K expression because ion concentrations in a solution can vary. Terms with values that can *vary* are included in K expressions, but terms that are constant are omitted.

- All K_{sp} expressions have a 1 in the denominator. The 1 is omitted as understood when writing the K_{sp} expression.

For the special case of a slightly soluble ionic solid dissolving in water, the following rules are used.

K_{sp} Rules

If a problem lists a K_{sp}, or if the reaction is a salt dissolving slightly in water,

1. The balanced equation is always written with one particle of the ionic solid on the left and its ions on the right.

2. The K expression for the reaction is termed the **solubility product**, symbol K_{sp}.

3. A K_{sp} expression has ion concentrations to powers multiplied in the numerator, but no term (a 1) in the denominator.

Applying those rules, solve this problem.

   Q. The K_{sp} value for $Co(OH)_2$ is 2.5×10^{-16}. Write the balanced equation for the reaction that this is a K value for, and then the K_{sp} expression.

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Answer

   This reaction is $1\, Co(OH)_2{}_{(s)} \; \leftarrow\leftarrow\rightarrow \; 1\, Co^{2+} \; + \; 2\, OH^{-}$ (goes slightly)

- In K_{sp} problems, for the separated *ions* in both the reaction equation and the K_{sp} expression, the aqueous *(aq)* state of the ions can be omitted as understood.

- The low K value means that the reaction goes only slightly: equilibrium strongly favors the reactants.

- The K_{sp} expression is: $K_{sp} = [Co^{2+}][OH^{-}]^2$

Practice A: Do every other problem now and the rest during your next study session. Check answers at the end of the lesson.

1. Write the K_{sp} expression for these reactions.

       a. $HgS(s) \leftleftarrows \rightarrow Hg^{2+} + S^{2-}$ b. $Al_2(CO_3)_3(s) \leftleftarrows \rightarrow 2\ Al^{3+} + 3\ CO_3^{2-}$

2. Write the reaction and K_{sp} expression for these salts dissolving slightly in water.

       a. AgI   b. $Sr(OH)_2$ c. Calcium phosphate   d. Copper (II) sulfide
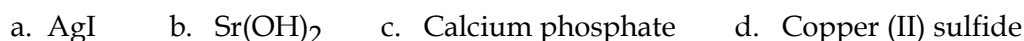
3. Label these compounds as *soluble* or *slightly soluble*.

       a. $AgNO_3$ b. $Fe(OH)_3$ c. Potassium phosphate   d. Silver chloride

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K_{sp} Math

Solving calculations that include K_{sp} values will require taking powers and roots of exponential notation. This math was covered in Lesson 28B. The following problems apply those rules to K_{sp} -type calculations. If you need a *rule* review, see Lesson 28B.

Practice B: Solve in your problem notebook. Convert final answers to scientific notation. Try every other problem, and more if you need more practice.

Do *not* use a calculator on these first four.

1. $(10^4)^{-3} =$ 2. $(2.0 \times 10^{-5})^3 \ =$

3. $(27 \times 10^{-6})^{1/3} \ =$ 4. $(16 \times 10^{-12})^{1/4} \ =$

On 5-8,

- first write an *estimated* answer and convert the estimate to scientific notation;
- then use a calculator as needed get a *final* answer in scientific notation.

5. The square root of $2.25 \times 10^{-10} =$ 6. The cube root of $6.4 \times 10^{-8} =$

7. $(5.1 \times 10^3)^2 \ =$ 8. $(1.6 \times 10^{-15})^{1/4} \ =$

Solve the following using a calculator as needed.

9. $(exact\ 3)(9.6 \times 10^{-11})^{1/2} \ =$ 10. $(exact\ 9)(8.1 \times 10^{-11})^{1/4} \ =$

11. $(exact\ 4\ )(7.5 \times 10^{-4})^3 \ =$

Solve problems 12-16 for x .

12. $4x^3 = 5.0 \times 10^{-16}$ 13. $(108)x^5 = 3.46 \times 10^{-17}$

14. $(2x)^2 (0.025) = 4.9 \times 10^{-14}$ 15. $(x) (0.20)^2 = 4.8 \times 10^{-19}$

16. $(3x)^3(2x)^2 = 2.62 \times 10^{-36}$

ANSWERS

Practice A

1a. $K_{sp} = [Hg^{2+}][S^{2-}]$ 1b. $K_{sp} = [Al^{3+}]^2 [CO_3^{2-}]^3$

2a. $AgI(s) \leftarrow\leftarrow\rightarrow Ag^+(aq) + I^-(aq)$ $K_{sp} = [Ag^+][I^-]$

  b. $Sr(OH)_2(s) \leftarrow\leftarrow\rightarrow Sr^{2+}(aq) + 2\,OH^-(aq)$ $K_{sp} = [Sr^{2+}][OH^-]^2$

  c. $Ca_3(PO_4)_2(s) \leftarrow\leftarrow\rightarrow 3\,Ca^{2+}(aq) + 2\,PO_4^{3-}(aq)$ $K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2$

  d. $CuS(s) \leftarrow\leftarrow\rightarrow Cu^{2+}(aq) + S^{2-}(aq)$ $K_{sp} = [Cu^{2+}][S^{2-}]$

3. Soluble are a. $AgNO_3$ and c. Potassium phosphate; Slightly soluble are b. $Fe(OH)_3$ and d. Silver chloride. See the solubility scheme in Lesson 13A.

Practice B

1. 10^{-12} 2. 8.0×10^{-15} 3. 3.0×10^{-2} 4. 2.0×10^{-3} 5. 1.50×10^{-5}

6. $= (16 \times 10^{-16})^{1/4} = 4.0 \times 10^{-3}$ 7. 2.6×10^7 8. 2.0×10^{-4} 9. 2.9×10^{-5}

10. 2.7×10^{-2} 11. $4\,(7.5 \times 10^{-4})^3 = 4\,(422 \times 10^{-12}) = 1690 \times 10^{-12} = \mathbf{1.7 \times 10^{-9}}$

12. $4x^3 = 5.0 \times 10^{-16}$; $x^3 = 1.25 \times 10^{-16} = 125 \times 10^{-18}$; $\boldsymbol{x = 5.0 \times 10^{-6}}$

13. $(108)x^5 = 3.46 \times 10^{-17}$; $x^5 = 3.46/108 \times 10^{-17} = 32.2 \times 10^{-20}$; $\boldsymbol{x = 2.00 \times 10^{-4}}$

14. $(2x)^2 (0.025) = 4.9 \times 10^{-14}$; $4x^2 = 198 \times 10^{-14}$; $x^2 = 49 \times 10^{-14}$; $x = \mathbf{7.0 \times 10^{-7}}$

15. $(x)(0.20)^2 = 4.8 \times 10^{-19}$; $x(0.040) = 4.8 \times 10^{-19}$; $x = 120 \times 10^{-19} = \mathbf{1.2 \times 10^{-17}}$

16. $(27x^3)(4x^2) = (108)x^5 = 2.62 \times 10^{-36}$; $x^5 = 0.0243 \times 10^{-36} = 243 \times 10^{-40}$; $x = \mathbf{3.0 \times 10^{-8}}$

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Lesson 35B: K_{sp} Calculations

Pretest: If you think you know this topic, try the last two problems at the end of the lesson. If you can do those problems, skip the lesson.

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K_{sp} Values

For ionic solids that dissolve only slightly in water, the concentration of the ions in the solution is low at equilibrium. K_{sp} *value*s will therefore be less than one: positive numbers with negative exponents when written in scientific notation.

  For example, in the reaction of slightly soluble silver chloride dissolving in water,

$$AgCl(s) \leftarrow\leftarrow\rightarrow Ag^+(aq) + Cl^-(aq) \qquad \text{(goes slightly)}$$
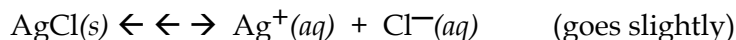
$$K_{sp} = [Ag^+][Cl^-] = \mathbf{1.6 \times 10^{-10}} \quad \text{at } 25^{\circ}C$$

K_{sp} values for a sample of slightly soluble ionic compounds are listed in the table below. As with all equilibrium constants,

- K_{sp} values have units, but the units are not included with K_{sp} values or used in K_{sp} calculations.
- If a concentration is calculated based on a K_{sp}, the unit *mol/L* must be added to the concentration.
- *K* values are difficult to measure precisely, and values may vary among textbooks. To match textbook answers, use the K_{sp} values in that text.

Solid	K_{sp} at 25°C
AgBr	5.0×10^{-13}
AgI	1.5×10^{-16}
Fe(OH)$_2$	1.8×10^{-15}
Ba$_3$(PO$_4$)$_2$	5.0×10^{-23}

Because a K_{sp} value varies with temperature, it must have a temperature attached, but by convention in K_{sp} problems, temperature is assumed to be *25°C* unless otherwise noted.

K_{sp} *WRECK* Steps

To solve K_{sp} calculations, use the fundamental rule for reactions that go to equilibrium rather than completion: Write the *WRECK* steps.

For the following example, write the *WRE* part of the *WRECK* steps, and then check your answer below.

Q. When solid silver sulfate is mixed with water, what is the [Ag$^+$] in the solution at equilibrium? (K_{sp} Ag$_2$SO$_4$ = 1.2×10^{-5})

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*W*ANTED: [Ag$^+$]

*R*xn. & *E*xtent: **1** Ag$_2$ SO$_4$*(s)* ← ← → 2 Ag$^+$ + 1 SO$_4^{2-}$ (goes slightly)

Next, to find the *C*oncentrations@equilibrium, we can either use a *rice* table or write the bottom row of the *rice* table by inspection. Let's try the *rice* table first.

In K_a calculations, for a weak acid ionizing slightly in water, *x* was defined as the small amount of *reactant that reacts*. For an ionic solid ionizing slightly in water, we define *x* in the same way. Since *x* is reactant used up, the reactant's *x* has a negative sign in the *C*hange row. We also assume that *initially* the reaction has not started, so there are no products.

Based on the reaction and rules above, fill in the empty boxes of the following table, then check your answer below.

Reaction			
Initial	mol/L solid	**0 M**	
Change (+,**—**)	**—** *x* **M**		
At **E**quilibrium			

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Reaction	1 Ag_2SO_4 (s)	2 Ag^+	1 SO_4^{2-}
Initial	mol/L solid	0 M	0 M
Change (+,−)	− x M	+ 2x M	+ x M
At Equilibrium	mol/L solid − x	+ 2x M	+ x M

This table follows the standard *rice* rules from Lesson 28G for reactions that go to equilibrium.

- Because coefficients show the ratios in which reactants are used up and products form, the coefficients in **R**eaction row 1 must match the numbers in front of the x terms in rows 3 and 4.

- In the **C**hange row, each reactant term must have the same *sign*, and each product term must have the *opposite* sign.

- The units in the table must be consistent: moles or mol/L. Mol/L can be used as a unit if all particles are in the same solution, as they are when an ionic solid dissolves slightly to form an aqueous solution.

Once the bottom row of the *rice* table is written in terms of x, complete the **K** step of the *WRECK* steps:

- Write the **K** equation: the expression (with [ ] symbols) and **K** value (if known).

- Write the *exact K* equation: substitute the x terms from the bottom *rice* row into the **K** expression.

- Solve the exact **K** equation to find the unknown value: **K** or x.

- If needed, use x to solve for the **W**ANTED symbol.

Try those steps based on the *rice* table above, then check your answer below.

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The **K** expression and value: $K_{sp} = [Ag^+]^2 [SO_4^{2-}] = 1.2 \times 10^{-5}$

The *exact K* equation: $K_{sp} = (2x)^2 (x) = 1.2 \times 10^{-5}$

Solve for x: $(4x^2)(x) = 1.2 \times 10^{-5}$

$$4x^3 = 1.2 \times 10^{-5}$$

$$x^3 = 0.30 \times 10^{-5} = 3.0 \times 10^{-6}$$

$$x = 1.44 \times 10^{-2}$$

Solve for the **W**ANTED symbol: $[Ag^+] = 2x = 2.9 \times 10^{-2}$ M

Significant figures: Since coefficients are exact, for terms such as $(2x)^2$ above in which the numbers are based on coefficients, those numbers are exact. Numbers based on coefficients do not limit the significant figures in an answer.

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The Solubility: Small x

For the reaction of a slightly soluble ionic solid dissolving in water, x is *defined* as the **solubility**: the small number of moles per liter that leave the solid.

> For a slightly soluble ionic solid dissolving in water: the solid's **solubility** = small x

Since solubility is the moles of solid that dissolve per liter, the unit of solubility is mol/L, and the unit *mol/L* (or its abbreviation *M*) must be added when solubilities are calculated using *K* equations.

In *rice* tables, the key definition is x. The rule is

> In K_{sp} calculations, when writing *rice* tables or *WRECK* steps,
>
> - Let $-x$ represent the small mol/L of the reactant used up in the reaction.
> - At equilibrium, let $[\text{solid}]_{eq.}$ = **mol/L solid** $-x$
> - Define the product concentrations using positive x terms.

The term *mol/L solid* can mean either the moles of solid added per liter of solution, or it can mean the density of the solid, measured in mol/L. The values will differ, and which value applies depends on the question being asked. However, in K_{sp} calculations, the value does not matter, because the value for *mol/L **solid*** is not included in K_{sp} equations.

Note that the *solubility* is not the same as the *solubility product*.

> **Solubility** of an ionic solid = small x in mol/L units.
>
> **Solubility product** = K_{sp} = [ions] multiplied, with no denominator and no units.

Writing [Ions]$_{eq.}$ By Inspection

Compared to general *K* calculations, K_{sp} calculations are simplified because an ionic solid formula is always on the reactant side of the balanced equation, and its coefficient is always one. On the right side are always its separated ions.

Because reactions with a K_{sp} have this simple and consistent form, at the **C** step of the *WRECK* steps, we can write the bottom *rice* row by inspection, rather than by writing a complete *rice* table. This is the same method that we used in K_a and K_b problems.

To simplify K_{sp} calculations: write the *first* term in the **C** row of the *WRECK* steps, which is the same as the first term in the *bottom* row of the *rice* table, as $\boxed{\text{mol/L solid} -x}$ (see the *rice* table above).

Using that rule, complete the *REC* steps for this ionic solid dissolving slightly in water.

$\quad$ *R*xn. & *E*xtent:$\qquad$ **1** Fe(OH)$_3$*(s)* $\quad \leftarrow \leftarrow \rightarrow$

$\qquad\qquad\qquad\qquad\qquad\qquad \wedge$

$\quad$ *C*onc@eq.:$\qquad\qquad\qquad\qquad\qquad$ ▌

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$Rxn.$ & $Extent$:   **1** Fe(OH)$_3$*(s)*   ← ← → **1** Fe^{3+} + **3** OH$^-$ (goes slightly)

$Conc$@eq.:   **mol/L solid** $- x$ ▌ $+ x$ | $+ 3x$

Try one more.

  Q. Write the REC steps for the slight ionization of silver phosphate.

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Tip: To determine the solid formula when given a name, it helps to write and balance the separated ions on the *products* side first.

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$Rxn.$ & $Extent$:   **1** _____   ← ← → 3 Ag$^+$ + 1 PO$_4{}^{3-}$ (goes slightly)

Complete the REC steps by inspection.

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$Rxn.$ & $Extent$:   **1** Ag$_3$PO$_4$*(s)*   ← ← → **3** Ag$^+$ + **1** PO$_4{}^{3-}$ (goes slightly)

$Conc$@eq.:   mol/L solid $- x$ $3x$ x

As was done above based on the *rice* table, a value of x can be solved by substituting the x terms into the K_{sp} equation.

Try this example. Write the complete *WRECK* steps. Write the **C**-step terms by inspection as done in the two REC step problems above. Find the value for x.

  Q. What is the solubility of strontium chromate (K_{sp} = 3.6 x 10^{-5}).

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WANTED: ? = **Solubility** = small x in mol/L

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$Rxn.$ & $Extent$: _____   ← ← →   Sr^{2+} +   CrO$_4{}^{2-}$ (goes slightly)

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$Rxn.$ & $Extent$:   **1** SrCrO$_4$*(s)*   ← ← → **1** Sr^{2+} + **1** CrO$_4{}^{2-}$ (goes slightly)

$Conc$@eq.:   mol/L solid $- x$ ▌ x | x

If needed, finish the calculation.

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At the **K** step:

*   Write the K equation: the K expression and K value.
*   Write the exact K equation, substituting the x terms above into the K expression.
*   Solve the exact K equation to find the unknown value.
*   Solve for the symbol **W**ANTED.

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K_{sp} = $[Sr^{2+}]$ $[CrO_4{}^{2-}]$ = $(x)(x)$ = x^2 = 3.6×10^{-5} = 36×10^{-6}

WANTED = x = 6.0×10^{-3} M = **solubility** = mol/L of $SrCrO_4$ that dissolves

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Summary

Nearly all **K calculations** are solved the same way.

1. Write the *WRECK* steps.

2. Find the **C**oncentrations at equilibrium, usually in terms of x, either using a *rice* table or by inspection.

3. Solve the **K** equation, then solve for the WANTED symbol.

K_{sp} is the special K for a slightly soluble salt dissolving in water.

1. In K_{sp} *WRECK* steps, write a balanced equation with *one* particle of the ionic *solid* on the *left*, its aqueous separated ions on the right, and (goes slightly).

2. K_{sp} = **solubility product**. A K_{sp} expression is written with [ions] multiplied in the numerator, but no term in the denominator.

3. For slightly soluble salts, x is the **solubility**: the small moles per liter that dissolve from the solid. At equilibrium, $[solid]_{eq.}$ = **mol/L solid** $- x$

4. **Solubility** of an ionic solid = small x. Add units of moles/liter.

   Solubility product = K_{sp} = [ions] multiplied, with no denominator and no units.

Practice: Do every other problem today, then the rest over the next few days.

1. For each of these slightly soluble salts dissolving in water, write the **R**eaction, its **E**xtent, the **C**oncentrations at equilibrium in terms of x, the K_{sp} expression in symbols, and the exact K_{sp} equation in terms including x. Then combine and simplify the x terms in the exact equation.

      a. CaF_2 b. $BaSO_4$ c. $Pb_3(PO_4)_2$

2. If the solubility of PbI_2 is 1.5×10^{-3} at 25°C, what is its K_{sp}?

3. Find $[Ca^{2+}]$ in a mixture of water and $Ca_3(PO_4)_2$ (K_{sp} = 1.3×10^{-32}) at equilibrium.

4. The K_{sp} of $MgCO_3$ is 6.8×10^{-6}.

   a. Find the solubility of $MgCO_3$.   b. Convert the solubility to nanomoles/mL.

5. Which has higher solubility: $AgCl$ (K_{sp} = 1.6×10^{-10}) or Ag_2CO_3 (K_{sp} = 8.1×10^{-12})?

ANSWERS

Practice A

1a.   **R**xn. & **E**xtent: $1\ CaF_2(s)\ \leftarrow\leftarrow\rightarrow\ 1\ Ca^{2+}\ +\ 2\ F^-$ (goes slightly)

      Conc@eq.:   mol/L solid $- x$ █ x | $2x$

      $K_{sp} = [Ca^{2+}]\,[F^-]^2\ =\ (x)(2x)^2\ =\ \mathbf{4x^3}$

1b.   **R**xn. & **E**xtent: $1\ BaSO_4(s)\ \leftarrow\leftarrow\rightarrow\ 1\ Ba^{2+}\ +\ 1\ SO_4^{2-}$ (goes slightly)

      Conc@eq.:   mol/L solid $- x$ █ x | x

      $K_{sp} = [Ba^{2+}]\,[SO_4^{2-}]\ =\ \mathbf{x^2}$

1c.   **R**xn. & **E**xtent: $1\ Pb_3(PO_4)_2(s)\ \leftarrow\leftarrow\rightarrow\ 3\ Pb^{2+}\ +\ 2\ PO_4^{3-}$ (goes slightly)

      Conc@eq.:   mol/L solid $- x$ █ $3x$ | $2x$
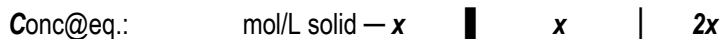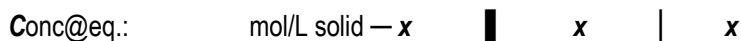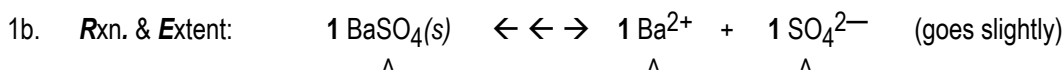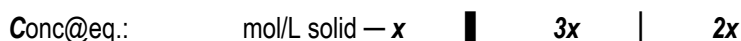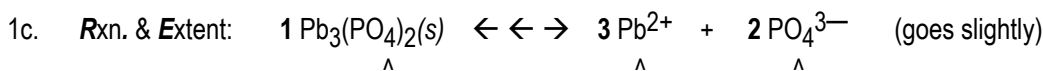
      $K_{sp} = [Pb^{2+}]^3[PO_4^{3-}]^2\ =\ (3x)^3(2x)^2\ =\ (27x^3)(4x^2)\ =\ \mathbf{(108)x^5}$

2.   In calculations for reactions that go to equilibrium, write the *WRECK* steps.

      WANTED: K_{sp}

      Rxn. & **E**xtent: $1\ PbI_2(s)\ \leftarrow\leftarrow\rightarrow\ 1\ Pb^{2+}\ +\ 2\ I^-$ (goes slightly)

      Conc@eq.:   mol/L solid $- x$ x $2x$
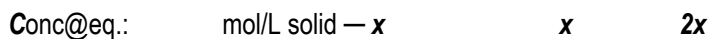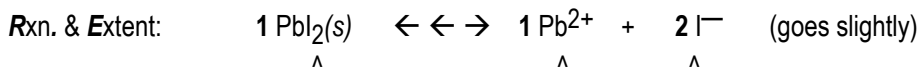
      $K_{sp} = [Pb^{2+}]\,[I^-]^2\ =\ (x)(2x)^2 = 4x^3$

      DATA: $1.5 \times 10^{-3}\ M = solubility = x$

      $K_{sp} = 4x^3 = 4\,(1.5 \times 10^{-3})^3 = 4\,(3.38 \times 10^{-9}) = 14 \times 10^{-9} = \boxed{\mathbf{1.4 \times 10^{-8} = K_{sp}}}$

3.   In calculations for reactions that go to equilibrium, write the *WRECK* steps.

      WANTED: $[Ca^{2+}]$

      Rxn. & **E**xtent: $1\ Ca_3(PO_4)_2(s)\ \leftarrow\leftarrow\rightarrow\ 3\ Ca^{2+}\ +\ 2\ PO_4^{3-}$ (goes slightly)

      Conc@eq.:   mol/L solid $- x$ $3x$ $2x$
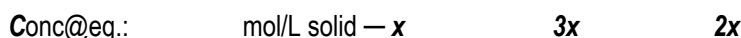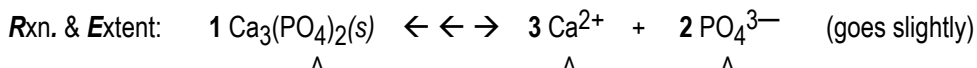
      $K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2\ =\ (3x)^3(2x)^2\ =\ (27x^3)(4x^2)\ =\ (108)x^5$

      $(108)x^5 = 1.3 \times 10^{-32}$; $x^5 = 0.0120 \times 10^{-32}$; $x^5 = 12 \times 10^{-35}$

      $x = 1.64 \times 10^{-7}$; $[Ca^{2+}] = 3x = \boxed{\mathbf{4.9 \times 10^{-7}\ M = [Ca^{2+}]}}$

4a. In calculations for reactions that go to equilibrium, write the *WRECK* steps.

WANTED: *solubility* = **x**   in mol/L

Rxn. & **E**xtent: **1** $MgCO_3(s)$ ← ← →   **1** Mg^{2+} +   **1** $CO_3{}^{2-}$ (goes slightly)

Conc@eq.:   mol/L solid — **x**   ▌   **x** | **x**
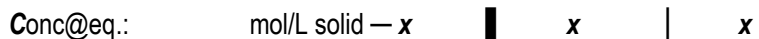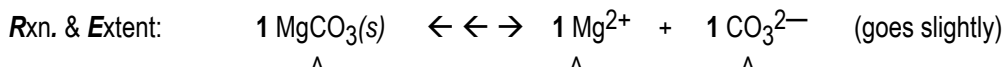
K_{sp} = $[Mg^{2+}] [CO_3{}^{2-}]$ = $(x)(x)$ = x^2 = 6.8×10^{-6}

$\boxed{x = 2.6 \times 10^{-3}\text{ M } = \text{ solubility}}$

The units of solubility, moles that dissolve per liter, must be added to the answer.

4b. ? $\dfrac{\text{nanomoles}}{\text{mL}}$ = $\dfrac{2.6 \times 10^{-3}\text{ mol}}{\text{L}}$ • $\dfrac{10^{-3}\text{ L}}{1\text{ mL}}$ • $\dfrac{1\text{ nanomole}}{10^{-9}\text{ mol}}$ = $\dfrac{2.6 \times 10^{3}\text{ nmol}}{\text{mL}}$

5. AgCl has the higher solubility *product* (K_{sp}), but that may not mean it has the higher *solubility* (**x**). Solve for the solubility of each compound.

  a. **W**ANTED: *solubility AgCl* = **x**

  Rxn. & **E**xtent: **1** $AgCl\ (s)$ ← ← →   **1** Ag^+ +   **1** Cl^- (goes slightly)

  Conc@eq.:   mol/L solid — **x**   ▌   **x** | **x**
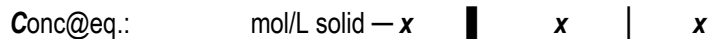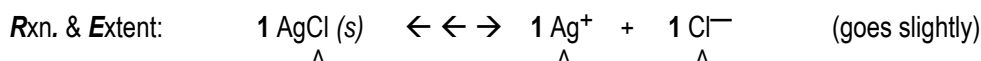
  K_{sp} = $[Ag^+] [Cl^-]$ = $(x)(x)$ = x^2 = 1.6×10^{-10}

  $\boxed{x = 1.3 \times 10^{-5}\text{ M } = \text{ solubility AgCl}}$

  b. **W**ANTED: *solubility* Ag_2CO_3 = **x**

  Rxn. & **E**xtent: **1** $Ag_2CO_3(s)$ ← ← →   **2** Ag^+ +   **1** $CO_3{}^{2-}$ (goes slightly)

  Conc@eq.:   mol/L solid — **x**   ▌   **2x** | **x**
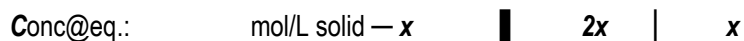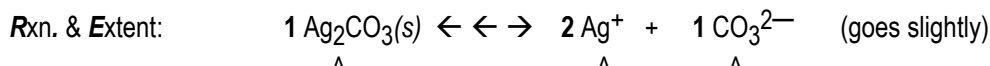
  K equation: K_{sp} = $[Ag^+]^2 [CO_3{}^{2-}]$ = 8.1×10^{-12}

  Exact K in terms of **x** : K_{sp} = $(2x)^2 (x)$ = 8.1×10^{-12}

  Solving for **x:** $(4x^2)(x)$ = 8.1×10^{-12}

                             $4x^3$ = 8.1×10^{-12}

                             x^3 = 2.02×10^{-12}

  $\boxed{x = 1.3 \times 10^{-4}\text{ M } = \text{ solubility } Ag_2CO_3}$

  The Ag_2CO_3, though it has a lower solubility *product* than AgCl, has the higher solubility.

* * * * *

Lesson 35C: Common Ions and Solubility

Prerequisites: If needed, review Lesson 28A on Le Châtelier's Principle.

*   *   *   *   *

Adding Solid

When a mixture of a solid salt and its dissolved ions is at equilibrium, the solution is *saturated*: the ion concentration is as high as theoretically possible. What happens to the [ions] in the solution if more of the same ionic *solid* is added to this solution?

The amount of the solid on the bottom of the solution increases, but the [ions] in the solution is already at its maximum when the solution is at equilibrium, so the [ions] does not shift. Changing the *amount* of the solid does not change the *concentration* of the solid (determined by its density), and does not shift the equilibrium.

Adding A Common Ion

In the laboratory, for mixtures of water and slightly soluble solids, we often want to cause ions that are dissolved in the solution to return to the solid. One way to cause a dissolved ion of interest to return to its solid is to add a *soluble* salt that contains the *other* ion in the ionic compound. Since that other ion that is the same in both the slightly soluble and the added soluble salt, it is a *common ion*.

> For example, in a mixture of solid silver bromide (AgBr) and water at equilibrium, some silver ion is dissolved in the solution above the solid. The equation for the solubility equilibrium is
>
> $$\textbf{1}\,AgBr(s)\ \leftarrow\leftarrow\rightarrow\ \textbf{1}\,Ag^+ + \textbf{1}\,Br^-\qquad (\text{goes slightly:}\ K_{sp} = 5.0 \times 10^{-13})$$
>
> If solid sodium bromide (NaBr) is added to the mixture of AgBr and water, it will dissolve ~100% and separate ~100% into Na^+ and Br^- ions.
>
> $$\textbf{1}\,NaBr(s)\ \rightarrow\rightarrow\ \textbf{1}\,Na^+ + \textbf{1}\,Br^-\qquad (\text{goes ~100\%})$$
>
> For AgBr and NaBr, Br^- is a common ion. Adding a substantial amount of NaBr substantially increases the $[Br^-]$ in the solution. Using Le Châtelier's Principle (Lesson 28A), write answers to the following questions.
>
>   1.   As Br^- ions from NaBr are added to the solution, in which direction will the AgBr solubility equilibrium shift: left or right?
>
>   2.   Will the $[Ag^+]$ ions dissolved in the solution increase or decrease?
>
>   3.   How will this shift change the amount of AgBr solid in the bottom of the beaker?
>
>   4.   How will this shift change the concentration of AgBr solid?
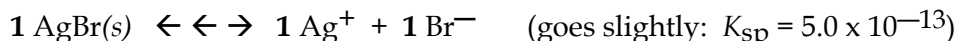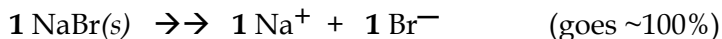
★   ★   ★   ★   ★

Answers

According to Le Châtelier's Principle, if the concentration of a component that appears on one side of an equilibrium equation is *increased*, the equilibrium shifts toward the opposite side of the equation.

In this case, adding Br^- ions shifts the AgBr equilibrium to the *left*, *decreasing* the $[Ag^+]$ in solution. For the $[Ag^+]$ to go down, silver ions must combine with Br^- ions and return to the surface of the solid, so the *amount* of solid AgBr goes up. However, the concentration of a solid is constant and is not changed by shifts in equilibrium.

In a solubility equilibrium, if a common ion is added:

the common ion shifts the *non*-common ion of the slightly soluble salt out of the solution and into the solid.

Practice A

1. Which of these compounds would you add to a mixture of solid AgI and water at equilibrium to reduce the $[Ag^+]$ in the solution?

    a. AgBr   b. KI   c. AgI   d. $AgNO_3$ e. NaI

2. Which of these compounds, when added to a solution of solid AgI at equilibrium with its dissolved ions, will reduce the $[I^-]$ in the solution?

    a. AgBr   b. KI   c. AgI   d. $AgNO_3$ e. NaI

Common Ion K_{sp} Calculations

To take advantage of the common ion effect to shift a solubility equilibrium, the [common ion] must be relatively high. A *soluble* salt that contains the common ion is required to create this high [common ion].

When a common ion is added to an equilibrium solution of a slightly soluble solid and its ions,

*   Le Châtelier's Principle predicts the *direction* that the equilibrium will shift.
* K_{sp} values can calculate *how much* the equilibrium will shift.

To solve K_{sp} calculations with common ion added, apply these rules:

*   If you see a K_{sp} value for a substance, write the *WRECK* steps for its slight ionization.
*   If a problem involves [ions] of two compounds, write the *REC* steps for both.

Common ion K_{sp} problems have two compounds, one with a *K* that calls for *WRECK* steps, the other a soluble ionic compound that calls for *REC* steps. Begin by writing the WANTED unit, and then the *REC* steps for each compound.

Fill in the *blanks* in the following table of the reactions that occur in this mixture with a common ion, then check your answers below.

Q. To a mixture of $Ba_3(PO_4)_2$ (K_{sp} = 5.0 x 10^{-23}) and water at equilibrium, 0.25 mol per liter of solid K_3PO_4 is added. Once the new equilibrium is established, what will be the solubility of the $Ba_3(PO_4)_2$?

*W*ANTED: _____

*R*xn. & *E*xtent: **1** $Ba_3(PO_4)_2(s)$ ← ← → **3** Ba^{2+} + **2** PO_4^{3-} (goes _____)

*C*onc@eq.:   mol/L solid − x ▐   _____ | _____

*R*xn. & *E*xtent: **1** $K_3PO_4(s)$ → →   **3** K^+ + **1** PO_4^{3-} (goes _____)

*C*onc@eq.:   ~~0.25 M~~ ***0 M***   ▐   _____ | _____

K_{sp} = [_____] — [_____] — = 5.0 x 10^{-23}

[Ba^{2+}] = _____ **M**
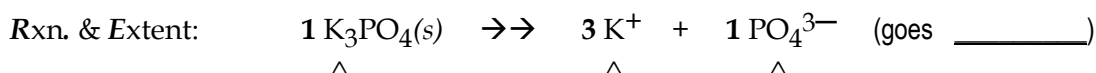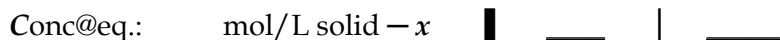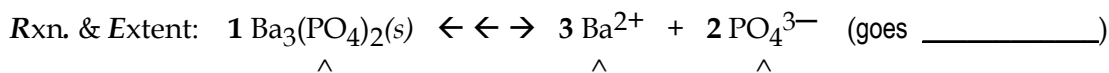
[PO_4^{3-}] = _____ **M** (exact) ≈ _____ **M** (approximate)

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Answer

Since barium phosphate has a small K_{sp} value, it is slightly soluble. From our solubility scheme (Lesson 13A), we know that potassium compounds are water soluble. We also know that compounds with metal atoms, including potassium, in an aqueous solution will separate ~100% into ions. If needed, adjust your work and complete the table.

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*W*ANTED: solubility $Ba_3(PO_4)_2$ = x in mol/L

*R*xn. & *E*xtent: **1 $Ba_3(PO_4)_2$**(s) ← ← → **3** Ba^{2+} + **2** PO_4^{3-} (goes ***slightly***)

*C*onc@eq.:   mol/L solid − x ▐   _3x_   ‖   _2x_

*R*xn. & *E*xtent: **1 K_3PO_4**(s)   → →   **3** K^+ +   **1** PO_4^{3-} (goes ***~100%***)

*C*onc@eq.:   ~~0.25 M~~ ***0 M***   ▐   _0.75 M_ | _0.25 M_
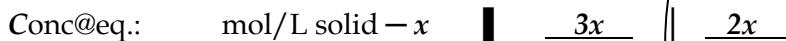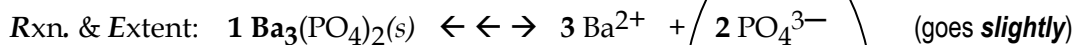
K_{sp} = [Ba^{2+}]^3[PO_4^{3-}]^2 = 5.0 x 10^{-23}

[Ba^{2+}] =   _3x_

[PO_4^{3-}] =   _0.25 M + 2x_   (exact) ≈ _0.25 M_   (approximate)

For problems with two or more reactions and/or lots of numbers, writing a DATA table below the equation, with each equation symbol and its DATA, is a good idea.

The common ion is supplied to the solution by both ionic compounds, but the largest contribution is due to the *soluble* salt.

For the [common ion], use the approximation rule: a small number added or subtracted from a large number does not substantially change the large number (see Lesson 30B). This rule applies to a small x *and* $2x$ and $3x$.

The steps for solving K equations are

- Solve the K equation using the approximation.

- Apply the 5% test to see if the approximation can be used.

- Then solve for the WANTED symbol.

Find the $Ba_3(PO_4)_2$ solubility in this solution that has common ion added.

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$$K_{sp} = [Ba^{2+}]^3 [PO_4^{3-}]^2 = 5.0 \times 10^{-23}$$

$$K_{sp} = (3x)^3 (0.25 \text{ M} + 2x) \approx (3x)^3 (0.25) = 5.0 \times 10^{-23}$$

<center>^ Exact   ^Approximate</center>

We could solve the exact equation for x using the quadratic formula, but the approximation solves more quickly. Solve for x using the *approximation* first.

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$$(3x)^3 (0.25) = 5.0 \times 10^{-23}$$

$$27x^3 = 20. \times 10^{-23}$$

$$x^3 = 0.741 \times 10^{-23} = 7.41 \times 10^{-24}$$

$$x = \boxed{1.9 \times 10^{-8} \text{ M} = \text{solubility } Ba_3(PO_4)_2}$$

When solving K_c, K_a, K_b, or K_{sp} calculations for concentration or solubility, always add *mol/L* (**M**) as the unit of the answer.

The value for solubility above is based on an approximation. K values have relatively high uncertainty, and as with K_a calculations, a 5% error in calculations is usually within the range of experimental error.

In a common ion calculation, error is introduced by ignoring the x term in the exact [common ion] at equilibrium, and this error can be measured by

$$\% \text{ } K_{sp} \text{ Common Ion Error} = 5\% \text{ test} \approx \frac{x \text{ or } 2x \text{ or } 3x}{[\text{common ion}]_{\text{mixed}}} \bullet 100\%$$

By using this equation, we can also use a *quick test* as the 5% test.

If the difference between the *exponents* of the [common ion] and the x term in the exact [common ion], with both written in scientific notation, is 3 or greater, the 5% test is passed, and the approximation may be used.

In this problem,

*   [common ion]$_{exact}$ = **0.25 + 2x**

*   [common ion] = 0.25 M = 2.5 x 10^{-1} M   and   2x = 3.8 x 10^{-9} M

so the exponent difference is 8, the ionization is much smaller than 5%, and the approximation is acceptable.

Summary: Adding a Common Ion to A Solubility Equilibrium

Rule: In a mixture of a slightly soluble ionic solid and its dissolved ions, to reduce the solution concentration of one ion, add a soluble salt that contains the *other* ion in the solid.

To solve a K_{sp} calculation with common-ion added,

*   As in all *K* calculations, write the *WRECK* steps.

*   Write *REC* steps for the ionization of *both* the slightly soluble and highly soluble salt.

*   Write a DATA TABLE under the K_{sp} equation. Include the *exact* and *approximate* [common ion].

*   Solve the K_{sp} equation first using the *approximate* [common ion] first, then do the 5% test.

Practice B: Do half now. Save a few for your next two study sessions.

1.   Change the equation to an approximation, then solve for x .

   a. $(x)(0.50 + 2x) = 2.0 \times 10^{-12}$

   b. $(2x)^2(0.25 + 3x) = 6.4 \times 10^{-7}$

2.   Into a 0.025 M Na_2CrO_4 solution, solid Ag_2CrO_4 (K_{sp} = 9.0 x 10^{-12}) is added. At equilibrium after mixing, some solid remains. Find the $[Ag^+]$ in the solution.

3.   Solid AgBr (K_{sp} = 5.0 x 10^{-13}) is added to a 0.30 M $AgNO_3$ solution. After equilibrium is reached between the solid and its ions, what is the $[Br^-]$ in the solution?

4.   What is the solubility of PbI_2 (K_{sp} = 1.4 x 10^{-8}) in a 0.20 M KI solution?

ANSWERS

Practice A

1.   In the solution above a slightly soluble ionic solid, to reduce the equilibrium concentration of one ion, add a soluble salt that contains the other ion. Above solid AgI, to reduce $[Ag^+]$, increase the $[I^-]$ substantially. The two compounds that ionize ~100% to form I^- are (b) **KI** and (e) **NaI** .

2. Above solid AgI, to reduce [I⁻], increase the [Ag⁺] substantially. The one compound that ionizes ~100% to form Ag⁺ is (d) **AgNO₃** .

Practice B

1a. $(x)(0.50 + 2x) = 2.0 \times 10^{-12}$ To approximate, **x** or **2x** or **3x** can be dropped if **x** is added or subtracted from a much larger number.

$(x)(\mathbf{0.50}) = 2.0 \times 10^{-12}$; $x = 2.0/0.50 \times 10^{-12} = \mathbf{4.0 \times 10^{-12}} = x$
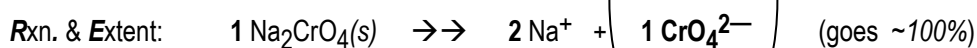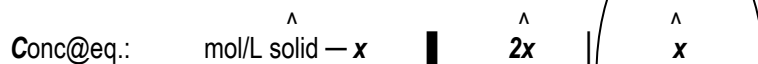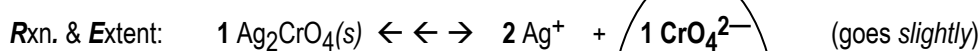
1b. $(2x)^2 (0.25 + 3x) = 6.4 \times 10^{-7}$

$(4x^2)(0.25) = 6.4 \times 10^{-7}$; $(x^2)(4 \times 0.25) = 6.4 \times 10^{-7}$

$x^2 = 6.4 \times 10^{-7} = 64 \times 10^{-8}$; $x = \mathbf{8.0 \times 10^{-4}}$

2. All Na compounds ionize ~100% in water. The small K_{sp} means that Ag_2CrO_4 is only slightly soluble.

   Solve *K* calculations using the *WRECK* steps. If two compounds are involved, write *REC* steps for both.

   Wanted: [Ag⁺]

   Rxn. & **E**xtent: 1 Ag₂CrO₄(s) ← ← → 2 Ag⁺ + 1 CrO₄²⁻   (goes *slightly*)

   Conc@eq.: mol/L solid — **x**   **|**   **2x** | **x**

   Rxn. & **E**xtent: 1 Na₂CrO₄(s) → → 2 Na⁺ + 1 CrO₄²⁻   (goes ~*100%*)

   Conc@eq.: ~~0.025 M~~ 0 M   **|**   0.050 M | **0.025 M**

   $K_{sp} = [Ag^+]^2 [CrO_4{}^{2-}] = 9.0 \times 10^{-12}$ Make a DATA TABLE with the equation symbols.

   $[Ag^+] = \mathbf{2x}$

   $[CrO_4{}^{2-}] = \mathbf{0.025\ M + x}$ (exact) ≈ **0.025 M** (approximate)

   Solve the *K* equation using the approximation first.

   $K_{sp} = (2x)^2 (0.025\ M) = 9.0 \times 10^{-12}$

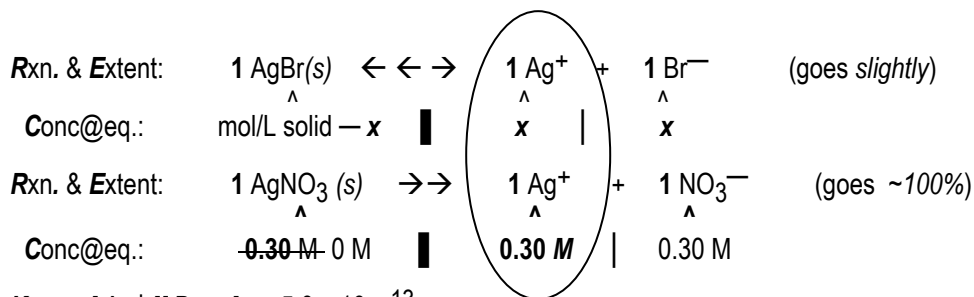 $4x^2 = 360 \times 10^{-12}$

   $x^2 = 90 \times 10^{-12}$

   $x = 9.5 \times 10^{-6}$

   ? = [Ag⁺] = 2x = 1.9 × 10⁻⁵ M

Since $(x/0.25)(100\%) = (9.5/0.25) \times 10^{-6} \times 10^2\% = 3.8 \times 10^{-3}\%$ is <5% , the approximation is acceptable.

3. All nitrate compounds ionize ~100% in water. The small K_{sp} means that AgBr is only slightly soluble.
   Solve *K* calculations using the *WRECK* steps. If two compounds are involved, write *REC* steps for both.

   Wanted: **[Br⁻]**

*R*xn. & *E*xtent: **1** AgBr*(s)* ← ← → **1** Ag$^+$ + **1** Br$^-$ (goes *slightly*)

*C*onc@eq.:   mol/L solid — *x* ▮ *x* | *x*

*R*xn. & *E*xtent: **1** AgNO$_3$ *(s)* →→ **1** Ag$^+$ + **1** NO$_3$$^-$ (goes *~100%*)

*C*onc@eq.:   ~~0.30 M~~ 0 M ▮ **0.30 *M*** | 0.30 M

K$_{sp}$ = [Ag$^+$][Br $^-$] = 5.0 x 10^{-13}

  [Ag$^+$] = **0.30 M + *x*** ≈ **0.30 M**

  [Br$^-$] = ***x***

Solve the *K* equation using the approximate value first.

K$_{sp}$ = 5.0 x 10^{-13} ≈ (*x*)(0.30)

  x = 16.7 x 10^{-13} = **1.7 x 10^{-12} M = [Br $^-$]**

The difference between [common ion] = 3.0 x 10^{-1} and *x* = ~10^{-12} is 11 which is greater than 3, so the approximation is acceptable.

4.   All potassium compounds ionize ~100% in water. The small *K*$_{sp}$ means that PbI$_2$ is only slightly soluble.

   Solve *K* calculations using the *WRECK* steps. If two compounds are involved, write *REC* steps for both.

    *W*anted: solubility of PbI$_2$ = small = ***x***

    *R*xn. & *E*xtent: **1** PbI$_2$*(s)* ← ← → **1** Pb^{2+} + **2** I$^-$ (goes *slightly*)

    *C*onc@eq.:   mol/L solid — *x* ▮ *x* | **2*x***

    *R*xn. & *E*xtent: **1** KI*(s)* →→ **1** K$^+$ + **1** I$^-$ (goes *~100%*)

    *C*onc@eq.:   ~~0.20 M~~ 0 M ▮ 0.20 *M* | **0.20 M**

    K$_{sp}$ = [Pb^{2+}] [I$^-$]^2 = 1.4 x 10^{-8} Make a DATA TABLE with the equation symbols.

      [Pb^{2+}] = ***x***

      [I$^-$] = **0.20 M + 2*x*** (exact) ≈ **0.20 M** (approximate)

    When *x* is small compared to the larger number, *x* or 2*x* or 3*x* added or subtracted may be omitted to obtain the approximation that simplifies calculations.

    Solve the *K* equation using the approximation first.

     K$_{sp}$ = (*x*) (0.20)^2 = 1.4 x 10^{-8}

            x(0.040) = 1.4 x 10^{-8}

               x = 35 x 10^{-8}

     ? = *x* = solubility = 3.5 x 10^{-7} M

    The difference between [common ion] = 2.0 x 10^{-1} and *x* = ~10^{-7} is 6 which is greater than 3, so the approximation passes the 5% test.

*   *   *   *   *

Lesson 35D: pH and Solubility

Adding Acid to Solutions of Slightly Soluble Salts

Some ions found in slightly soluble salts do not react as acids and bases. These ions include

- Cl^-, Br^-, and I^-.

Those three ions are conjugates of the strong acids HCl, HBr, and HI. Conjugates of strong acids are such weak bases that they are essentially pH neutral.
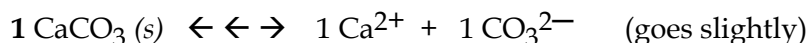
Other ions found in slightly soluble salts can act as acids and bases. Most of these ions are basic. The basic ions include

- OH^-, F^-, S^{2-}, CO_3^{2-}, and PO_4^{3-}.

> Adding *acid* to an equilibrium that includes a *base* will shift the equilibrium. The acid will use up basic particles and reduce the [base]. This reduction in the [base] will shift the equilibrium as predicted by Le Châtelier's Principle.

Based on the above, write answers to this problem, then check your answers below.

Q. Solid $CaCO_3$ is slightly soluble in water.

$$1\ CaCO_3\ \textit{(s)}\ \leftarrow\leftarrow\rightarrow\ \ 1\ Ca^{2+}\ +\ 1\ CO_3^{2-}\qquad \text{(goes slightly)}$$

If a strong acid is added to the above system at equilibrium, what will happen to the

- a. $[CO_3^{2-}]$ in the solution?
- b. $[Ca^{2+}]$ in the solution?
- c.   The amount of solid $CaCO_3$ in the mixture?

★ ★ ★ ★ ★

Answer

a. Carbonate ions are bases (see Lesson 14E), and bases react with strong acids. Adding acid will therefore use up CO_3^{2-} in the solution and cause the $[CO_3^{2-}]$ to decrease.

b. If the concentration of a component that appears on one side of an equilibrium equation is *decreased*, the equilibrium shifts *toward* that side of the equation. Since adding acid decreases the $[CO_3^{2-}]$, the equilibrium above shifts to the right, causing the $[Ca^{2+}]$ to increase.

c. Shifting the equilibrium to the right, the only way that the $[Ca^{2+}]$ can increase is for more solid $CaCO_3$ to dissolve.

Practice A

1. For mixtures of water and these slightly soluble salts, which will have its solubility equilibrium shifted by the addition of a strong acid to the solution?

    a. $CaCl_2$ b. CaF_2 c. AgI d. Ag_2CO_3 e. $Ba_3(PO_4)_2$

2. To a mixture of water and solid $Sr_3(PO_4)_2$ at equilibrium, strong acid is added. What will be the change in the

    a. $[PO_4^{3-}]$ in the solution?   b. $[Sr^{2+}]$ in the solution?

pH and Slightly Soluble Hydroxides

For slightly soluble salts that contain *hydroxide* ions, calculations can solve for unknown quantities including salt solubility, cation concentrations, solution pH, and the K_{sp} of the salt.

Using the rules for pH and K_{sp}, try this calculation. If you get stuck, read the answer until unstuck, then complete the problem.

Q. In a mixture of solid $Mg(OH)_2$ ($K_{sp} = 1.5 \times 10^{-11}$) and water at equilibrium,

     a. $[OH^-] = ?$ b. pH = ?

     c. Will adding strong acid increase or decrease the $[Mg^{2+}]$ in the solution?

     d. What will be the $[Mg^{2+}]$ if acid is added to adjust the pH to 10.0?
         (Try this step without a calculator.)

★ ★ ★ ★ ★

Answer

a. In calculations for reactions that go to equilibrium, write the *WRECK* steps.

*W*ANTED: $[OH^-]$

*R*xn. & *E*xtent: $1\,Mg(OH)_2(s)$ $\longleftarrow\longleftarrow\longrightarrow$ $1\,Mg^{2+}$ + $2\,OH^-$ (goes slightly)

    *C*onc@eq.:   mol/L solid $- x$ ▌ x | $2x$

$K_{sp} = [Mg^{2+}][OH^-]^2 = 1.5 \times 10^{-11}$

   $[Mg^{2+}] = x$ $[OH^-] = 2x$

$K_{sp} = (x)(2x)^2 = 4x^3 = 1.5 \times 10^{-11}$

            $x^3 = 0.375 \times 10^{-11} = 3.75 \times 10^{-12}$

            $x = 1.55 \times 10^{-4}$

$? = [OH^-] = 2x = \boxed{3.1 \times 10^{-4}\,M = [OH^-]}$

b. WANTED = pH   Know $[OH^-]$ from part a.

Write: $\boxed{pOH \equiv -\log[OH^-] \text{ and } [OH^-] \equiv 10^{-pOH}}$ and $\boxed{pH + pOH = 14.00}$

$pOH \equiv -\log[OH^-] = -\log(3.1 \times 10^{-4}) = 3.51; pH = 14.00 - 3.51 = \boxed{10.49 = pH}$

c. For the reaction: $1\,Mg(OH)_2(s)$ $\leftarrow\leftarrow\rightarrow$ $1\,Mg^{2+} + 2\,OH^-$ (goes *slightly*)

adding acid uses up OH^-, shifting the equilibrium to the right, increasing the $[Mg^{2+}]$.

d. *W*ANTED: $[Mg^{2+}]$

WRECK steps – see above.

DATA: $pH = 10.0$, so $pOH = 4.0$ and $[OH^-] \equiv 10^{-pOH} = 10^{-4.0} = 1.0 \times 10^{-4}\,M$

$K_{sp} = [Mg^{2+}][OH^-]^2 = 1.5 \times 10^{-11}$

$[Mg^{2+}] = ?$ $[OH^-] = 1.0 \times 10^{-4}\,M$

$K_{sp} = [Mg^{2+}](1.0 \times 10^{-4})^2 = 1.5 \times 10^{-11}$

$[Mg^{2+}](1.0 \times 10^{-8}) = 1.5 \times 10^{-11}$

$[Mg^{2+}] = \dfrac{1.5 \times 10^{-11}}{1.0 \times 10^{-8}} = \mathbf{1.5 \times 10^{-3}\,M}$

Practice B

1. In a mixture of solid AgOH ($K_{sp} = 2.0 \times 10^{-8}$) and water,

   a. $[Ag^+] = ?$ b. $[OH^-] = ?$ c. $pH = ?$

   d. If a strong acid is added to the solution, will the $[Ag^+]$ increase or decrease?

   e. What will be the $[Ag^+]$ if acid is added to adjust the pH to 9.5?

   f. Compare answers to *parts a* and *e*. Was your prediction in *answer d* correct?

ANSWERS
Practice A

1a. $CaCl_2$ contains Cl^- ion which is not basic, so acid will *not* shift the solubility equilibrium.

1b. CaF_2 forms F^- ion which is basic and will react with acids, so acid *will* shift the equilibrium.

1c.   AgI in solution forms I^- ion which is not basic, so acid will not shift the solubility equilibrium.

1d. Ag_2CO_3 contains $CO_3{}^{2-}$, and 1e. $Ba_3(PO_4)_2$ contains $PO_4{}^{3-}$. Both of those ions are basic and will react with acids, so acid will shift their solubility equilibrium.
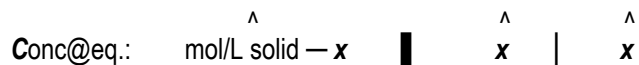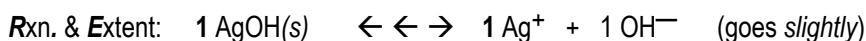
2.   In water, the initial solubility reaction is

$$1 \ Sr_3(PO_4)_2(s) \quad \leftarrow\leftarrow\rightarrow \quad 3 \ Sr^{2+} \ + \ 2 \ PO_4{}^{3-} \quad \text{(goes \textit{slightly})}$$

$PO_4{}^{3-}$ is a basic ion and will be used up when combined with acids, so the $[PO_4{}^{3-}]$ will decrease.

The decrease of $[PO_4{}^{3-}]$ on the right side shifts the equilibrium to the right, increasing the $[Sr^{2+}]$ dissolved in the solution.

Practice B

1a,b.   In calculations for reactions that go to equilibrium, write the *WRECK* steps.

WANTED: $[Ag^+]$

Rxn**.** & **E**xtent: **1** AgOH*(s)* $\leftarrow\leftarrow\rightarrow$ **1** Ag^+ + **1** OH^- (goes *slightly*)

               ^   ^   ^

  Conc@eq.:   mol/L solid $- \, x$ ▌ x | x

K_{sp} = $[Ag^+][OH^-]$ = 2.0×10^{-8}

  Equation DATA table: $[Ag^+]$ = x = $[OH^-]$

K_{sp} = $(x)(x)$ = x^2 = 2.0×10^{-8}

x = **1.4×10^{-4} M** = **$[Ag^+]$** = **$[OH^-]$** = *part b* answer

1c.   WANTED = pH   Know $[OH^-]$

Write: $\boxed{\text{p}\textbf{OH} \equiv - \log[\textbf{OH}^-] \text{ and } [\textbf{OH}^-] \equiv 10^{-\text{p}\textbf{OH}}}$ and $\boxed{\text{pH} + \text{pOH} = 14.00}$

$\text{p}\textbf{OH} \equiv - \log[\textbf{OH}^-] = - \log\,(1.4 \times 10^{-4}) = 3.85$; **pH** = $14.00 - 3.85$ = $\boxed{\textbf{10.15} = \textbf{pH}}$

1d.   Since AgOH has a very small K_{sp}, it is slightly soluble in water. The solubility reaction is:

    AgOH*(s)* $\leftarrow\leftarrow\rightarrow$ **1** Ag^+ + **1** OH^- (goes *slightly*)

Adding acid causes $[OH^-]$ to decrease. According to Le Châtelier's Principle, if the concentration of a component that appears on one side of an equilibrium equation is *decreased*, the equilibrium shifts toward that side of the equation.

Adding acid therefore shifts the equilibrium above to the right and causes the $[Ag^+]$ to *increase*.

1e.   **W**ANTED: $[Ag^+]$

WRECK steps – see above.

DATA: pH = 9.5, so pOH = 4.5 and $[\textbf{OH}^-] \equiv 10^{-\text{p}\textbf{OH}}$ = $10^{-4.5}$ = **3.16×10^{-5} M** = **$[OH^-]$**

K_{sp} = $[Ag^+][OH^-]$ = 2.0×10^{-8}

  $[Ag^+]$ = **?** $[OH^-]$ = 3.16×10^{-5} M

K_{sp} = $[Ag^+]\,(3.16 \times 10^{-5})$ = 2.0×10^{-8}

      $[Ag^+]$ = $\dfrac{2.0 \times 10^{-8}}{3.16 \times 10^{-5}}$ = 0.633×10^{-3} = $\boxed{\textbf{6.3} \times \textbf{10}^{-4} \textbf{ M} = \textbf{[Ag}^+\textbf{]}}$

1f.   Without added acid, **$[Ag^+]$ = 1.4×10^{-4} M .** After adding acid to lower the pH from 10.15 to 9.5, **$[Ag^+]$ = 6.3×10^{-4} M .** The $[Ag^+]$ increased with added acid, as predicted.

* * * * *

Lesson 35E: Quantitative Precipitation Prediction

In Module 13, we learned a simplified scheme to predict whether precipitation will take place when two solutions are combined. Our predictions were based on an arbitrary but convenient division: if a possible product has a solubility of less than 0.1 mol/L in water, it is termed insoluble and will precipitate. These general rules allowed us to make accurate precipitation predictions in cases when solutions with concentrations at or near 0.2 M are combined.

In this lesson, our goal is to predict whether precipitation will occur when solutions that have a *wide range* of concentrations are combined.

Precipitation Prediction

By definition, when solutions of dissolved ions are combined, **precipitation** occurs *if* a precipitate both forms *and* persists after stirring.

When two solutions of ions are combined, to determine whether a precipitation occurs, use these steps.

1. Since solubility predictions involve a K (the K_{sp}), write the *WRECK* steps. Include the K_{sp} equations for precipitate(s) that are predicted based on solubility schemes (see Lesson 13C).

2. Find Q: substitute into the K_{sp} expression the ion concentrations in solution *after* the solutions are combined, but *before* the ions react, then calculate a value for Q.

3. If $Q > K_{sp}$, the precipitate forms *and* persists after stirring.

    If $Q < K_{sp}$, persistent precipitate will *not* form.

    When $Q = K_{sp}$, the precipitate begins to persist after stirring.

These rules rely on the *reaction quotient* (Q) defined in Lesson 28H : Q is the number obtained by substituting into the *K expression* the concentrations in a mixture that may not be at equilibrium.

Apply those three steps to the following problem, then check your answer below.

Q. If 1.0×10^{-3} moles of Ag^+ ions are combined with 1.0×10^{-5} moles of Cl^- ions in 1.0 liters of solution, will AgCl ($K_{sp} = 1.6 \times 10^{-10}$) precipitate?

★ ★ ★ ★ ★

Answer

For *K* calculations, write the *WRECK* steps. If the reaction has a K_{sp}, that reaction is always one formula unit of an ionic solid dissolving slightly in water to form separated ions.

To predict precipitation, compare *Q* for the mixture to K_{sp} for the precipitate.

   *W*ANTED: *Q*

   *R*xn. & *E*xtent: **1** AgCl *(s)*   ← ← →   **1** Ag^+ + **1** Cl^- (goes slightly)

                         ^   ^   ^

    *C*onc@eq.:   mol/L solid $- x$ ▮ x | x

$K_{sp} = [Ag^+][Cl^-] = \mathbf{1.6 \times 10^{-10}}$

$Q = ([Ag^+]_{\text{after combining, before reacting}})([Cl^-]_{\text{after combining, before reacting}})$

   $[Ag^+] = 1.0 \times 10^{-3}$ moles/liter

   $[Cl^-] = 1.0 \times 10^{-5}$ moles/liter

   $Q = (1.0 \times 10^{-3})(1.0 \times 10^{-5}) = \mathbf{1.0 \times 10^{-8}}$

In calculations involving *Q*, as with *K*, the numbers have units but by convention the units are omitted from *Q* values and during *Q* calculations.

   Since $Q = 1.0 \times 10^{-8}$ is greater than $K_{sp} = 1.6 \times 10^{-10}$, AgCl precipitate persists.

* * * * *

Predicting the Point When Precipitation Begins

Comparing *Q* to K_{sp} can predict both weather a precipitate will form *and* the point at which precipitate will form, when solutions is combined.

Apply the 3 steps for precipitation prediction to the following problem. If you get stuck, read a little of the answer, adjust your work, and then complete the problem.

  Q. Solid sodium sulfate is slowly stirred into a solution of 0.020 moles of Ag^+ dissolved in 1.0 liters of solution. At what $[SO_4{}^{2-}]$ will Ag_2SO_4 precipitate form? (K_{sp} $Ag_2SO_4 = 1.2 \times 10^{-5}$)

★ ★ ★ ★ ★

Answer

In this problem, it is helpful to write the sodium sulfate reaction. Sodium compounds dissolve and ionize ~100% in water. Given a name rather than a formula for a salt, write first the separated ions, then the solid formula (for review, see Lesson 7C).

       1 $Na_2SO_4(s)$ →→ **2** Na^+ + **1** $SO_4{}^{2-}$ (goes ~*100%*)

By adding *solid* sodium sulfate that then dissolves, we do not cause a substantial change in the volume of the solution.

For *K* calculations, begin by writing the *WRECK* steps. Then, to find the point at which precipitation persists after stirring, apply the

> **Rule:** Precipitate forms and persists when the substance being added reaches the concentration at which $Q = K_{sp}$.

> *W*ANTED: $[SO_4{}^{2-}]$ when $Q = K_{sp}$
>
> *R*xn. & *E*xtent: $1\ Ag_2SO_4(s) \ \leftarrow\leftarrow\rightarrow\ \ 2\ Ag^+\ +\ \ 1\ SO_4{}^{2-}$ (goes slightly)
>
> ^   ^   ^
>
> *C*onc@eq.: $mol/L\ solid - x$ $\blacksquare$ $2x$ | x
>
> $K_{sp}\ =\ [Ag^+]^2\,[SO_4{}^{2-}]\ = 1.2 \times 10^{-5}\ =\ Q$ at start of precipitation
>
> $[Ag^+]\ = 0.020\ mol/L\ =\ 2.0 \times 10^{-2}\ M$;
>
> $[SO_4{}^{2-}]\ = ?\ =\ \dfrac{1.2 \times 10^{-5}}{[Ag^+]^2}\ =\ \dfrac{1.2 \times 10^{-5}}{(2.0 \times 10^{-2})^2}\ =\ \dfrac{1.2 \times 10^{-5}}{4.0 \times 10^{-4}}\ =\ \mathbf{3.0 \times 10^{-2}\ M}$

> **Summary:** To predict whether *combining* ions will produce a precipitate,
>
> 1. Since K_{sp} is involved, write the *WRECK* steps for the possible precipitate.
>
> 2. Calculate Q, using [ions] after combining, but before reacting.
>
> 3. Compare **Q** to K_{sp}.   If Q is equal or larger, precipitation is predicted.

Practice A: Problem 2 is more challenging.

1. How many moles of solid $AgNO_3$ must be mixed into a 1.0 liter solution containing 0.0200 moles of Na_2CrO_4 before precipitate forms? ($K_{sp}\ Ag_2CrO_4\ = 9.0 \times 10^{-12}$)

2. How many grams of solid NaI must be mixed into a 1.0 liter solution containing 0.040 moles of $Pb(NO_3)_2$ before persistent solid forms? ($K_{sp}\ PbI_2 = 1.4 \times 10^{-8}$)

Solution Concentrations After Combining

In the problems above, the data lists *moles* of substances, plus the volume of the *final* solution after the substances are combined but before they react. Given such data, the concentrations needed to find Q values are easily calculated.

However, in predicting precipitation, most problems supply the concentrations and volumes of the two solutions *before* they are combined. Combining solutions changes the ion concentrations. To solve such calculations, the rules are:

> 1. For solution reactions, in Q and K and *rice* calculations, *mol/L* must be concentrations *after* solutions are combined, but *before* they react.

To find concentrations after combining, we will need rule

> 2. When solutions of *different* dissolved substances are *combined*, each substance is *diluted*.

To find those diluted concentrations, the rule is:

> 3. When solutions are combined, volumes add.

For all but highly concentrated solutions, we can safely assume that 30.0 mL of one aqueous solution added to 20.0 mL of another will result in a volume of 50.0 mL, even if water is a product or reactant of a reaction that occurs when the solutions are combined.

Calculating the diluted concentrations can be done in several ways (see Lesson 12B). Two methods are 1) solve by inspection and 2) use the dilution equation.

1. *If* the solutions that are combined have simple *volume* ratios, the molarity of the substances or ions after combining can often be written by inspection.

    The easiest case: for two solutions that contain different substances and ions, if *equal* volumes of the two solutions are combined, the concentration of each substance or ion in the combined solution is *one-half* its concentration before they were combined.

    > Try this example: If 50.0 mL of 0.60 M Ag^+ is mixed with 50 mL of 0.20 M Cl^-,

    $[Ag^+]_{\text{after combining, before reacting}}$ = _____

    $[Cl^-]_{\text{after combining, before reacting}}$ = _____

* * * * *

    If the volumes combined are equal, the concentrations are cut in half.

    $[Ag^+]_{\text{after combining, before reacting}}$ = 1/2 x 0.60 M Ag^+ = 0.30 M Ag^+

    $[Cl^-]_{\text{after combining, before reacting}}$ = 1/2 x 0.20 M Cl^- = 0.10 M Cl^-

2. If the dilution does not involve easy volume multiples, the quickest way to find the diluted concentrations is to use the dilution equation:

    (Volume concentrated)(Molarity concentrated) = (Volume diluted)(Molarity diluted)

    written in symbols as $\boxed{V_C \times M_C = V_D \times M_D}$ and memorized by recitation:

    > "In dilution, volume times molarity equals volume times molarity."

    For precipitation predictions in which solutions of two substances are combined, we are usually given the volume and molarity of each solution before they are combined, when both solutions are more *concentrated*.

    To find the ion concentrations after combining (M_D) that are needed to calculate Q, first calculate the volume of the *one* solution that exists *after* the solutions are combined. That diluted volume (V_D) is the volume in which *all* of the ions are dissolved after the

solutions are combined. To find V_D, simply add the volumes of the solutions that are mixed together.

Then, to find the concentration of any particle after combining (M_D), use the dilution equation solved for M_D:

$$? M_D = \frac{V_C \times M_C}{V_D}$$ Try those steps on this sample calculation:

Q. If 150.0 mL of 0.0400 M $Pb(NO_3)_2$ is combined with 50.0 mL of 0.0500 M $CaCl_2$ solution, in the solution after combining but before any reaction takes place,

   a. $[Pb(NO_3)_2]$ = ?   b. $[CaCl_2]$ = ?   c. $[Cl^-]$ = ?

   d. *After* the reaction takes place, will there be a precipitate of $PbCl_2$?
       (K_{sp} $PbCl_2$ = 1.5 x 10^{-5})

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Answer

   a. First calculate the volume of the single solution that exists after combining.

      150.0 mL + 50.0 mL = **200.0 mL** = V_D for all particles – after combining. Then,

      WANTED: ? = $[Pb(NO_3)_2]_{diluted}$ = M_D

      The dilution equation is $\boxed{V_C \times M_C = V_D \times M_D}$

      $? M_D = \dfrac{V_C \times M_C}{V_D}$ = $\dfrac{150.0 \text{ mL} \times 0.0400 \text{ M}}{200.0 \text{ mL}}$ = **0.0300 M** = $[Pb(NO_3)_2]_{diluted}$

★ ★ ★ ★ ★

   b. WANTED: ? = $[CaCl_2]_{diluted}$ = M_D

      $? M_D = \dfrac{V_C \times M_C}{V_D}$ = $\dfrac{50.0 \text{ mL} \times 0.0500 \text{ M}}{200.0 \text{ mL}}$ = **0.0125 M** = $[CaCl_2]_{diluted}$

★ ★ ★ ★ ★

   c. WANTED: ? = $[Cl^-]_{diluted}$

      The chloride ion is created by the separation of soluble, diluted $CaCl_2$ into its ions. Either solve by inspection or use the *REC* steps below.

      *R*xn. & *E*xtent: 1 $CaCl_2$ *(s)* → →   1 Ca^{2+} +   2 Cl^- (goes ~100%)
                              ^   ^   ^
      *C*onc@eq.:   ~~0.0125 M~~ 0 M   ▌ 0.0125 *M* | **0.0250 M**
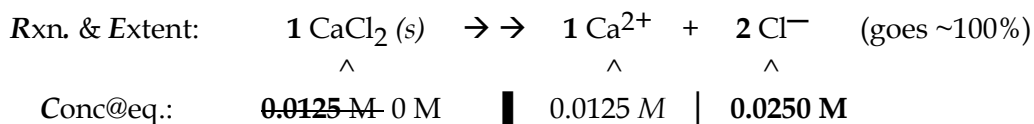
      ? = $[Cl^-]_{diluted}$ = **0.0250 M**

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   d. *W*ANTED: *Q* compared to K_{sp}. If $Q > K_{sp}$, a precipitate *will* form.

      In calculations that involve a *K*, write the *WRECK* steps.

Rxn. & Extent: **1** $PbCl_2(s)$ ⭠⭠➝ **1** Pb^{2+} + **2** Cl^- (goes slightly)

Conc@eq.:   mol/L solid $- x$ ▮ x | $2x$
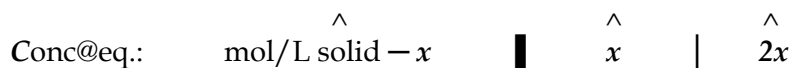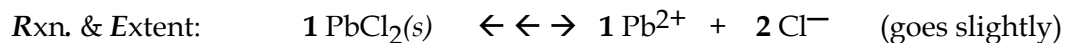
K_{sp} = $[Pb^{2+}][Cl^-]^2$ = Q expression

To calculate Q, use the concentrations in the reaction mixture *after* combining and diluting, but *before* reacting.

$[Pb^{2+}]$ = **0.0300 M**   by inspection from $[Pb(NO_3)_2]$ in answer a.

$[Cl^-]$ = **0.0250 M** from part c.

$Q = \textbf{(0.0300)(0.0250)}^2$ = $(3.00 \times 10^{-2})(2.50 \times 10^{-2})^2$ = $(3.00 \times 10^{-2})(\textbf{6.25} \times 10^{-4})$ =

= 18.8×10^{-6} = 1.9×10^{-5} which is > K_{sp} = 1.6×10^{-5}

The mixture *will* form persistent precipitate.

* * * * *

In the problem above, we calculated the diluted concentrations, then wrote the *WRECK* steps. In most problems, the steps will not be in a requested order, and it will be easier to write the *WRECK* steps first. The K_{sp} expression will then identify the specific concentrations after dilution that must be calculated to find the value for Q.

Summary: To predict whether *combining* ion solutions will produce a precipitate:

1. Since a K (K_{sp}) is involved, write the *WRECK* steps for the possible precipitation(s).

2. Calculate Q using the [*diluted* ions] after combining, but before reacting.

3. Compare Q to K_{sp}. If Q is larger, the precipitate is predicted to form.

Practice B

1. If 100.0 mL of 0.010 M Ag^+ is combined with 100.0 mL of 0.40 M $SO_4{}^{2-}$, will a precipitate form? (K_{sp} Ag_2SO_4 = 1.2×10^{-5})

2. If 150.0 mL of 0.10 M Pb^{2+} is combined with 100.0 mL of 0.0200 M Cl^-, will there be a precipitate of $PbCl_2$ (K_{sp} = 1.5×10^{-5})?

Saturated Solutions Not At Equilibrium

If a solid is at equilibrium with its ions in an aqueous solution, the saturated solution can be **decanted** (carefully poured off, leaving the solid behind) into a separate container. The decanted solution is still *saturated* with its ions, but if there is no solid in the container, the solution in the new container is not at solubility equilibrium.   For equilibrium to exist, all of the products and reactants must be present.

Similarly, if an ionic solid is mixed with water and all of the solid dissolves, the system cannot be at solubility equilibrium. A solubility equilibrium must have some solid present.

Theoretical Versus Actual Results

In K_{sp} calculations, as with most calculations in general chemistry, our goal is to get *close* to an accurate prediction of what experimental results will be. Error can be introduced from many sources, including:

- The equations we use are often based on models that assume ideal behavior, when actual behavior is not ideal.

- Calculations may not take into account all of the factors that may have impact on results.

For example,

- We assume that salts predicted to be soluble by our solubility rules ionize ~100% in solution, but some in some solutions the salt may effectively ionize less than 100%.

- In common-ion calculations, if an added soluble salt is not pH neutral, the equilibrium shifts will be affected by pH changes as well as [common-ion].

- Some solutions can become **supersaturated.** In those cases, the dissolved particle concentrations are higher than they would be theoretically, based the predictions of when precipitation should occur based on K_{sp} values or solidification should occur based on melting points.   In solutions with liquid components, nearly always, no solid is present, so the solution is not at solubility equilibrium. Supersaturated solutions will generally go to the conditions predicted at equilibrium if a "seed crystal" of the solid can be added. The crystal serves as a template on which particles in the solution can fit into geometry needed to form the solid. Without a seed crystal, persuading a solution to crystallize when it should can be one of the interesting challenges of laboratory chemistry.

In upper-level chemistry courses, we consider these factors in more detail. In the meantime, our general chemistry rules will result in *generally* accurate predictions of what truth (experimental results) will be.

Practice C

1. When 25.0 mL of 2.0×10^{-4} M K_2SO_4 is combined with 75.0 mL of 1.0×10^{-4} M $BaCl_2$, if $BaSO_4$ ($K_{sp} = 1.1 \times 10^{-10}$) does not precipitate, is the solution supersaturated?   As always, show your work and explain your reasoning.

ANSWERS

Practice A

1.   **W**ANTED: mol $AgNO_3$

>   *Strategies*:   There are three reactions to consider. First, the two soluble compounds dissolve and separate into ions ~100%. Then, as one substance is added, persistent precipitate forms when $Q = K_{sp}$.
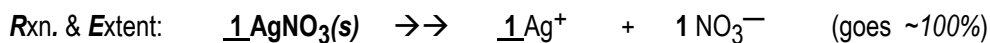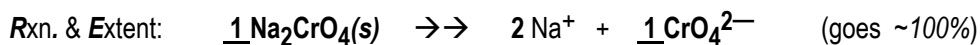>
>   Since a K is involved, write the *WRECK* steps for the formation of the precipitate.
>
>   Since the problem supplies solid formulas, and ion formulas are needed for K and Q, write the *REC* steps for the formation of the ions.

If needed, use those steps to complete the problem, then check below.

* * * * *

First, the two soluble solids ionize.

Rxn. & **E**xtent:	$\underline{1}\,Na_2CrO_4(s)$	$\rightarrow\rightarrow$	$2\,Na^+$ +	$\underline{1}\,CrO_4{}^{2-}$	(goes ~*100%*)
	^		^	^	
Conc@eq.:	$\cancel{0.0200\,M}$ 0 M ▎		0.0400 M │	**0.0200 M**	

Rxn. & **E**xtent:	$\underline{1}\,AgNO_3(s)$	$\rightarrow\rightarrow$	$\underline{1}\,Ag^+$ +	$1\,NO_3{}^-$	(goes ~*100%*)
	^		^	^	
Conc@eq.:	$\cancel{??\,M}$ 0 M ▎		**? M (Wanted)** │	?? M	

Then precipitate forms and ionizes *slightly*. For slight reactions, complete the *WRECK* steps.

Rxn. & **E**xtent:	$1\,Ag_2CrO_4(s)$	$\leftarrow\leftarrow\rightarrow$	$2\,Ag^+$ +	$1\,CrO_4{}^{2-}$	(goes *slightly*)
	^		^	^	
Conc@eq.:	mol/L solid $-\,x$ ▎		$2x$ │	x	
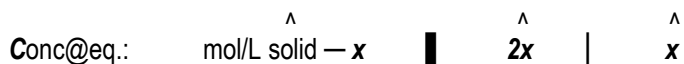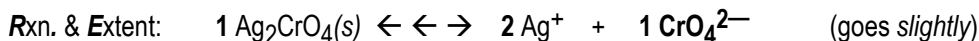
$K_{sp} = [Ag^+]^2\,[CrO_4{}^{2-}] = 9.0 \times 10^{-12}$

The goal is moles of $AgNO_3$ added when $Q = K_{sp}$.

Solving $Q = K_{sp}$ for $[Ag^+]$ will get us close to moles $AgNO_3$.

Make a DATA TABLE with the equation symbols.

$[Ag^+]_{as\ combined,\ before\ reacting}$ = **2x**

$[CrO_4{}^{2-}]_{formed\ in\ solution}$ = **0.0200 mol/L**   from the first reaction above.

$Q = K_{sp} = (2x)^2\,(0.0200\ M) = 9.0 \times 10^{-12}$

$\qquad 4x^2 = 450 \times 10^{-12}$

$\qquad\ \ x^2 = 112 \times 10^{-12}$

$\qquad\ \ \ x = 10.6 \times 10^{-6}$

  ? = $[Ag^+]$ = 2x = 21.2×10^{-6} M **= 2.1 x 10^{-5} M** when persistent precipitation starts.

From the ionization equation for $AgNO_3$ above:

$[Ag^+]_{as\ mixed}$ **= 2.1 x 10^{-5} M** = $[AgNO_3]_{mixed}$ = **mol AgNO$_3$** added per 1.0 L soln**. = WANTED**

2.   In calculations for reactions that go to equilibrium, write the *WRECK* steps.

   WANTED: g NaI

   DATA: 149.9 g NaI = 1 mol NaI   (grams prompt)

   Strategies: To find grams, find moles first.

                 Precipitation begins when $Q = K_{sp}$.

                 Since the moles of NaI will be in a 1.0 L solution, the moles NaI will equal the [NaI]. Since Na compounds ionize ~100% in water, $[NaI]_{mixed} = [I^-]_{formed}$ in solution.

                 If you know some of the steps, but maybe not all at the beginning of a problem, do some steps that get you closer to the answer unit or symbol, then look for ways to finish, working forward from what is known and backward from what is WANTED.

   * * * * *

   Rxn. & **E**xtent: $1 PbI_2(s)$ $\leftarrow \leftarrow \rightarrow$ $1 Pb^{2+}$ + $2 I^-$ (goes slightly)

                                                    ^   ^   ^

   Conc@eq.:   mol/L solid — **x**   ▌   **x** | **2x**

   K_{sp} = $[Pb^{2+}] [I^-]^2$ = 1.4×10^{-8} = Q at start of persistent precipitation

      $[Pb^{2+}]$ = 0.040 M   To find $[I^-]$, find $[I^-]^2$ in equation above first

      $[I^-]^2 = \dfrac{1.4 \times 10^{-8}}{[Pb^{2+}]} = \dfrac{1.4 \times 10^{-8}}{4.0 \times 10^{-2}} =$ 0.350×10^{-6} = **35.0 x 10^{-8}**

      $[I^-] = (35.0 \times 10^{-8})^{1/2}$ = **5.92 x 10^{-4} M = $[I^-]$**

   But what was wanted was grams NaI added. Find moles NaI added first.

   * * * * *

   Moles of soluble NaI added per 1.0 L = $[NaI]_{mixed} = [I^-]_{in\ solution}$ = **5.92 x 10^{-4}**

   From the moles NaI that need to be added, find grams.

   * * * * *

   ? g NaI = **5.92 x 10^{-4}** mol NaI • $\dfrac{149.9\ g\ NaI}{1\ mol\ NaI}$ = **8.9 x 10^{-2} g NaI** = **0.089 g NaI**

   Since the supplied K_{sp} had 2 sf, round the final answer to 2 sf.

Practice B

1.   <u>Steps</u>: To predict precipitation after combining, write the *WRECK* steps for the possible pcpt.; find Q using *diluted* concentrations, compare Q to K_{sp} .

   WANTED: ***Q***

   Rxn. & **E**xtent: $1 Ag_2SO_4(s)$ $\leftarrow \leftarrow \rightarrow$ $2 Ag^+$ + $1 SO_4^{2-}$ (goes slightly)

                                                    ^   ^   ^

     Conc@eq.:   mol/L solid — **x**   ▌   **2x** | **x**

   K_{sp} = $[Ag^+]^2 [SO_4^{2-}]$ = 1.2×10^{-5} = ***Q***

   When solutions are combined, the dissolved substances are diluted.

To calculate Q, we need the [ions] after combining, but before reacting.

Since the two solutions have *equal* volumes, combining them cut their [ions] in half.

$[Ag^+]$after combining, before reacting $= $ 1/2 x 0.010 M Ag^+ $= $ 0.0050 M Ag^+

$[SO_4{}^{2-}]$after combining, before reacting $= $ 1/2 x 0.40 M $SO_4{}^{2-}$ $= $ 0.20 M $SO_4{}^{2-}$

$Q = [Ag^+]^2 [SO_4{}^{2-}] = (5.0 \times 10^{-3})^2 (2.0 \times 10^{-1}) = $ 50. x 10^{-7}

$= $ 5.0. x 10^{-6} which is less than K_{sp} $= 1.2 \times 10^{-5}$, so pcpt. should not form.

2. **W**ANTED: Precipitation prediction: compare Q to K_{sp} .

Rxn. & **E**xtent: **1** $PbCl_2(s)$ $\leftarrow \leftarrow \rightarrow$ **1** Pb^{2+} + **2** Cl^- (goes slightly)
                                    ^   ^   ^

Conc@eq.:   mol/L solid $- x$ ▌ x | $2x$
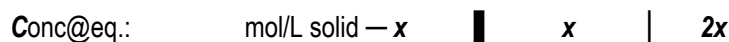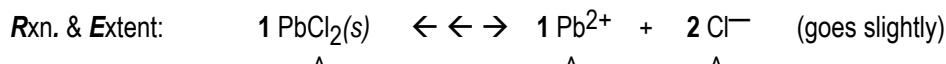
$K_{sp} = $ 1.5 x 10^{-5} $= [Pb^{2+}] [Cl^-]^2$ $= Q$ to calculate using [*diluted* ions]

The dilution equation: $\boxed{V_C \times M_C = V_D \times M_D}$

$[Pb^{2+}]$diluted $= $ **? M_D** $= \dfrac{V_C \times M_C}{V_D}$ $= \dfrac{150.0\ mL \times 0.10\ M}{250.0\ mL\ total}$ $= $ **0.060 M Pb^{2+}**

$[Cl^-]$diluted $= $ **? M_D** $= \dfrac{V_C \times M_C}{V_D}$ $= \dfrac{100.0\ mL \times 0.020\ M}{250.0\ mL\ total}$ $= $ **0.0080 M Cl^-**

$Q = [Pb^{2+}] [Cl^-]^2$ $= $ **$(0.060)(0.0080)^2$** $= (6.0 \times 10^{-2})(8.0 \times 10^{-3})^2$

$= (6.0 \times 10^{-2})(64 \times 10^{-6}) = 384 \times 10^{-8} = $ **3.8 x 10^{-6}** $= Q$

which is *less* than $K_{sp} = 1.5 \times 10^{-5}$ so the mixture will *not* form a precipitate.

Practice C

1. To be supersaturated means that the solution should precipitate, but it does not. If this solution does not precipitate, the question is whether it should. Begin by calculating whether the solutions should precipitate when combined.

Steps: To predict precipitation after combining, write the *WRECK* steps for the *possible* pcpt.; find Q using *diluted* concentrations, compare Q to K_{sp} .

WANTED: Precipitation prediction: compare diluted Q to K_{sp}

Rxn. & **E**xtent: **1** $BaSO_4\ (s)$ $\leftarrow \leftarrow \rightarrow$ **1** Ba^{2+} + **1** $SO_4{}^{2-}$ (goes slightly)
                                    ^   ^   ^

Conc@eq.:   mol/L solid $- x$ ▌ x | $2x$
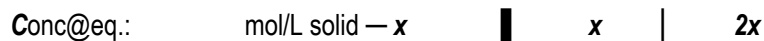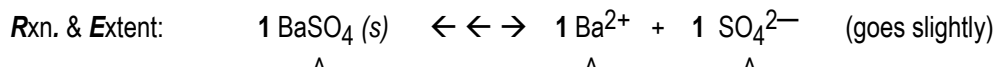
$K_{sp} = $ 1.1 x 10^{-10} $= [Ba^{2+}] [SO_4{}^{2-}]$ $= Q$ to calculate using [*diluted* ions]

The dilution equation is $\boxed{V_C \times M_C = V_D \times M_D}$

$BaCl_2$ is in solution (soluble) and ionizes ~100%, so: **1** $BaCl_2 \rightarrow \rightarrow$ **1** Ba^{2+} + **2** Cl^-

1 $[Ba^{2+}]$diluted therefore equals **1** $[BaCl_2]$diluted

$[Ba^{2+}]_{dil.} = [BaCl_2]_{dil.} = \textbf{? M}_D = \dfrac{V_C \times M_C}{V_D} = \dfrac{75.0 \text{ mL} \times 1.0 \times 10^{-4} \text{ M}}{100.0 \text{ mL total}} = \textbf{7.5 x 10}^{-5}\textbf{ M Ba}^{2+}$

Since all potassium compounds are water soluble & ionize ~100%: $\textbf{1 } K_2SO_4 \rightarrow\rightarrow 2\textbf{ K}^+ + \textbf{1 } SO_4{}^{2-}$

$[SO_4{}^{2-}]_{diluted}$ therefore equals $[K_2SO_4]_{diluted}$

$[SO_4{}^{2-}]_{dil.} = [K_2SO_4]_{dil.} = \textbf{? M}_D = \dfrac{V_C \times M_C}{V_D} = \dfrac{25.0 \text{ mL} \times 2.0 \times 10^{-4} \text{ M}}{100.0 \text{ mL total}} = \textbf{5.0 x 10}^{-5}\textbf{ M SO}_4{}^{2-}$

$\textbf{Q} = [Ba^{2+}] [SO_4{}^{2-}] = (7.50 \times 10^{-5})(5.00 \times 10^{-5}) = 37.5 \times 10^{-10} = \textbf{3.75 x 10}^{-9} = \textbf{Q}$

which is greater than $K_{sp} = 1.1 \times 10^{-10}$. This means that the mixture should precipitate. *If* it does not, the solution would be supersaturated.

* * * * *

Summary: Solubility Equilibrium

1. Nearly all **K calculations** are solved in the same way.

   a. Write the *WRECK* steps.

   b. Find the **C**oncentrations at equilibrium for the terms in the *K* expression, usually in terms of x, either using a *rice* table or by inspection.

   c. Solve the **K** equation, then solve for the WANTED symbol.

2. K_{sp} is the special *K* for a slightly soluble salt dissolving in water.

   a. In the K_{sp} *WRECK* steps, write a balanced equation with *one* particle of the ionic solid on the left, its aqueous separated ions on the right, and (goes slightly).

   b. K_{sp} = **solubility product**. A K_{sp} expression is written with [ions] multiplied in the numerator, but no term in the denominator.

3. For a slightly soluble ionic solid dissolving in water: the solid's **solubility** = small x

   Solubility is the moles of solid that dissolve per liter. The unit *mol/L* (or M) must be added to calculated solubilities.

4. **Solubility** of an ionic solid **=** small x. Add units of moles/liter.

   Solubility product = K_{sp} without units. During **K** calculations, units are omitted.

5. When writing the *rice table* or the *WRECK* steps in K_{sp} calculations,

   a. Let $-x$ represent the small mol/L of the reactant that is used up in the ionization reaction.

   b. At **E**quilibrium, **[solid]$_{eq.}$ = mol/L solid** $-x$

   c. Define the product concentrations using positive x terms.

6. When a common ion is added to a solubility equilibrium:

    a. **Rule**: In a mixture of a slightly soluble ionic solid and its dissolved ions, to reduce the solution concentration of one ion, add a soluble salt that contains the *other* ion in the solid.

    b. To solve a K_{sp} calculation with common-ion added,

    - As in all *K* calculations, write the *WRECK* steps.

    - Write *REC* steps for the ionization of *both* the slightly soluble and soluble salt.

    - Write a DATA TABLE under the K_{sp} equation. Include the *exact* and *approximate* [common ion].

    - Solve the K_{sp} equation first using the approximate [common ion].

    - If the difference between the exact and approximate [common ion] is greater than 5%, solve the exact quadratic.

7. Adding *acid* to a solution at equilibrium that includes *basic* particles will reduce the [base] and shift the equilibrium in accord with Le Châtelier's Principle.

    Basic ions include OH^-, F^-, S^{2-}, CO_3^{2-}, and PO_4^{3-}.

8. To predict whether *combining* solutions will produce a precipitate:

    a. Since K_{sp} is involved, write the *WRECK* steps for the possible precipitate.

    b. Calculate *Q* using the [*diluted* ions] *after* combining, but *before* reacting.

    c. Compare *Q* to K_{sp}. If *Q* is equal or larger, precipitate is predicted to form and persist.

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Module 36 — Thermodynamics

Prerequisites: If needed, review Lessons 21A and 22A on phases, energy, and ΔH.

Pretest: If you think you know a lesson topic in this module, try the last two problems in each problem set in the lesson. If you can do those problems, skip the lesson.

* * * * *

Lesson 36A: Review: Energy and Heats of Reaction

Timing: Calorimetry, heat and heat of reaction (ΔH) calculations were covered in Modules 21 and 22. Begin this Module when you are assigned problems that involve entropy (**S**) or free energy *(g)*.

* * * * *

Thermodynamics, Energy, and Enthalpy

Thermodynamics includes the study of energy (E), enthalpy (H), entropy (S) and free energy *(g)*. Let us briefly review the rules for energy and enthalpy changes (from Modules 21 and 22).

1.   To study thermodynamics, we divide the universe into two parts:

- The **system** is the *particles* of interest, which may be molecules or ions.

- The **surroundings** is the environment outside of the system.

> Universe = system + surroundings

In chemical changes, the impact on the system and its surroundings is often accounted for separately.

2.   Energy is the capacity to do work. The Law of Conservation of Energy is: Energy can neither be created nor destroyed (except in nuclear reactions). This means that in any physical or chemical process,

> $\Delta E_{universe} = E_{final} - E_{initial} = \mathbf{0}$

However, energy can be transferred between substances and to and from the surroundings. Energy can also change its form during chemical or physical processes.

3.   Forms of energy include *potential* energy, defined as stored energy, and *kinetic* energy, defined as energy of motion.   Kinetic energy (KE) = ½ (mass) (velocity)^2

4.   Chemical substances can store energy in the attractions (bonds) between atoms, molecules, and ions. During chemical reactions and phase changes, when bonds break and form, energy can be stored or released.

5.   One way to store energy in a substance is to change its phase. The solid phase of a substance always has less stored (potential) energy than its liquid phase, which always has less potential energy than its gas phase.

> Potential energy of a substance: **solid < liquid < gas**

6. When a substance is in *one* phase (all solid, liquid, or gas), adding or removing energy will change the average kinetic energy of its particles (its *temperature*), but not its potential energy.

7. During a phase change, when *two* phases are present, adding or removing energy changes the potential energy, but not the average kinetic energy (temperature), of the particles.

8. Energy (E), heat (*q*), and work (*w*) in the SI system are measured in joules (J).

9. In any physical or chemical change: $\boxed{\Delta E_{system} = q + w}$

10. In chemistry, measurements of heat, work, and changes in energy and enthalpy are assigned signs from the perspective of the *system*.

    - If heat is added to the system, *q* is given a positive sign. If a reaction or process releases heat from the system to the surroundings, *q* is given a negative sign.

    - If work is done on the system, such as in compressing a gas, *w* is positive. If a system does work, such as an expanding gas moving a piston that is under pressure, the system loses energy and *w* is negative.

11. In the case of PV work by a gas, $\boxed{w = -\ P_{external}\ \Delta V_{system}}$

    In converting from PV-work units to energy units: $\boxed{1 \text{ liter} \bullet \text{atm} = 101 \text{ joules}}$

12. If a thermodynamic symbol has no subscript, assume the subscript is *system*.

13. Enthalpy (H) is defined as $\boxed{H = E + PV}$

    and the change in enthalpy in a process = $H_{final} - H_{initial}$ = $\boxed{\Delta H = \Delta E + \Delta(PV)}$

    if work is limited to PV work.

14. For reactions in which the external pressure on a system is held constant and work is limited to PV work, ΔH will measure the *heat flow* into or out of the system.

    $\boxed{\Delta H = q = \text{"heat of reaction"}}$.

15. In a reaction, if pressure and temperature are held constant and the change in volume is small, and/or if the work term is much smaller than *q* (true for most reactions), then ΔH will approximate the change in the potential energy of the system, which will approximate the heat flow into or out of the system. $\boxed{\Delta H \approx \Delta E_{potential} \approx q}$

Practice A: Refresh your memory on the rules and sign conventions above, then answer these questions from memory.

1. From the perspective of the particles in a system,

    a. if heat is removed from the particles, is the sign of *q* positive *or* negative ?

    b. If gas particles are compressed by a piston that is under external pressure, is the sign of *w* positive *or* negative ?

2. If a substance is melted, but no work is done,

    a. is the sign of *q* positive *or* negative ?

    b. Is the sign of Δ*E*   positive *or* negative ?

    c. Is the reaction exothermic *or* endothermic?

    ━━━

16. In equations that include energy terms, the coefficients are in *moles*.

17. Because the energy content of a substance varies with its phase, in energy equations the *phase* of each particle must be shown: *(s)*, (1), *(g)*, or *(aq)*.

18. In **exo**thermic reactions, energy is *released* into the environment, and the energy term

     *   EITHER is shown with a *positive* sign on the *products* side;

     *   OR (preferred) with a *negative ΔH* value written *after* the equation.

19. In **endo**thermic reactions, energy must be *added*, and the energy term

     *   EITHER is shown with a *positive* sign on the *reactants* side of the equation,

     *   OR with a *positive ΔH* written *after* the reaction.

20. Reactions involving energy or heat can be *reversed*. To represent the reversed reaction, write equation is backwards), and if a ΔH is included, *change its sign*.

21. All reaction coefficients and energy terms can be multiplied or divided by a number. If a ΔH notation is attached, do the same to the value of ΔH.

22. <u>Hess's law</u>: Equations with energy terms can be added to produce a new equation.

     *   Like particles on the same side in different equations can add, and on opposite sides can cancel.

     *   ΔH values add or subtract according to their signs.

23. When ΔH for an equation is not known, it can be found by adding together equations for which ΔH is known.

     *   Write the reaction equation WANTED, then a dotted line below it.

     *   Write the *first* coefficient and substance formula below the dotted line.

     *   Find an equation with a known ΔH that includes that first formula. Adjust its direction and coefficients to put the dropped particle and its coefficient on the side where it is WANTED. Modify and include ΔH.

     *   Add other equations and their known ΔH values arranged to cancel particles not wanted, and add to result in the equation WANTED.

24   In a *formation* equation, the reactants are all *elements* in their *standard state* at 25°C and 1 atm pressure, and the product is *one mole* of a compound.

25. The *heat* of formation (ΔH°$_f$) of a compound is the heat required or released when one mole of the compound is formed from its elements in their standard state.

26. All elements in their standard state are assigned a heat of formation of *zero* kJ/mole.

27. The standard enthalpy value for a compound (ΔH°) is its ΔH°$_f$.

Practice B: If you need help on these, review Module 22.

1 Use these "known" reactions to fill in the blanks below.

$$H_2\,(g)\ +\ 1/2\,O_2(g)\ \rightarrow\ H_2O(l) \qquad\qquad \Delta H = -\,285.8\ \text{kJ} \qquad\qquad (1)$$

$$H_2(g)\ +\ 1/2\,O_2(g)\ \rightarrow\ H_2O(g) \qquad\qquad \Delta H = -\,241.8\ \text{kJ} \qquad\qquad (2)$$

$$1/2\,N_2\,(g)\ +\,O_2\,(g)\ \rightarrow\ NO_2\,(g) \qquad\qquad \Delta H = +\,33.8\ \text{kJ} \qquad\qquad (3)$$

a. $2\,N_2(g)\ +\,4\,O_2\,(g)\ \rightarrow\ 4\,NO_2(g)$ **ΔH** = _____

b. $3\,H_2O(g)\ \rightarrow\ 3\,H_2(g)\ +\ 3/2\,O_2(g)$ **ΔH** = _____
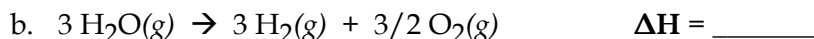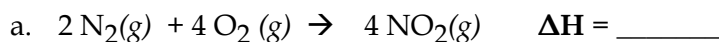
2. Which of the three known reactions above are endothermic?

3. For *n*-octane, the heat of combustion is

$$C_8H_{18}(l)\ +\ 25/2\,O_2(g)\ \rightarrow\ 8\,CO_2(g) + 9\,H_2O(g) \qquad \Delta H = -\,5450.\ \text{kJ}$$
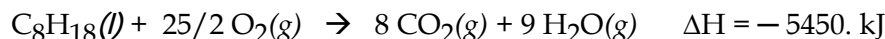
Use the above equation plus the table values below to find the heat of formation for *n*-octane.

Formula	$\Delta H°_f$ in kJ/mole
$H_2O(g)$	$-\,241.8$
$CO_2(g)$	$-\,393.5$

28. <u>ΔH Summation Equation</u>

By definition: $\Delta H_{reaction} = \Delta H_{products} - \Delta H_{reactants}$

If heats of formation are known for all of the substances in a reaction, the ΔH of the reaction can be found by substituting $\Delta H°_f$ values into:

ΔH = [sum of (coefficient x $\Delta H°$) of *products*] $-$ [sum of (coefficient x $\Delta H°$) of *reactants*]

which can also be written as

$$\Delta H_{reaction}\ =\ \Sigma\,c_{product}\,\Delta H_{product}\ -\ \Sigma\,c_{reactant}\,\Delta H_{reactant}$$

Practice C: If you need additional review, see Lesson 22D.

1. The equation for the burning of *n*-butane is:

$$C_4H_{10}(g)\ +\ 13/2\,O_2(g)\ \rightarrow\ 4\,CO_2(g)\ +\ 5\,H_2O(g)$$
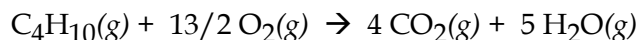
Use the summation equation and the values at the right to calculate ΔH.

Formula	$\Delta H°_f$ in kJ/mole
$C_4H_{10}(g)$	$-\,30.0$
$CO_2(g)$	$-\,393.5$
$H_2O(g)$	$-\,241.8$

ANSWERS

Practice A

1 a.   If heat is removed from the particles, the sign of q is **negative.** The particles lose energy.

   b.   If a gas is compressed by a piston that is under pressure, the sign of w is **positive** . The environment has done work on the system, and in the process the system gains internal energy. In the equation $\boxed{w = -\ P_{external}\ \Delta V_{system}}$, ΔV is negative, and P must be positive, so w is positive.

2. a. q is **positive** . In melting, the system gains heat.

   b. $\Delta E = q + w$. If q is positive and w is 0, ΔE must be **positive**. If the system gains heat with no work involved, the system gains energy, and ΔE for the system must be positive.

   c.   If the system gains heat, the reaction is **endo**thermic.

Practice B

1a. $2\,N_2\,(g)\ + 4\,O_2\,(g)\ \rightarrow\ 4\,NO_2\,(g)$ **ΔH = + 135.2 kJ**
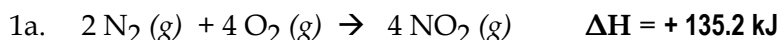
   Table reaction # 3 is quadrupled.

   SF: Multiplying by an exact number does not change the *place* with doubt.

1b. $3\,H_2O(g) \rightarrow 3\,H_2\,(g)\ +\ 3/2\,O_2(g)$ **ΔH = + 725.4 kJ**
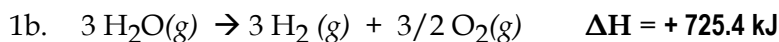
   Table reaction **#2** is tripled and written backwards, so the sign is reversed. Be careful to distinguish the gas/liquid/solid states.

2.   Only **(3)**

3.   The heat of *formation* of n-octane is WANTED:

   $$8\,C(s) +\ 9\,H_2(g)\ \rightarrow\ C_8H_{18}(l)\qquad \Delta H = \textbf{?}$$

★   ★   ★   ★   ★
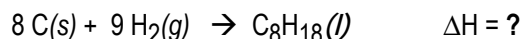
   In burning (combustion) reactions, the O_2 coefficients should work as a check if the other added equations are correct. Here, the **25/2** O_2 total on both sides cancels.

$8\,C(s) +\ 9\,H_2(g)\ \rightarrow\ C_8H_{18}(l)$ $\Delta H = \textbf{?}$		(wanted equation)
$8\,C(s) +\ \textbf{8}\,O_2(g)\ \rightarrow\ 8\,CO_2(g)$	$\Delta H = -\ \textbf{3,148.0 kJ}$	(table rxn. x8)
$8\,CO_2(g) + 9\,H_2O(g) \rightarrow\ C_8H_{18}(l) +\ \textbf{25/2}\,O_2(g)$	$\Delta H = +\ 5450.$ kJ	(supplied rxn reversed)
$9\,H_2(g) +\ \textbf{9/2}\,O_2(g)\ \rightarrow 9\,H_2O(g)$	$\Delta H = -\ 2,176.2$ kJ	(table reaction x9)
$8\,C(s) +\ 9\,H_2(g)\qquad \rightarrow\ C_8H_{18}(l)$	$\Delta H = \textbf{+ 126 kJ}$	(wanted equation)

Practice C

1. $C_4H_{10}(g)\ +\ 13/2\,O_2(g)\ \rightarrow\ 4\,CO_2(g)\ +\ 5\,H_2O(g)$
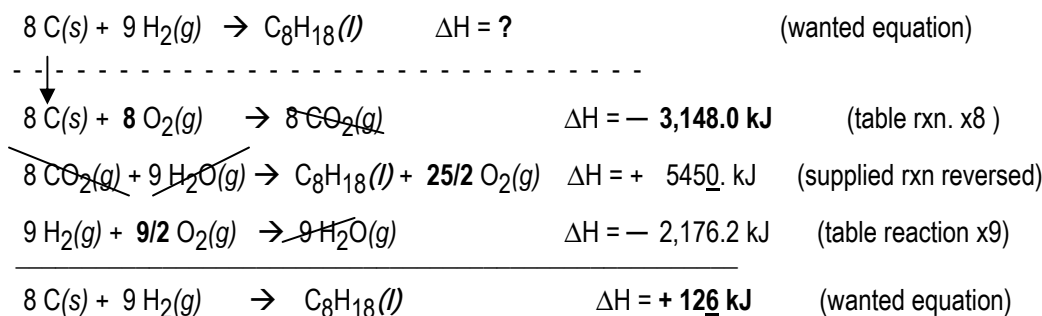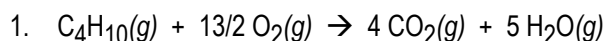
   ΔH = (sum of ΔH° values of *products*) — (sum of ΔH° values of *reactants*)

   $= [\,4(-393.5\ kJ) + 5(-241.8)\,]\ -\ [\,(-30.0 + 13/2(0)\,]\ =\ -1574.0 - 1209.0 + 30.0 = \textbf{-2,753.0 kJ}$

★   ★   ★   ★   ★

Lesson 36B: Entropy and Spontaneity

Introduction To Thermodynamics

Thermodynamics is the study of why things in the physical universe happen as they do: why some processes go to completion, some go partially, and others do not go at all. Thermodynamics suggests ways to adjust conditions so that chemical reactions go in a direction that adds value to materials.

Theoretical Versus Empirical Relationships

Some of the laws of thermodynamics can be derived from kinetic-molecular theory: Newton's laws applied to molecules as they move and collide. Other thermodynamic equations remain in essence empirical: found by trial and error to predict the behavior of objects around us.

Though the *why* of thermodynamics may not be clear in all cases, many of the relationships in thermodynamics can be expressed by relatively simple equations. If you commit these fundamentals to memory, you will be able to solve problems. At this point, that's the goal. Additional courses in science will increase your understanding.

Entropy

All chemical reactions are, in theory, reversible: In a closed system, they all proceed to equilibrium, though the equilibrium mixture can strongly favor the reactants or the products.

In determining whether or not a reaction will go, or the direction in which a reaction mixture will shift, we must consider three factors in the reaction: its change in enthalpy (ΔH), its temperature (T), and its **change in entropy** (ΔS).

To begin to understand **entropy** (symbol **S**), it helps to have experience with the mathematics of probability and statistics. Let us begin with words and analogies that may be more familiar.

Comparing two systems, the system with *higher* entropy is the one in which the energy is more dispersed. This is generally the one in which the particles are in arrangements that are more *probable* in terms of statistics. This condition may be described as

* more mixed, random, or chaotic;
* less well-ordered;
* having more freedom of motion;
* having more options in terms of positions for the particles to occupy.

For example: For a given amount of a substance, with other variables being equal,

* the gas phase has higher *entropy* than the solid. Why? In the solid, the particles are locked in place in a highly ordered crystal. In the gas, the particles have more freedom to move about and mix.
* Particles of a gas have a higher entropy in a larger container than a smaller one. In the larger, they have more freedom to move about and more positions to occupy.

- Gas particles have more entropy at *lower* pressure than at higher pressure. At lower pressure there is more empty space between the particles, so the particles have more available space to occupy.

- In a chemical reaction, the side of the balanced equation that has *more* gas molecules (as determined by *adding* the gas particle coefficients) generally has higher entropy. More particles offer more options for mixing, and the arrangements of the particles can be more random.

- Larger molecules tend to have more energy than similar smaller molecules. In larger molecules, there are more ways to distribute the energy of the atoms.

Practice A: Learn the rules above, *then* try these problems.

1. Circle the system in each pair below that has lower enthalpy during the change between the two phases.

   a. Steam *or* liquid water   b. CO_2 gas *or* solid CO_2

2. Circle the system or side in each pair below that is predicted to have higher entropy.

   a. Ice or liquid water   b. CO_2 gas *or* solid CO_2

   c. At the same temperature: 1 mole of gas at 1 atm *or* 1 mole of gas at 2 atm

   d. At the same temperature: 1 mole of gas in 1.0 liters *or* 1 mole of gas in 2.0 L

   e. A deck of cards in order *or* a deck of cards shuffled

   f. 4 heads in a row *or* 2 heads and 2 tails in any order

   g. $N_2O_4(g)$ $\longleftrightarrow$ $2\ NO_2(g)$ h. $CaO(s)$ + $CO_2(g)$ $\longleftrightarrow$ $CaCO_3(s)$

   i. CH_4 *or* C_4O_{10}

Spontaneity

If a chemical process occurs without intervention from its surroundings, the process is said to be **spontaneous**. The direction that is spontaneous is the direction that the reaction will go. In many reactions, the direction that is spontaneous will depend on the temperature and pressure conditions under which the reaction is run.

In other usages, spontaneous may connote something that happens fast. In chemistry, a spontaneous process will go, but it may go quickly or slowly. The laws of thermodynamics determine the direction of a reaction, but the rules of kinetics determine its speed.

Spontaneous Direction: The Second Law

All systems *tend* to go to minimum potential energy. For example, in a vacuum, without opposing forces, all objects fall toward the center of the earth. As an object falls, it loses gravitational potential energy.

However, this tendency does not mean that systems will *always* go to lower potential energy.

For example, the gas phase of a substance has higher potential energy than its liquid phase (Lesson 21A), yet a drop of a liquid left in the open evaporates, going from the lower potential energy liquid phase to the higher potential energy gas phase.

Why would a system go to higher potential energy? The potential energy change of the system is a factor, but in many cases it is not the controlling factor deciding whether a process occurs.

The rule which predicts the direction in which *all* changes occur is termed

---

The Second Law of Thermodynamics

A process will be spontaneous if it *increases* the *entropy* of the universe.

Other ways to state the second law may help with understanding:

* In a spontaneous process, energy is always dispersed.
* During change, the energy of the universe always goes toward the more probable condition.
* Every change increases the entropy of the universe.
* Processes that do not increase the entropy of the universe don't happen.

In equation form, the second law can be represented as

$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} = $ *Positive* for spontaneous change   (Eq. 1)

One implication of this equation is that during a spontaneous change, a *system* may or may *not* go to higher entropy. If the change takes the *system* to lower entropy, the change may be spontaneous if the change takes the *surroundings* to higher entropy.

Each physical and chemical change can be assigned a positive or negative value for the resulting *change* in entropy (ΔS) of the system, its surroundings, and the universe.

* If $\Delta S_{universe}$ is positive, the change, process, or reaction is spontaneous.
* If $\Delta S_{universe}$ is negative, the change, process, or reaction is spontaneous in the *opposite* direction.
* If $\Delta S_{universe}$ is zero, net change does not occur, and the system is at equilibrium.

In thermodynamics, we must be attentive to changes in both a system and its surroundings. However, by convention in chemistry, if a subscript is *not* attached to an H, S, ΔH, or ΔS symbol, it is understood that the subscript is *system*.

$\Delta S_{surroundings}$

If a process or reaction is carried out with no net change in temperature and pressure, the change in the entropy of the *surroundings* is determined by the change in enthalpy of the *system* and the temperature during the change. This relationship is:

$$\Delta S_{surroundings} = -\frac{\Delta H}{T}$$ when P and T are constant,   (Eq. 2)
and T is *absolute* temperature.

Let's consider some implications of this equation.

- If a reaction or process is *exo*thermic, the sign of its ΔH is negative. Since absolute temperature (T) is always positive, for any *exo*thermic reaction the overall sign on the right side of the equation must be positive, and the change in the entropy of the surroundings on the left must be positive.

    This can be thought of as, if a system loses energy, the surroundings assume a more probable state, such as becoming more mixed up and random.

- The larger is the positive or negative change in enthalpy (ΔH) of a system during a process, the larger is the positive or negative change in entropy of its surroundings. However, because the **T** term is in the denominator, as the temperature at which a process occurs is increased, the effect of ΔH on $\Delta S_{surroundings}$ decreases.

To summarize:

> Exothermic processes increase the entropy of the surroundings. Endothermic processes decrease the entropy of the surroundings.
>
> Increasing temperature decreases the impact of ΔH on $\Delta S_{surroundings}$.

Equation 2 also supplies *units* that measure a change in entropy. Try this example.

Q. When referring to one substance, the SI units of ΔH are joules per mole. For a process involving one substance, in equation 2, what must be the units of ΔS?

★ ★ ★ ★ ★

Since T is measured in kelvins, and the units on both sides of an equation must be the same:

$$\Delta S_{surr.} = -\frac{\Delta H}{T} = -\;\Delta H \cdot \frac{1}{T} = \frac{joules}{mole} \cdot \frac{1}{kelvins} = \mathbf{J/mol \cdot K} \;\; or \;\; \mathbf{J \cdot mol^{-1} \cdot K^{-1}}$$

In general:

> The SI *units* of ΔS when referring to one substance are joules *per* (mol · K) , written as J/mol·K or J·mol^{-1}·K^{-1}.
>
> In the case of a chemical reaction involving more than one substance, the SI *unit* of ΔS is written as J/K or J·K^{-1}, with reaction coefficients understood to be in moles.

Use equation 2 for the following calculation.

Q. For the melting of one mole of ice: $H_2O(s) \rightarrow H_2O(l)$ $\Delta H = + 6.03$ kJ/mol

Find $\Delta S_{surroundings}$ for melting carried out at 0°C and standard pressure.

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Answer

WANTED: $\Delta S_{surr.}$

DATA: $\Delta H = +6.03$ kJ/mol

         $0°C = 273$ K   **T**

The equation that relates these symbols, when P and T are constant, is

$$\boxed{\Delta S_{surr.} = -\frac{\Delta H}{T}} = -6.03 \frac{\text{kJ}}{\text{mol}} \cdot \frac{1}{273\text{ K}} = -0.0221 \text{ kJ/mol·K} = -22.1 \text{ J/mol·K}$$

Practice B: Learn the rules and equations above, *then* try these problems.

1. To change 22.0 grams of dry ice (solid CO_2) to its gas phase at $-78°C$ and 1 atm pressure, 7.65 kJ of heat is added.

   a. Is the ΔH for this reaction positive or negative?

   b. What is the ΔH value for this sublimation of dry ice, in kJ/mol?

   c. What is the $\Delta S_{surr.}$ for this process?

2. For an endothermic process,

   a. Will the sign of $\Delta S_{surr.}$ be positive or negative? Explain your reasoning.

   b. How will $\Delta S_{surr.}$ change at higher temperature?

3. If $x = -$ energy/time, what are the SI units of x ?

Predicting Spontaneity From the Change to the System

In equation form, the second law of thermodynamics is stated as

$$\boxed{\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} = \textbf{Positive for spontaneous change}} \quad \text{(Eq. 1)}$$

If we substitute equation 2 into equation 1, we can write

$$\boxed{\Delta S_{universe} = \Delta S_{system} - \frac{\Delta H_{system}}{T} = \text{Positive for spontaneous change}} \quad \text{(Eq. 3)}$$

In this form, all of the changes needed to predict spontaneity are measured from the perspective of the system: the particles involved in the process.

Note from Equation 3 that as T increases, the value of $\Delta H/T$ decreases. This means that

> As temperature increases, ΔH becomes relatively less important, and ΔS becomes relatively more important, in determining whether a process will be spontaneous.

Using equation 3, write answers to the following question.

   Q1. If a reaction is exothermic, and the products are more random,

      a. Will $\Delta H/T$ be positive or negative?   b. Will the reaction be spontaneous?

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   <u>Part a.</u>   If the reaction is exothermic, **ΔH** must be a negative number.

            T is absolute temperature which is always a positive number.

            A negative **ΔH** over a positive **T** must equal a negative number.

If needed, adjust your work and complete *part b*.

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   <u>Part b.</u>   Since Δ**H/T** in part a is a negative number, $-\Delta$**H/T** must be a *positive* number.

            If the products of a reaction are more random, the system has gained entropy, and the change in the system's entropy (**ΔS**) is a *positive* number.

            Since **ΔS** is positive and $-\Delta$**H/T** is positive, their sum must be positive, which means that **ΔS$_{universe}$** is positive and the process is spontaneous.

Apply the logic of equation 3 to answer this question. Write your reasoning.

   Q2. If a reaction is *endo*thermic, and the products are more random, will the reaction be spontaneous?

★ ★ ★ ★ ★

   If the reaction is endothermic, **ΔH** must be positive. **T** is always positive.

   A positive **ΔH** over a positive **T** must be positive, so $-\Delta$**H/T** must be *negative*.

   If the system becomes more random, it gains entropy, so the change in the system's entropy (**ΔS**) is *positive*.

   If **ΔS** is positive and $-\Delta$**H / T** is negative, whether the sum is positive or negative will depend on which is the larger number: the positive entropy change or the number after the minus sign in $-\Delta$**H / T**.   The answer is: whether the reaction is spontaneous will depend on the *values* of ΔH, ΔS, and T.

By applying this "logic of signs" to the other two possibilities of signs for ΔH and ΔS, we can summarize with these general rules:

Systems *tend* to go to lower enthalpy and higher entropy.

   • If a process takes a system to both lower enthalpy (is exothermic) *and* higher entropy, the process is always spontaneous (always goes toward the products).

   • If a process takes a system to higher enthalpy (is endothermic) *and* lower entropy, the reactants are favored, and the process will not go.

   • If there is a conflict between the tendencies to lower enthalpy and higher entropy, the magnitude of ΔH, ΔS, and T will determine whether the reaction goes.

Summary: Rules Involving Entropy

From the following, be able to apply the rules and write of the equations from memory.

Rules

1. *Entropy* (S): Comparing two systems, in the system with higher entropy, the particles

   - are in arrangements that are more *probable*; mixed, random, or chaotic;
   - are less well-ordered;
   - have more freedom of motion;
   - have more options in terms of positions for the particles to occupy.
   - Gas particles of a substance have higher entropy than solid particles.
   - Other variables being equal, a gas has more entropy at lower pressure and higher volume.

2. The second law of thermodynamics: A process will be spontaneous if it increases the entropy of the universe.

3. The *units* of ΔS, per mole, are joules per (mol·K), written as J/mol·K or $J \cdot mol^{-1} \cdot K^{-1}$.

4. Systems *tend* to go to lower enthalpy and higher entropy.

   - If a process takes a system to both lower enthalpy (is exothermic) *and* higher entropy, the process is spontaneous (goes toward the products).
   - If a process takes a system to higher enthalpy *and* lower entropy, the process will not go forward, but instead goes backwards.
   - If there is a conflict between the tendencies to lower enthalpy and higher entropy, the magnitude of ΔH, ΔS, and T will determine whether the process goes.

Equations

Eq. 1. $\boxed{\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} = \textbf{Positive for spontaneous change}}$

Eq. 2. $\Delta S_{surroundings} = -\dfrac{\Delta H_{sys.}}{T}$ when P and T are constant, and T is absolute.

Eq.3. $\Delta S_{universe} = \Delta S_{system} - \dfrac{\Delta H_{sys.}}{T}$ = Positive for spontaneous change

(for reaction in which P and T are constant)

Practice C: Write your answer and reasoning.

1. As you play solitaire with a deck of shuffled cards, what is the sign of ΔS for the cards? What is the sign of ΔH for your body?

2. If a reaction at constant temperature and pressure is *endo*thermic, and the products are less random,

   a. will the reaction be spontaneous?

   b. Will the reverse reaction be spontaneous?

3. If a reaction at constant temperature and pressure is *endo*thermic and the products have higher entropy, will the reaction go?

ANSWERS

Practice A

1a. **liquid water**: the gas phase of a substance has the highest PE. During a phase change, temperature is constant, and ΔH is approximately equal to the change in potential energy.

1b. **Solid.** Potential energy must be added to change a solid to a gas.

2a. liquid water: the liquid phase has less structure than the solid.

2b. gas: The molecules in the gas phase have more freedom of motion.

2c. 1 atm.   2d. 2 liters   2e. The shuffled deck has less order.   2f. 2 heads and 2 tails is more probable.

2g. The right side, with twice as many particles, has more possible arrangements.

2h. The left side. Entropy is usually higher on the side with more gas molecules.

2i. For molecules with similar composition, the larger molecule (C_4H_{10}) will generally have higher entropy.

Practice B

1a. If energy is added to the system, as is always true to change a solid substance to its gas phase, ΔH must be positive.

1b. WANTED: ΔH in kJ/mol   (use kJ to be consistent with the unit in the DATA)

DATA: 7.65 kJ added = 22.0 **g CO_2** sublimated   (2 measures of same process)

44.0 g CO_2 = 1 mol CO_2 (g CO_2 in data = grams prompt)

SOLVE: $\dfrac{kJ}{mol} = \dfrac{7.65\ kJ}{22.0\ g\ CO_2} \cdot \dfrac{44.0\ g\ CO_2}{1\ mol\ CO_2} = +\ 15.3\ \dfrac{kJ}{mol\ CO_2} = \Delta H$

1c. WANTED: $\Delta S_{surr.}$

DATA: ΔH = + 15.3 kJ/mol

−78°C = 195 K   **T**

The equation that relates these symbols, when P and T are constant, is

$$\boxed{\Delta S_{surr.} = -\ \dfrac{\Delta H}{T}} = -\ 15.3\ \dfrac{kJ}{mol} \cdot \dfrac{1}{195\ K} = -\ 0.0785\ kJ/mol \cdot K = -\ 78.5\ J/mol \cdot K$$

2a. For an endothermic process, ΔH is positive, and T can only be positive, so $-\Delta H/T$ must be *negative*, and that equals $\Delta S_{surr.}$.

2b. As T increases, the magnitude of $\Delta S_{surr.}$ (the value of the number after its sign, whether positive or negative) decreases. For an endothermic process, $\Delta S_{surr.}$ is negative, but as temperature increases it will be less negative.

3. The units must be the same on both sides of an equation. Since the SI unit for energy is joules and time is seconds, the units of **x** must be **joules/second**.

Practice C

1. In solitaire, you take a random deck and put it into order. The entropy of the cards decreases, so ΔS is negative. As you order the cards, your body must burn energy. Burning is an exothermic reaction with a negative ΔH.

2a. If the products are less random, ΔS_{system} is a negative number. If the reaction is endothermic, ΔH_{system} is positive, ($\Delta H_{system}/T$) must be positive, and $\Delta S_{system} - (\Delta H_{system}/T)$ is negative minus a positive, which must be more negative. Since the right side is negative, $\Delta S_{universe}$ is negative, and the process is not spontaneous.

2b. When the process goes backwards, all of the Δ_{system} signs reverse. For reverse process, $\Delta S_{universe}$ is positive and the process is spontaneous.

3. If the reaction is endothermic, ΔH_{system} is positive, and ($\Delta H_{system}/T$) must be positive. If the products are more random they have higher entropy, and ΔS_{system} is a positive number. $\Delta S_{system} - (\Delta H_{system}/T)$ is then a positive minus a positive. Whether the result is positive or negative depends on which of the positive terms is larger. Without more information, you can't say whether the reaction will go.

* * * * *

Lesson 36C: Free Energy

Defining Free Energy

Our second law equation:

$$\boxed{\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} = \textbf{Positive for spontaneous change}}$$

is true for all changes. When measuring chemical reactions and processes, we generally try to hold temperature and pressure constant. If we do, the equation

$$\Delta S_{universe} = \Delta S_{system} - \frac{\textbf{ΔH}_{\textbf{system}}}{\textbf{T}} = \text{Positive for spontaneous change} \qquad \text{(Eq. 3)}$$

allows us to predict which processes will be spontaneous based on measurements of the *system* alone.

A third way to predict spontaneity is to define a function termed **free energy** (symbol **G**) that combines enthalpy, entropy, and temperature:

$$\boxed{\textbf{G = H} - \textbf{TS}} \qquad\qquad\qquad \text{(Equation 4)}$$

Free energy is also called **Gibbs free energy**, after the 19th century Yale physicist J. Willard Gibbs whose work laid the foundation for much of modern thermodynamics.

In chemical processes, the quantity of interest is the *change* in the free energy of a system, defined as

$$\boxed{\Delta\textbf{G} = \Delta\textbf{H} - \textbf{T}\Delta\textbf{S}} \qquad \text{at constant temperature.} \qquad \text{(Equation 5)}$$

ΔG is the energy of the system that is *free* (available) to do work. Each Δ symbol is measured from the perspective of the particles (the system), so by convention the subscripts are omitted.

To find the SI units of ΔG, apply the laws of dimensional homogeneity:

*   Terms to be added or subtracted must have the same dimensions (units); and

*   On both sides of an equation, the units must be the same.

Based on the equation above, the units of the ΔH, ΔG, and — TΔS terms must be the same. In energy relationships, coefficients and amounts are understood to be *moles*.

These rules mean

> The SI units attached to ΔH and ΔG may always be *joules*, with "per moles shown" understood.
>
> When referring to *one* mole of *one* substance, the units of ΔH and ΔG may be stated as either *joules* or *joules/mol* .

Using ΔG To Predict Direction

ΔG values quickly indicate whether a chemical process is spontaneous. To explore why, begin by solving $\boxed{\Delta G = \Delta H - T\Delta S}$ for **ΔS,** then check your answer below.

* * * * *

There are several ways to do the algebra. One is

$$\boxed{\Delta G = \Delta H - T\Delta S}$$

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

$$\Delta S \text{ sys.} = \frac{\Delta G - \Delta H}{-T} = \frac{-(\Delta G - \Delta H)}{-(-T)} = \frac{\Delta H - \Delta G}{T} = \frac{\Delta H}{T} - \frac{\Delta G}{T}$$

Now substitute the final terms on the right above in place of **ΔS**$_{sys.}$ in Eq. 3, then simplify.

* * * * *

Eq. 3: $\Delta S_{universe} = \Delta S_{sys.} - \dfrac{\Delta H_{sys.}}{T}$ = Positive for spontaneous change
when P and T are constant

$\Delta S_{universe} = \dfrac{\Delta H}{T} - \dfrac{\Delta G}{T} - \dfrac{\Delta H_{sys.}}{T} = - \dfrac{\Delta G}{T}$ = Positive for spontaneous change
when P and T are constant

Or $\boxed{\Delta S_{universe} = - \dfrac{\Delta G}{T} = \text{Positive for spontaneous change} \atop \text{when P and T are constant}}$ (Eq. 6)

For a process at constant T and P to be spontaneous, what must be the sign of **ΔG ?**

* * * * *

T is always positive. **— ΔG / T** must be positive for spontaneous change, and that will happen only if **ΔG** is *negative*.

Based on this "logic of signs," we can write three general rules:

Using ΔG to Predict Direction: For a process at constant temperature and pressure,

- ★   if **ΔG** is *negative,* the process will be spontaneous (*go* toward the products).

- •   if ΔG is *positive*, the process will not go or go backward (favors the reactants).

- ★   if ΔG is *zero*, no net change will occur (the process is at equilibrium).

Using $\boxed{\Delta G = \Delta H - T\Delta S}$, the temperature at which a process will be at *equilibrium* can be calculated if ΔH and ΔS are known. Try the following example.

>   **Q.** For the melting of ice at 1 atm pressure, ΔH = +6.03 kJ/mol and ΔS = + 22.1 J/mol·K .
>   Calculate the temperature at which this phase change will be at equilibrium.

★ ★ ★ ★ ★

Answer: To solve with equations:

1.   List the WANTED unit and its *symbol*, list the DATA, label each item of DATA with symbols based on its units, then solve using an equation that includes both the WANTED and DATA symbols.

2.   In the DATA table, convert to *consistent* units.

In thermodynamics problems, the supplied DATA units are often not consistent. If you write a DATA table and convert to consistent units in the table *before* you start to solve, it will simplify your work.

★ ★ ★ ★ ★

>   WANTED: temperature at equilibrium   **T**

>   DATA: **ΔH** = +6.03 **kJ**/mol

>   **ΔS** = + 22.1 **J**/mol·K = + 0.0221 **kJ**/mol·K

>   As the consistent energy unit, you may convert to *either* J or kJ. Converting to the larger unit (kJ in this case) will simplify significant figures.

>   RULE: The system is at equilibrium when **ΔG = 0**

>   The equation that uses those four symbols is $\boxed{\Delta G = \Delta H - T\Delta S}$

>   When the value of a variable is zero, a quick way to solve is to substitute the zero into the fundamental equation, solve for the WANTED symbol in symbols, *then* substitute the data.

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

> $\Delta H = T\Delta S$

> $? = T = \dfrac{\Delta H}{\Delta S}$ = 6.03 $\dfrac{kJ}{mol}$ • $\dfrac{mol \cdot K}{0.0221\ kJ}$ = 273 K

>   This answer means that if you have ice and water at 273 K and 1 atm pressure, the molecules will neither freeze nor melt.

Within the data uncertainty, this answer is consistent with what we know about phase changes. Since 273.15 K (0°C) is the temperature at 1 atm pressure where solid and liquid water coexist, if the surrounding temperature is also kept at 273.15 K, heat will neither enter nor leave the water molecules, and a mixture of ice and liquid water will remain at equilibrium.

In general,

> For a substance in a closed system, at the T and P of a phase change, equilibrium exists between the phases, and $\Delta G = 0$.

Practice A: Learn the rules above, then apply the rules to these problems from memory.

1. For the boiling of water at 1 atm pressure and a temperature of 100°C,

    a. If the heat of vaporization is 2260 J/g, what is ΔH for the reaction, in kJ/mol ?

    b. If ΔS for the vaporization is 109 $J \cdot mol^{-1} \cdot K^{-1}$, find ΔG for the reaction.

2. Complete the following table. At constant P and T:

If ΔH is	and ΔS is	then ΔG is (+ or − or ?)	And process goes *fwd*, *backward*, or *?*
Positive (+)	Negative (−)		
(+)	(+)		
(−)	(−)		
(−)	(+)		

Shifting the Direction of a Reaction

In chemistry, one of our goals is to be able to cause a reversible reaction to go in the direction we would like. The form of the equation $\boxed{\Delta G = \Delta H - T\Delta S}$ helps us to adjust conditions to favor one side of a reaction equation or the other.

According to $\boxed{\Delta G = \Delta H - T\Delta S}$, as we lower the temperature of a reaction toward absolute zero, the term $T\Delta S$ becomes smaller. If we increase the temperature at which a reaction is run, the term $T\Delta S$ becomes larger. Let's summarize as:

> When trying to shift a reaction direction, to make the *entropy* change more important, raise the temperature.

This rule is most important in a reaction where the tendencies of enthalpy and entropy oppose each other.

For example, for the reaction of melting ice: $H_2O(s) \rightarrow H_2O(l)$

$$\Delta H = +6.03 \textbf{ kJ}/mol \text{ and } \Delta S = +0.0221 \textbf{ kJ}/mol \cdot K$$

Enthalpy, being positive, opposes the reaction. Entropy, being positive, favors the reaction. To get the reaction to go, should temperature be increased or decreased?

★ ★ ★ ★ ★

Since entropy favors what we want, to make entropy more important, raise the temperature. This matches our experience with this reaction, that to get ice to melt, we raise its temperature.

To *measure* how temperature makes a difference, try this calculation.

Q. Use the data above to calculate ΔG for the melting of ice, first at −10°C, then at +10°C.

★ ★ ★ ★ ★

Answer

at −10°C, $\boxed{\Delta G = \Delta H - T\Delta S}$ $= + 6.03$ kJ/mol $-$ **(263 K)**$(+ 0.0221$ kJ·mol^{-1}·K$^{-1})$

$= + 6.03$ kJ/mol $-$ **5.81** kJ·mol^{-1} $= + 0.22$ kJ/mol   (positive ΔG = *no go*)

at +10°C, $\boxed{\Delta G = \Delta H - T\Delta S}$ $= + 6.03$ kJ/mol $-$ **(283 K)**$(+ 0.0221$ kJ·mol^{-1}·K$^{-1})$

$= + 6.03$ kJ/mol $-$ **6.25** kJ·mol^{-1} $= - 0.22$ kJ/mol   (negative ΔG = reaction *goes*)

This, too, matches our experience: ice does not melt at −10°C, but does melt at +10°C.

Summary: Rules Involving Free Energy

1. G is free energy. ΔG is the energy of the system that is available to do work.

2. $\boxed{G = H - TS}$ and $\boxed{\Delta G = \Delta H - T\Delta S}$ at constant temperature.

3. When referencing a single substance, the unit of ΔG may be *joules* or *joules/mole*.

   When referencing more than one substance, the unit of ΔG is *joules* .

4. For a process at constant temperature and pressure:

   ★   if **ΔG** is *negative,* the process will be spontaneous (*go* toward the products).

   •   if ΔG is *positive*, the process will go backward or not go (favors the reactants).

   ★   if ΔG is *zero*, no net change occurs (the process is at equilibrium).

5. For a substance in a closed system, at the T and P of a phase change, equilibrium exists between the phases, and $\Delta G = 0$.

6. To shift a reaction direction by making the entropy change more important, increase the temperature.

Practice B

1. To favor the products of a reaction, would you raise or lower the temperature if

   a. ΔH is negative and ΔS is negative?

   b. ΔH is positive and ΔS is negative?

2. To boil water: $H_2O(l) \rightarrow H_2O(g)$

    a. What must be the sign of ΔH?   b. What must be the sign of ΔS?

    c. Will increasing temperature make ΔG more positive or more negative?

3. To boil water at 1.0 atm pressure, at what temperature does ΔG change from positive to negative?

ANSWERS

Practice A

1a. WANTED: **ΔH** in kJ/mol

    Heat of vaporization is a ΔH, but this ΔH is in J/g. *Convert* to the WANTED unit.

    DATA: 2,260 J = 1 **g H_2O** sublimated   (2 measures of same process)

              18.0 g H_2O = 1 mol H_2O (**g H_2O** in data = grams prompt)

    SOLVE: $\dfrac{kJ}{mol} = \dfrac{2,260\ J}{1\ g\ H_2O} \cdot \dfrac{18.0\ g\ H_2O}{1\ mol\ H_2O} \cdot \dfrac{1\ kJ}{10^3\ J} = \mathbf{+\ 40.7}\ \dfrac{\mathbf{kJ}}{\mathbf{mol}\ H_2O}$

    If energy from the surroundings must be added, as is always true to change a liquid to its gas phase, ΔH must be given a positive sign.

1b. WANTED: **ΔG** in kJ/mol   (the units of ΔG and ΔH are the same)

    DATA: + 40.7 **kJ**/mol = **ΔH**

              100°C = 373 K = **T**

              109 J·mol^{-1}·K^{-1} = **ΔS** = **0.**109 **kJ**·mol^{-1}·K^{-1} (make units consistent in DATA table)

    SOLVE: The equation that uses all four of those symbols is

    $$\boxed{\Delta G = \Delta H - T\Delta S}$$

    $\mathbf{\Delta G} = +\ 40.7\ kJ/mol\ -\ \mathbf{(373\ K)}(+\ \mathbf{0.}109\ \mathbf{kJ}$·mol^{-1}·K$^{-1})$

    $= +\ 40.7\ kJ/mol\ -\ \mathbf{(40.7\ kJ}$·mol$^{-1})$

    $= \boxed{\ 0\ \text{kJ/mol} = \mathbf{\Delta G}\ }$

    Is the answer reasonable? At the boiling point of a liquid, in a closed system, equilibrium exists between the liquid and gas phases. At equilibrium, $\Delta G = 0$.

2. The equation that relates these variable is $\boxed{\Delta G = \Delta H - T\Delta S}$, and T must be positive.

If ΔH is	and ΔS is	then ΔG is (+ or − or ?)	And process goes *fwd*, *backward*, or ?
Positive (+)	Negative (−)	**+**	**backward**
(+)	(+)	**?**	**?**
(−)	(−)	**?**	**?**
(−)	(+)	**−**	**forward**

Practice B

1. To encourage a reaction to go, you want ΔG to be negative. $\boxed{\Delta \text{G} = \Delta \text{H} - \text{T}\Delta \text{S}}$

    a. When ΔH helps and ΔS hurts, decrease the importance of ΔS by lowering T.

    b. If ΔH is positive and ΔS is negative, the (— TΔS) term must be positive. Since both terms are positive, and you need the result to be negative, the reaction does not go. Lowering the temperature will make ΔG a smaller positive number, and may shift a mixture toward the products a bit, but the mixture will favor the reactants.

2a. To boil water, heat must be added. The reaction is therefore endothermic, and ΔH must be **positive**.

2b. When a substance goes from a liquid to a gas, entropy increases. ΔS must be **positive**.

2c. From experience, we know that adding heat tends to make boiling go. Increasing temperature therefore tends to make the ΔG of boiling negative.

From the equation $\boxed{\Delta \text{G} = \Delta \text{H} - \text{T}\Delta \text{S}}$, since ΔH and ΔS are both positive, the way to make the ΔG more likely to be negative is to **increase T**.

3. At 1.0 atm, water starts to boil at 100ºC. As temperature changes, for a chemical equation that is a phase change, ΔG will switch between negative and positive (have a value of zero) at the temperature of the phase change (such as the melting point or boiling point). At that temperature, if the system is closed (no heat enters or leaves), the two phases are at equilibrium.

* * * * *

Lesson 36D: Standard State Values

The rules for standard states were covered in Lesson 22D. Let us briefly review.

Standard States

For *thermodynamic* measurements, for substances to be in their **standard state,**

- *elements* must be at **25ºC** and 1 atm pressure and (in most cases) in the phase and/or solid structure that is most stable.

- *Compounds* that are *gases* must be at *one atmosphere* pressure.

- *Substances in solutions* must have a concentration of *one* mol/L.

- *Solid and liquid compounds* are in their standard state under nearly all conditions if they are in the form that is most stable at 25ºC and 1 atm pressure.

Standard *conditions* in thermodynamic calculations should assume a temperature of 25ºC unless otherwise noted.

Standard State Enthalpy Values

Each substance has a characteristic value for its *enthalpy of formation*, symbolized as $\Delta \text{H}^{\text{o}}_{\text{f}}$. The º symbol means that the values apply to a substance in its *standard* state.

Absolute enthalpy cannot be measured, but we can measure *changes* in enthalpy (ΔH). To design a scale to calculate ΔH, each *element* in its standard state is arbitrarily assigned a $\Delta \text{H}^{\text{o}}_{\text{f}}$ value of *zero* kJ/mol. This choice for zero is arbitrary but convenient: in calculations, we can assign a $\Delta \text{H}^{\text{o}}_{\text{f}}$ value of zero to every *element* by inspection.

The standard state enthalpy (ΔH^o_f) of each *compound* is then defined as the ΔH of its *formation* reaction: the reaction in which one mole of the compound is formed from its elements, with all substances in their standard states.

    <u>Example</u>: The formation equation for carbon dioxide gas is

$$C(s) + \ O_2(g) \ \rightarrow \ CO_2(g) \qquad \Delta H \ = \ \mathbf{\Delta H^o_f} \ = \ -393.5 \text{ kJ/mol}$$

The standard state enthalpy (ΔH^o_f) of a compound is the *difference* between its enthalpy and the ΔH^o_f = *zero* of its elements. A ΔH^o_f value does not change with changes in temperature and pressure as long as the substance remains in the same phase.

ΔH^o_f has a different value if the substance is in a different phase: its gas phase has a higher enthalpy than its liquid phase, which has a higher enthalpy than its solid phase.

The symbol $\mathbf{\Delta H}$ may be attached to any reaction. An enthalpy change may be given the symbol $\mathbf{\Delta H^o}$ if all substances involved are in their standard states. The symbol ΔH^o_f applies only to the heat of formation of a substance: the enthalpy change of its formation reaction.

Standard State Entropy Values

Substances can also be assigned **standard entropy (S^o)** values. To do so, we start from the

> **<u>Third Law of Thermodynamics</u>**
>
> The entropy (S) of a perfect crystal of a substance is *zero* at absolute zero (0 K).

This definition of a zero point for entropy is logical. In a crystal with no deformities, the particles of a substance are in their most ordered state possible.

In addition, at absolute zero, the motion of particles (their translation, vibration, and rotation) is zero.

Unlike ΔH values, entropy values change with temperature. Compared to its perfect crystal at absolute zero, the *disorder* of a substance increases as its temperature increases because the *motion* of its particles increases. Motion makes it possible for the particles to move to more positions, which increases their entropy.

Since any substance in a real situation will be warmer than absolute zero (which cannot be reached), it will always have more motion than at absolute zero. Entropy values for a substance in a real situation must therefore be higher than zero: *positive* numbers.

Every substance can be assigned a *standard* entropy value $\mathbf{S^o}$ that represents the entropy of the substance at 25°C and 1 atm pressure. Though S^o values will always be positive, the *change* in S ($\mathbf{\Delta S}$) during a reaction or process may be positive *or* negative.

Tables of the thermodynamic characteristics of substances list ΔH^o_f and S^o values for compounds. The use of the Δ in front of the H^o but not the S^o is an indication that the enthalpy values are relative to an arbitrary zero, while entropy values are relative to a logical zero.

Since entropy varies with temperature, it is important to distinguish between generic entropy S and standard state entropy S^o. However, ΔH and a ΔH^o values for a process will usually be the same, since ΔH values are not temperature dependent.

Calculating Thermodynamic Changes During Reactions

If table values for ΔH^o_f and S^o for substances are known, the ΔH and ΔS^o for chemical reactions can be calculated. Two fundamental equations are the state functions:

$$\boxed{\Delta H = \Delta H_{final} - \Delta H_{initial}} \quad \text{and} \qquad \text{(Equation 7)}$$

$$\boxed{\Delta S^o = S^o_{final} - S^o_{initial}} \qquad \text{(Equation 8)}$$

In *state functions*, only the initial and final values matter.

When applying the equations above to chemical reactions,

- ΔH_{final} = sum of (*c*oefficient *times* $\Delta H^o_{f\ product}$) terms = $\sum c_{products}\ \Delta H^o_{f\ products}$

- $S^o_{initial}$ = the sum of the (coefficient times $S^o_{reactant}$) terms = $\sum c_{reactants}\ S^o_{reactants}$

To find the overall ΔH and ΔS^o changes in a reaction, we can use

$$\Delta H_{reaction} = \sum c_{products}\ \Delta H^o_{f\ products} - \sum c_{reactants}\ \Delta H^o_{f\ reactants} \qquad \text{(Equation 9)}$$

$$\Delta S^o_{reaction} = \sum c_{products}\ S^o_{products} - \sum c_{reactants}\ S^o_{reactants} \qquad \text{(Equation 10)}$$

The meaning of these equations will be more clear when applied to an example.

Q. For the reaction

$2\ CO(g) + O_2(g) \rightarrow 2\ CO_2(g)$
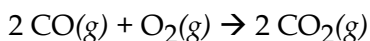
carried out at 25°C and 1 atm pressure, based on the table at the right, calculate

a. $\Delta H_{reaction}$

b. $\Delta S^o_{reaction}$

c. $\Delta G^o_{reaction}$

Substance	ΔH^o_f (kJ/mol)	S^o (J/mol·K)
CO(g)	− 110.5	198
O₂(g)	0	205
CO₂(g)	− 393.5	214

Use equations 9 and 10 above. If you need a hint, read a part of the answer below, then complete the problem.

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a. WANTED: $\Delta H_{reaction}$

$\Delta H_{reaction} = \sum c_{products}\ \Delta H^o_{f\ products} - \sum c_{reactants}\ \Delta H^o_{f\ reactants}$

$= (2)(\mathbf{\Delta H^o_f}\ \text{of}\ CO_2(g)\ ) - [\ (2)(\mathbf{\Delta H^o_f}\ \text{of}\ CO(g)) + (1)(\mathbf{\Delta H^o_f}\ \text{of}\ O_2(g))\ ]$

$= (2\ \mathbf{mol})(-393.5\ \mathbf{kJ/mol})\ -[\ (2)(-110.5)\ +\ (1)(0)\ ]$

$= (-787.0\ \mathbf{kJ})\ -\ [(-221.0)\ ]\ =\ \mathbf{-566.0\ kJ}$

For reactions, coefficients are in moles and ΔH values are in J or kJ .

b. WANTED: $\Delta S^{\circ}{}_{reaction}$

$$\Delta S^{\circ}{}_{reaction} = \sum c_{products}\, S^{\circ}{}_{products} - \sum c_{reactants}\, S^{\circ}{}_{reactants}$$

$$= (2 \text{ mol })(214 \textbf{ J/mol·K}) - [\,(2)(198) + (1)(205)\,]$$

$$= (\,428\,) - [\,601\,] = \textbf{−173 J/K}$$

For reactions, ΔS values are in J/K (or kJ/K) , with *per moles shown* understood.

Does the negative value for the entropy change makes sense? The rule is that the side with *more* gas molecules has *more* entropy. In this reaction, we go from three gas molecules to two. Going to fewer gas molecules, entropy should decrease, and it does.

c. WANTED: $\textbf{ΔG}^{\circ}{}_{reaction}$

Strategy: We know **ΔH** and **ΔS** for the reaction from parts a and b. What known equation relates ΔG, ΔH, and ΔS?

★ ★ ★ ★ ★

$\boxed{\textbf{ΔG = ΔH — TΔS}}$ is true for all values, whether in standard states or not.

$\boxed{\textbf{ΔG = ΔH — TΔS}}$ $= \textbf{−566.0 kJ} - (\textbf{298 } \text{K})(\textbf{−173 J/K})$

$$= -566.0 \text{ kJ} - (-\textbf{51,600 J})$$

$$= -566.0 \textbf{ kJ} + 51,600 \textbf{ J}$$

These last two numbers *cannot* be added directly. If you leave out the units, you may miss that the units are not consistent, and you may add them by mistake.

To *add* or *subtract* two values, they must have the same units (see Lesson 2D). In most thermodynamic calculations, the arithmetic and significant figures will be easier if you

- include the units, watch the units, and

- *early* in each calculation, convert all **J** to **kJ** (by moving the decimal 3 places left).

For relatively simple equations, you do not need to write a DATA table with every equation, but if you do not, you should convert to consistent units by inspection as *early* as possible in the calculation. Whenever unit manipulations become complex, it is best to write out a DATA table under each equation, then convert to consistent units in the table before attempting to solve.

In the last addition line above, converting **J** to **kJ** by inspection, then finish.

★ ★ ★ ★ ★

$$\textbf{ΔG} = -566.0 \textbf{ kJ} + 51,600 \textbf{ J}$$

$$= -566.0 \textbf{ kJ} + \textbf{51.6 kJ} = \boxed{-514.4 \textbf{ kJ} = \textbf{ΔG}^{\circ}}$$

Since all of the calculations in parts a, b, and c above are based on ΔH° and S° values, the calculated values of ΔG ΔH, ΔS are also ΔH°, ΔS° and ΔG° values, the values for these variables at 1 atm pressure and 25°C.

Summary: Rules For Standard State ΔH and ΔS Calculations

1.   The entropy (S) of a perfect crystal of a substance is zero at absolute zero (0 K).

2. $\Delta H_{reaction} = \sum c_{products} \Delta H°_{f\ products} - \sum c_{reactants} \Delta H°_{f\ reactants}$

3. $\Delta S°_{reaction} = \sum c_{products} S°_{products} - \sum c_{reactants} S°_{reactants}$

Practice: Learn the rules above, then try the problem.

1. -26.3 kJ $+ 29.0$ J $=$

2. For the Haber Process reaction

   $N_2(g) + 3\,H_2(g) \rightarrow 2\,NH_3(g)$
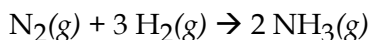
   carried out at 25°C and 1 atm pressure,

   a. Based on the equation above, predict whether the change in entropy will be positive or negative. Explain your reasoning.

   b. Use the table values at the right to calculate

Substance	ΔH°$_f$ (kJ/mol)	S° (J/mol·K)
$N_2(g)$	0	192
$H_2(g)$	0	131
$NH_3(g)$	-46	193

   i. $\Delta H_{reaction}$ ii. $\Delta S°_{reaction}$ iii. $\Delta G°_{reaction}$

   c. Was your prediction for the sign of the change in entropy correct?

ANSWERS

1. -26.3 kJ $+ 29.0$ J $=$ -26.3 kJ $+ 0.0290$ **kJ** $=$ $-26.\underline{2}71$ kJ $=$ $-$**26.3 kJ**
   (When adding, round to the highest place with doubt.)

2. a.   The reaction goes from 4 moles of gas to 2 moles. Entropy should decrease; the change in entropy (ΔS) should be a negative number.

   bi.   WANTED: $\Delta H_{reaction}$

   $\Delta H_{reaction}$ $=$ $\sum c_{product} \Delta H°_{f\ product} - \sum c_{reactant} \Delta H°_{f\ reactant}$

   $=$ (2 mol)(-46 kJ/mol) $-[\,(1)(0) + (3)(\,0\,)\,]$

   $=$ (-92 kJ) $-$ [0] $=$ $-$**92 kJ**

   For reactions that make more than one mole of one product, coefficients are in moles and ΔH values are in J or kJ .

   bii.   WANTED: $\Delta S°_{reaction}$

   S values are temperature dependent, but since this reaction is run at standard thermodynamic conditions, and the values in the table are **S°** values, the table values may be used to solve.

$$\Delta S^o{}_{reaction} \quad = \quad \sum c_{product} \, S^o{}_{product} \; - \; \sum c_{reactans} \, S^o{}_{reactant}$$

$$= \quad (2 \text{ mol})(193 \text{ J/mol·K}) \; - \; [\,(1)(192) \; + \; (3)(131)\,]$$

$$= \quad (\, 386 \text{ J/K}\,) \; - \; [\, 192 + 393\,] \; = 386 - 585 = -\mathbf{199} \ \mathbf{J/K}$$

For reactions that make more than one mole of one product, coefficients are in moles and ΔS values are in J/K , per moles shown.

biii.   WANTED: **ΔG°***reaction*

Strategy: We know **ΔH** and **ΔS** for the reaction from parts a and b. What known equation relates ΔG, ΔH, and ΔS?

$$\boxed{\Delta G = \Delta H - T\Delta S} \quad = -\mathbf{92} \ \mathbf{kJ} \; - \; (\mathbf{298} \text{ K})(-\mathbf{199} \ \mathbf{J/K})$$

$$= -92 \ \text{kJ} \; - \; (-\mathbf{59{,}300} \ \mathbf{J})$$

$$= -92 \ \text{kJ} \; + \; \mathbf{59.3} \ \mathbf{k}\text{J}$$

$$\Delta G = \quad \boxed{-33 \ \mathbf{kJ} = \mathbf{\Delta G^o}}$$

The reaction made 2 moles of ammonia. Per mole, this ΔG would be −16 kJ/**mol** .

Since all values were for substances in their standard states, this ΔG is also a **ΔG°**.

c.   ΔS*reaction* was predicted to be negative, and it is.

* * * * *

Lesson 36E: Adding ΔG° Equations

Prerequisites: If you have any difficulties with this lesson, review Lesson 22C on Hess's Law and 22D on formation reactions.

* * * * *

ΔG° Versus ΔH

ΔG° values for chemical reactions were calculated in the previous lesson using table values for ΔH° and S°. A second way to calculate ΔG° values for reactions is to add the ΔG°$_f$ values for substances.

Both ΔH and ΔG are state functions: dependent on only the characteristic values of the initial state (reactants) and final state (products). This means that many of the rules that apply to ΔH calculations can be applied to ΔG calculations.

If the ΔG° of a reaction is known, ΔG°*reaction* values

- have the same units as ΔH;

- are written after the reaction with a positive or negative sign;

- change sign when the reaction is written backwards;

- multiply when coefficients are multiplied;

- can be added in the same way that ΔH values were added using Hess's law, and

- can be calculated by the summation method using

$$\Delta G^o{}_{reaction} = \sum c_{product} \, \Delta G^o{}_{f \, product} - \sum c_{reactant} \, \Delta G^o{}_{f \, reactant} \quad \text{(Eq. 11)}$$

Also similar to ΔH,

- the $\Delta G^o{}_f$ for *elements* in their standard state (at 25°C and 1 atm pressure) is defined as *zero* kJ/mol , and

- the $\Delta G^o{}_f$ for compounds, which can be found in tables, is equal to the change in free energy that occurs in the *formation* reaction: in which one mole of the compound is formed at 25°C and 1 atm from elements in their standard state.

As in ΔH calculations, the SI *units* of ΔG that are attached to chemical reactions:

- Assume that coefficients are in moles;

- Are written as J or **kJ** , with "per moles shown" understood; and

- May also be written as *J/mol* or as *kJ/mol* if referencing *one* mole of *one* substance.

Unlike ΔH values, ΔG values change with temperature. However, since ΔG° values must be measured at 25°C and 1 atm pressure, temperature is a factor in **ΔG** calculations, but is *not* a factor in ΔG° calculations.

The above rules can be summarized by this general rule:

> For calculations reversing, multiplying, or adding reaction equations with ΔG° values attached, follow the rules for ΔH.

Try this problem. If you need a hint, read a part of the answer below, then finish.

Q. If $2 \, SO_2 \, (g) + O_2(g) \rightarrow 2 \, SO_3(g) \qquad \Delta G^o = -142$ kJ
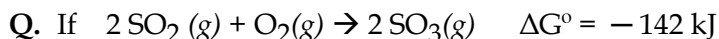
and $\Delta G^o{}_f$ for $SO_2(g) = -300.$ kJ , calculate $\Delta G^o{}_f$ for $SO_3(g)$.

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Hint 1: When given a mixture of ΔG° equations and $\Delta G^o{}_f$ values, use the Hess's law method to solve.

★ ★ ★ ★ ★

Hint 2: Write out the formation equations and attach their $\Delta G^o{}_f$ values.

★ ★ ★ ★ ★

Hint 3: WANT: $1/8 \, S_8(s) + 3/2 \, O_2(g) \rightarrow 1 \, SO_3(g) \qquad \Delta G^o = \textbf{?} \qquad$ (formation rxn.)

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Hint 4: WANT: $1/8 \, S_8(s) + 3/2 \, O_2(g) \rightarrow \, SO_3(g) \qquad \Delta G^o = ?$

$$\text{- - -} \downarrow \text{- -}$$

$1/8 \, S_8(s) + \, 1 \, O_2(g) \rightarrow 1 \, SO_2(g) \qquad \Delta G^o = -300.$ kJ

★ ★ ★ ★ ★

WANT: $1/8\ S_8(s) + 3/2\ O_2(g) \rightarrow 1\ SO_3(g)$ $\Delta G^o = ?$ (formation rxn.)

- -

$1/8\ S_8(s) + 1\ O_2(g) \rightarrow 1\ SO_2(g)$ $\Delta G^o = -300.\ kJ$ (formation rxn.)

$1\ SO_2(s) + 1/2\ O_2(g) \rightarrow 1\ SO_3(g)$ $\Delta G^o = -71\ kJ$ (1/2 of given rxn.)

_____

$1/8\ S_8(s) + 3/2\ O_2(g) \rightarrow 1\ SO_3(g)$ $\Delta G^o = \textbf{−371 kJ/mol} = \Delta G^o{}_f$
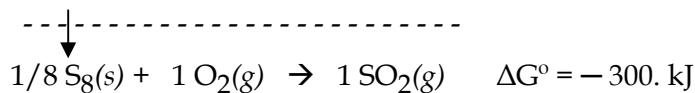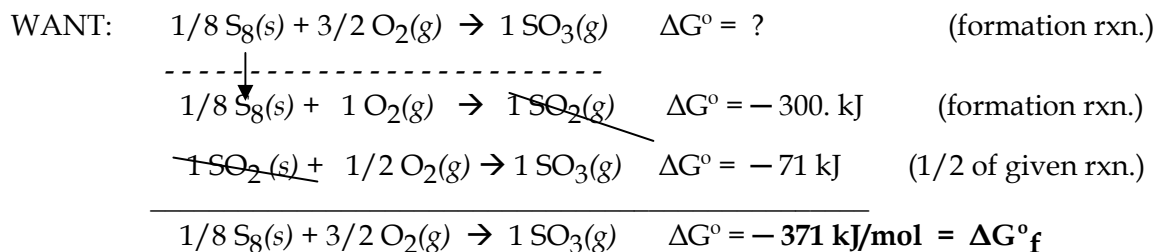
Since the WANTED reaction makes a single mole of product, the unit may be kJ or kJ/mol.

Note that in combustion reactions, if we do not worry about O_2 until the final adding of the reactions, the final O_2 coefficient serves as a check that the equations are added correctly.

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Practice: Learn the rules above, then try these problems.

1. If $N_2(g) + 4\ H_2(g) + Cl_2(g) \rightarrow 2\ NH_4Cl(s)$ $\Delta G^o = -406\ kJ$,

   find $\Delta G^o{}_f$ for $NH_4Cl(s)$.

2. Use the values in the table to find ΔG^o for

   $2\ NO(g) + O_2(g) \rightarrow 2\ NO_2(g)$
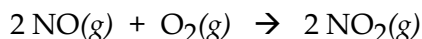
Substance	$\Delta G^o{}_f$ (kJ/mol)
$NO(g)$	+ 87
$NO_2(g)$	+ 52

3. Given this ΔG^o for the burning of methyl alcohol,

   $CH_3OH(l) + 3/2\ O_2(g) \rightarrow 1\ CO_2(g) + 2\ H_2O(g)$ $\Delta G^o = -686\ kJ$
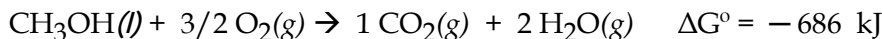
   plus the free energies of formation for the compounds on the right, find the free energy of formation of the methyl alcohol.

Substance	$\Delta G^o{}_f$ (kJ/mol)
$H_2O(g)$	− 229
$CO_2(g)$	− 394

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ANSWERS

1. The given reaction makes 2 moles of $NH_4Cl(s)$. A $\Delta G^o{}_f$ will be for the formation reaction of $NH_4Cl(s)$, which is the given reaction multiplied by 1/2. $\Delta G^o{}_f = 1/2 \times -406\ kJ = \textbf{−203 kJ/mol}$

2. As with ΔH , there are two ways to find ΔG^o : adding the equations by the Hess's law method, or using the summation equation. If you know the $\Delta G^o{}_f$ values (here you do), summation is generally faster.

   A key is: elements in their standard state, such as $O_2(g)$, have $\Delta G^o{}_f = \textbf{0}$.

   $$\Delta G^o{}_{reaction} = \sum c_{product} \Delta G^o{}_{f\ product} - \sum c_{reactant} \Delta G^o{}_{f\ reactant}$$

   $$= (2\ mol)(+52\ kJ/mol) - [(2)(+87) + (1)(0)]$$

   $$= (+104\ kJ) - [+174] = -\textbf{70. kJ}$$

3. The substance being burned (reacted with O_2) is CH_3OH .

    When given a mixture of $\Delta G°$ equations and $\Delta G°_f$ values, use the Hess's law method to solve.

    WANT: $1\ C(s)\ +\ 2\ H_2(g)\ +\ 1/2\ O_2(g)\ \rightarrow\ 1\ CH_3OH(l)$ $\Delta G°$ = **?**   (formation rxn.)

    $1\ C(s)\ +\ 1\ O_2(g)\ \rightarrow\ 1\ CO_2(g)$ $\Delta G°$ = $-$ 394 kJ   (formation rxn.)

    $1\ CO_2(g)\ +\ 2\ H_2O(g)\ \rightarrow\ CH_3OH(l) + 3/2\ O_2(g)$ $\Delta G°$ = $+$ 686 kJ   (given reversed)

    $2\ H_2\ (g)\ +\ 1\ O_2(g)\ \rightarrow\ 2\ H_2O(g)$ $\Delta G°$ = $-$ 458 kJ   (formation x 2)

    _____

    $1\ C(s) + 2\ H_2(g)\ +\ 1/2\ O_2(g)\ \rightarrow\ 1\ CH_3OH(l)$ $\Delta G°$ = $-$ **166 kJ/mol = $\Delta G°_f$**

* * * * *
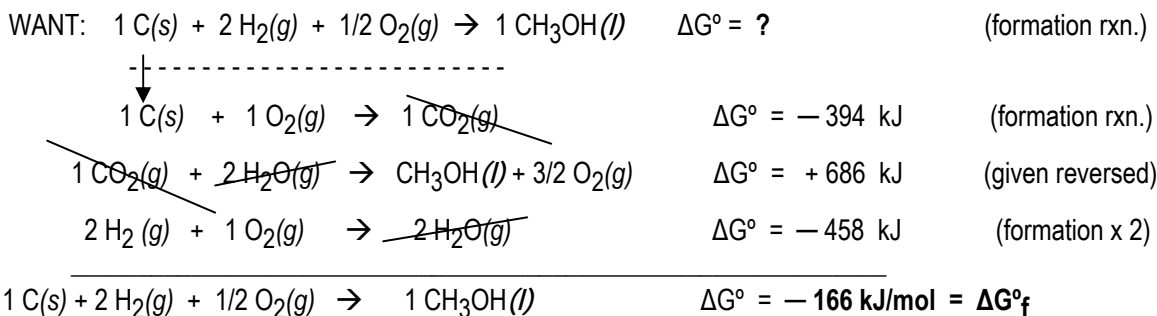
Lesson 36F: Free Energy at Non-Standard Conditions

Prerequisites: You may want to review Lesson 27D on natural logs (ln) to complete the calculations in this lesson.

* * * * *

The Non-Standard Free Energy of Reactions

For a *reaction* involving either gases that are not at standard (1 atm) pressure or solutions that are not at 1 mol/L concentration, the free energy change can be calculated using

$$\Delta G_{reaction} = \Delta G°_{reaction} + RT\ \ln(Q)$$ (Equation 12)

In this equation, Q is the *reaction quotient*: the value obtained when concentrations *or* partial pressures are substituted into the K expression for the reaction (see Lesson 28H).

Let's learn how to use this equation by example.

Q. Using Equation 12 and the table values at the right, find the $\Delta G_{rxn.}$ at 25°C for

$$2\ CO(g) + O_2(g) \rightarrow 2\ CO_2(g)$$
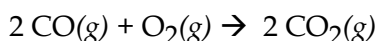
with gas partial pressures = 2.0 atm for each reactant and 10.0 atm for CO_2.

Substance	$\Delta G°_f$ (kJ/mol)
$CO_2(g)$	$-$ 394
$CO(g)$	$-$ 137

Solving with equation 12, especially the first time, let us use our methodical steps.

1. Write the WANTED symbol and unit.

2. Write the equation that uses the WANTED and DATA symbols. Below the equation, list in a data table each symbol in the equation.

3. Fill in the data table. If needed, either in the data table if it fits, or below the table, solve to find the value of each symbol in the table. Put a ? after the WANTED symbol.

Do those steps, then check your answer below.

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WANT: $\Delta G_{rxn.}$ in kJ   (Since the table data is in kJ, pick a consistent WANTED unit)

DATA: $\boxed{\Delta G_{rxn.} = \Delta G^{\circ}_{rxn.} + RT \ln(Q)}$ is the one equation we know using $\Delta G_{rxn.}$

A condition for the use of this equation: it solves based the *coefficients* of the balanced equation in moles. Though the units used *during* the calculation may be *per mole*, for a *reaction*, the final units will be J or kJ, with *per moles shown* by the coefficients as understood.

$\Delta G_{rxn.}$ in kJ = ? = WANTED

$\Delta G^{\circ}_{rxn.}$ =

R =

T =

$\ln(Q)$ =

Below the DATA table, do any long calculations needed to fill in the DATA.

a. to find $\Delta G^{\circ}_{rxn.}$, use the summation equation. Do that step, then check below.

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$\Delta G^{\circ}_{reaction}$ = $\sum c_{product} \Delta G^{\circ}_{f\ product} - \sum c_{reactants} G^{\circ}_{f\ reactant}$

= (2 mol)(-394 kJ/mol) $-$ [(1)(0) + (2)(-137)]

= (-788 kJ) $-[-274]$ = -514 **kJ**

The unit for ΔG° for a *reaction* can be *J* or *kJ* , with *per moles shown* as understood.

b. **R =** ?   We need a value for R. We have used several in the past, including

R = 0.0821 L·atm/mol·K = 8.31 kPa·L/mol·K = 62.4 L·torr/mol·K

Which is the best R term to *start* from in this problem so that units are consistent?

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Since the problem has pressure units in atm, start from the R that uses *atm*.

R = 0.08206 L·atm/mol·K

(To help with rounding, we will use a more precise R here)

However, by the *end* of a $\Delta G_{rxn.}$ problem, to have consistent units, we will need to convert the unit *liter·atm* in R to *joules*. To do so, use the PV-work conversion

$\boxed{1 \text{ liter} \bullet \text{atmosphere} = 101.3 \text{ joules}}$

We will need this new R value in every $\Delta G_{rxn.}$ problem. Try the conversion now.

Q.   Convert **0.08206 L·atm**/mol·K   to   **J**/mol·K .

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WANTED = **?** $\dfrac{\text{J}}{\text{mol·K}}$ = **0.08206** $\dfrac{\text{L·atm}}{\text{mol·K}}$ • $\dfrac{\text{101.3 J}}{\text{1 L·atm}}$ = 8.314 **J**/mol·K

The rule will be: in ΔG_{rxn}, or other problems that mix *joules* and R, use

$$\boxed{R = 8.31 \text{ J/mol·K} \quad or \quad 0.00831 \text{ kJ/mol·K}} \qquad \text{(Equation 13)}$$

In each problem, choose the R value that has units consistent with other DATA. Which value should be entered in the DATA table for this problem?

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$R = 0.00831 \text{ kJ/mol·K}$ is consistent with the unit supplied.

Continue to fill in the DATA table for the equation,

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T in K $= 25°C + 273 = 298$ K

c. $\ln(Q) = ?$ An important rule is:

> When K or Q are calculated:
> - Gas pressures must be measured in *atmospheres*.
> - Concentrations must be measured in *moles/liter*.
> - Concentrations and pressures for solids, solvents, and pure liquids are given values of **1.**
> - Values are substituted into K and Q expressions without units.

This rule assures that Q calculations are based on units that are consistent with the defined standard conditions of *one atmosphere* pressure and *one mole/liter* concentration.

Calculate a value for Q in this problem, then check your answer below.

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To find Q, substitute the gas partial pressures into the K expression for the reaction.

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$$Q = \frac{(P\ CO_2)^2}{(P\ CO)^2 \cdot (P\ O_2)} =$$

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$$Q = \frac{(P\ CO_2)^2}{(P\ CO)^2 \cdot (P\ O_2)} = \frac{(10.0)^2}{(2.0)^2\ (2.0)} = \frac{100.}{8} = 12.5$$

Now finish the data table.

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$\ln(Q) = \ln(12.5) = \mathbf{+\ 2.526}$

Especially in logarithmic calculations, it is a good idea to carry an extra significant figure until the final step of a sequential calculation.

With the DATA table now complete, solve for the WANTED symbol.

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$$\boxed{\Delta G_{rxn.} = \Delta G^{\circ}_{rxn.} + RT \ln(Q)}$$

$$= -514 \text{ kJ/mol} + (0.00831 \text{ kJ/mol·K})(298 \text{ K})(+2.526)$$

$$= -514 \text{ kJ/mol} + 6.26 \text{ kJ/mol}$$

$$= -508 \text{ kJ} \quad \text{(for reactions, units include } per \text{ } moles \text{ } shown \text{ as understood)}$$

Done!

Let's summarize.

If $\boxed{\Delta G_{rxn.} = \Delta G^{\circ}_{rxn.} + RT \ln(Q)}$ is the equation, use this DATA table:

$\Delta G_{rxn.}$ in **kJ** (per moles shown) =

$\Delta G^{\circ}_{rxn.}$ in **kJ** = (find using $\sum$ with table values *or* $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$)

R = **8.31 J**/mol·K *or* **0.00831 kJ**/mol·K (choose the one with consistent units)

T in K = °C + 273 =

ln(*Q*) = (use gas P in *atm*, [ ] in *M*, [solid] = [liquid] = **1 ,** and no units)

Practice: Learn the rules in the summary above, then apply the rules to these problems from memory.

1. Using the table values at the right,

    a. find $\Delta G^{\circ}_{rxn.}$ for $N_2O_4(g) \rightarrow 2 NO_2(g)$

    b. find the $\Delta G_{rxn.}$ at 25°C, with partial pressures of 101 kPa for N_2O_4 and 505 kPa for NO_2 .

Substance	ΔG°_f (kJ/mol)
$N_2O_4(g)$	+ 98
$NO_2(g)$	+ 51

2. In the equation $\boxed{\Delta G_{rxn.} = \Delta G^{\circ}_{rxn.} + RT \ln(Q)}$ as the [products] in a reaction mixture becomes very large compared to the [reactants], state whether the following will increase or decrease, and state your reasoning.

    a. The value of Q b. The value of $\ln(Q)$ c. The value of $RT \ln(Q)$

    d. The value of ΔG_{rxn} e. The tendency of the reaction to form more products.

3. Under standard-state conditions,

    a. all terms substituted into a K expression to calculate Q have what value and units?

    b. Under those standard-state conditions, what is the calculated value for Q ?

    c. Using the Q value in *part b*, simplify $\boxed{\Delta G_{rxn.} = \Delta G^{\circ}_{rxn.} + RT \ln(Q)}$.

ANSWERS

1a. To find $\Delta G^o{}_{rxn.}$ from table values, use the summation equation.

$\Delta G^o{}_{rxn.}$ = $\sum c_{products} \Delta G^o{}_{f\ products}$ − $\sum c_{reactants} \Delta G^o{}_{f\ reactants}$

   = (2 mol)(+ 51 kJ/mol) − [(1)(+ 98))]

   = (+ 102) − [98] = **+ 4 kJ**

1b. If $\Delta G_{rxn.}$ and $\Delta G^o{}_{rxn.}$ are in the data, the equation is likely to be

$\boxed{\Delta G_{rxn.} = \Delta G^o{}_{rxn.} + RT\ \ln(Q)}$ If that is the equation, use this data table:

   $\Delta G_{rxn.}$ in **kJ/mol** = **?**

   $\Delta G^o{}_{rxn.}$ in **kJ/mol** = **+ 4 kJ**   from *part a*

   R = **0.00831 kJ**/mol·K   (Choose the R with consistent units)

   T in K = 298 K

   ln(Q) = **?** Q = ? = $\dfrac{(P_{NO_2})^2}{(P_{N_2O_4})}$

   (substitute gas pressures converted to **atm**, concentrations to **M**, solid = liquid = **1**)

   ? $P_{N_2O_4}$ in atm = 101 kPa = **1.00 atm** by definition

   ? P_{NO_2} in atm = 505 kPa · $\dfrac{1\ atm}{101\ kPa}$ = **5.00 atm**

   $K = \dfrac{(P_{NO_2})^2}{(P_{N_2O_4})}$ = Q = $\dfrac{(5.00)^2}{(1.0)}$ = **25.0**

   ln(Q) = ln(25) = **+ 3.22**

$\boxed{\Delta G_{rxn.} = \Delta G^o{}_{rxn.} + RT\ \ln(Q)}$

   = **+ 4 kJ**/mol + 0.00831 **kJ**/mol·K(298 K)(**+ 3.22)**

   = **+ 4 kJ**/mol + **7.97 kJ**/mol

   = **+ 12 kJ/moles shown**   (adding; doubt in ones place)

2a. Since Q = [products] / [reactants] , Q gets larger.   2b. As Q increases, ln(Q) increases.

2c. Since R and T are positive, and ln(Q) is positive if $Q>1$, which it is if [products]>[reactants}, RT ln(Q) must be positive and get larger as Q increases.

2d. As RT ln(Q) gets to be a larger positive value, the value of $\Delta G_{rxn.}$ must increase. It may be a negative value, but it will shift in a more positive direction.

2e. As $\Delta G_{rxn.}$ shifts in a more positive direction, the tendency to shift toward making more products decreases. All reactions go toward equilibrium: a *mix* of reactants and products. When [products] becomes higher than it would be at equilibrium, the direction of the reactant shifts toward reactants.

3a. Under standard-state conditions, solution concentrations = 1 M and gas pressures = 1 atm . All solid and liquid concentrations and pressures are assigned a value of 1 in the Q equation. Since units are omitted when calculating K and Q , the value for all terms under standard conditions = **1 without units.**

3b. Under standard-state conditions, Q is a ratio in which all of the values are 1, so $Q = 1$.

3c. $\ln(Q) = \ln(1) = \ln(e^0) = \mathbf{0}$, so $\boxed{\Delta G_{rxn.} = \Delta G^{\circ}_{rxn.} + RT \ln(Q)}$ $= \Delta G_{rxn.} = \Delta G^{\circ}_{rxn.} + RT(\mathbf{0}) = \mathbf{\Delta G^{\circ}_{rxn.}}$

Under standard-state conditions, $\boxed{\Delta G_{rxn.} = \Delta G^{\circ}_{rxn.}}$

* * * * *

Lesson 36G: Free Energy and *K*

Prerequisites: You may want to review Lesson 27D on natural logs (both *e* and ln functions) for the calculations in this lesson.

* * * * *

ΔG and Equilibrium

For reactions with a very large *K,* equilibrium so strongly favors the products that a limiting reactant is close to 100% used up. Reaction calculations can then be handled by the relatively simple steps of stoichiometry. Stoichiometry solves reaction calculations quickly when compared to the *WRECK* steps and/or *rice* tables needed in *K* calculations.

However, even for reactions that *strongly* favor the reactants or products, a very large or very small *K* value can be written.

In a closed system,

- *all* reaction mixtures go to equilibrium,

- at equilibrium, $\Delta G = 0$, and

- in a reaction mixture that is at equilibrium, $Q = K$.

Therefore, since $\boxed{\Delta G_{rxn.} = \Delta G^{\circ}_{rxn.} + RT \ln(Q)}$

at equilibrium, this equation becomes $\Delta G_{rxn.} = \mathbf{0} = \Delta G^{\circ}_{rxn.} + RT \ln(K)$

Or, to simplify: $\boxed{\Delta G^{\circ}_{rxn.} = -RT \ln(K)}$ (Equation 14)

In calculations using gas partial pressures, the *K* is a K_p. For calculations based on concentrations, , the *K* is a K_c. If the *K* type is unspecified, K_c is understood.

Equation 14 means that knowing values for any two of the three variables in the equation: $\Delta G^{\circ}_{rxn.}$, T, or *K*, we can calculate the third.

Try this example.

Q. For a reaction at 25°C and standard pressure, $\Delta G^{\circ}_{rxn.} = -20.0$ kJ. What is the *K* value for the reaction?

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WANT: **K**

The equation that links $\Delta G^{\circ}_{rxn.}$ and K is $\boxed{\Delta G^{\circ}_{rxn.} = -RT \ln(K)}$

DATA: **$\Delta G^{\circ}_{rxn.}$ = −20.0 kJ**

       R = 0.00831 **kJ/**mol·K

       T in K = 25ºC + 273 = **298 K**

       ln(K) = **?**

SOLVE:

$$\ln(K) = \frac{\Delta G^{\circ}_{rxn.}}{-RT} = \frac{\Delta G^{\circ}_{rxn.}}{-R} \cdot \frac{1}{T} = \frac{-20.0 \text{ kJ}}{\text{mol}} \cdot \frac{\text{mol·K}}{-0.00831 \text{ kJ}} \cdot \frac{1}{298 \text{ K}} = \boxed{+8.076}$$

Separating the terms in the formula helps with unit cancellation (see Lesson 17C).

Since $x = e^{\ln(x)}$, $K = e^{\ln(K)} = e^{(8.076)} = $ **3,220** = $\boxed{\textbf{3.22 x } 10^3 = K}$

Finding K from ΔG°_{f} Table Values

Small values for concentrations and pressures can be difficult to determine experimentally. As a result, values for equilibrium constants can be difficult to determine directly. Equation 14 is especially important because it allows us to calculate equilibrium constants from values that can be calculated by other means. If ΔG°_{f} values are known (and many can be looked up in tables), a $\Delta G^{\circ}_{reaction}$ value can be found using the summation equation. From $\Delta G^{\circ}_{reaction}$, a K value can be calculated.

Try this example.

  Q. For the Haber Process reaction,

      a. find $\Delta G^{\circ}_{rxn.}$ for

          $N_2(g) + 3 H_2(g) \rightarrow 2 NH_3(g)$

Substance	ΔG°_{f} (kJ/mol)
$NH_3(g)$	− 16.7
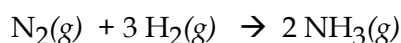
      b. find the value K value for the reaction at standard temperature.

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      a. Given free energies of formation, either use the summation reaction.

$$\Delta G^{\circ}_{rxn.} = \sum c_{products} \Delta G^{\circ}_{f\ product} - \sum c_{reactant} \Delta G^{\circ}_{f\ reactant}$$

$$= (2 \text{ mol })(-16.7 \text{ kJ/mol}) - [\,(1)(0) + (3)(\,0\,)\,]$$

$$= (-33.4 \text{ kJ}) - [0] = \textbf{−33.4 kJ}\ \text{per stated moles}$$

      or, since this reaction is double the formation equation, double ΔG°_{f}.

      b. The equation that links $\Delta G^{\circ}_{rxn.}$ and K is $\boxed{\Delta G^{\circ}_{rxn.} = -RT \ln(K)}$

         DATA: **$\Delta G^{\circ}_{rxn.}$ = − 33.4 kJ**   from *part a*

                R = 8.31 J/mol·K = **0.00831 kJ/**mol·K

T in K = $25°C + 273 = $ **298 K**

ln(K) = ?

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SOLVE:

$$\ln(K) = \frac{\Delta G°_{rxn.}}{-RT} = \frac{-33.4 \text{ kJ}}{\text{mol}} \cdot \frac{\text{mol·K}}{-0.00831 \text{ kJ}} \cdot \frac{1}{298 \text{ K}} = +13.49 = \ln(K)$$

WANTED **= K =** $e^{\ln(K)} = e^{(13.49)} = $ | **7.22 x 10⁶ = K** |

To summarize:

If | $\Delta G°_{rxn.} = -RT \ln(K)$ | is the equation, use this data table:

$\Delta G°_{rxn.}$ in kJ = (find using $\sum$ with table values *or* **$\Delta G° = \Delta H° - T\Delta S°$**)

R $= 8.31$ **J**/mol·K *or* 0.00831 **kJ**/mol·K (use the one with consistent units)

T in K = $°C + 273 =$

ln(K) = To find *K*, first find ln(*K*), then use $K = e^{\ln(K)}$

Practice: Commit to memory equation 14, then try these problems.

1. If $K = 1$ for a reaction, calculate $\Delta G°_{rxn.}$. (You should not need a calculator).

2. In mammals, internal temperature is generally 38°C. At this temperature, $\Delta G°_{rxn.}$ for $H_2O(l) \leftleftarrows \rightarrow H^+(aq) + OH^-(aq)$ is 80.5 kJ . Find the value of *K* for this reaction at mammalian normal temperature.

3. For $Fe(s) + 3/2 \, O_2(g) \leftarrow\rightarrow Fe_2O_3(s)$, at 25°C, $\Delta H°_{rxn.} = -826$ kJ and $K = 2.6 \times 10^{130}$. Find the value of $\Delta S°_{rxn.}$

4. Complete this problem if you are majoring in the physical sciences or engineering.

   If 1 pascal (Pa) = 1 newton/meter², 1 newton = 1 kg · m · s⁻², 1 joule = 1 kg · m² · s⁻², and one atm = 101 kPa, use those equalities to calculate the number of joules in one liter · atm.

ANSWERS

1. WANT: $\Delta G°_{rxn.}$

   Know: T, *K*

   The equation that relates those variables is | $\Delta G°_{rxn.} = -RT \ln(K)$ |

DATA:

  $\Delta G^\circ_{rxn.}$ in **kJ** = **?**

  R = 8.31 **J**/mol·K = **0.00831 kJ**/mol·K   (pick consistent units)

  T in K = 25ºC + 273 = **298 K**

  ln(K) = ln(1) = ln(e^0) = **0** ,

  This simplifies $\boxed{\Delta G^\circ_{rxn.} = -RT \ln(K)}$ to $\Delta G^\circ_{rxn.} = -RT\ (0) = \boxed{0 = \Delta G^\circ_{rxn.}}$

At standard conditions, all terms in a Q equation have a value of 1, so Q = 1. *If* the value of K is also one, then when conditions are standard, the system is at equilibrium, and $\Delta G = \Delta G^\circ = 0$.

2. WANT: K

   Know: T, $\Delta G^\circ_{rxn.}$

   The equation that relates those variables is $\boxed{\Delta G^\circ_{rxn.} = -RT \ln(K)}$

   DATA:

   $\Delta G^\circ_{rxn.}$ in **kJ** = + 80.5 kJ

   R = 8.31 **J**/mol·K = **0.00831 kJ**/mol·K   (pick consistent units)

   T in K = 38ºC + 273 = **311 K**

   ln(K) $= \dfrac{\Delta G^\circ_{rxn.}}{-RT} = \dfrac{+\ 80.5\ \text{kJ}}{\text{mol}} \cdot \dfrac{\text{mol·K}}{-\ 0.00831\ \text{kJ}} \cdot \dfrac{1}{311\ \text{K}} = -\ 31.14$

   SOLVE: ***WANTED*** **=** $K = e^{\ln(K)} = e^{(-31.14)}$ = $\boxed{\textbf{2.97 x 10}^{-14}\ =\ K = K_W}$

   At 25ºC, K_W = **1.0 x 10^{-14}** . At higher temperatures, more HOH bonds break, [ions] are higher, and K_W is higher.

3. WANT: **$\Delta S^\circ_{rxn.}$**   Know: T, K, ΔH°

   The equations that relates those variables are $\boxed{\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ}$ and $\boxed{\Delta G^\circ_{rxn.} = -RT \ln(K)}$

   You can combine the equations, but if you choose to solve them separately, the math will be more familiar.

   First solve the equation that has **one** unknown value. Which equation is that?

★   ★   ★   ★   ★

   Since you know R, T, and K, use them find $\Delta G^\circ_{rxn.}$

   DATA: $\boxed{\Delta G^\circ_{rxn.} = -RT \ln(K)}$

     $\Delta G^\circ_{rxn.}$ in **kJ** = ?

     R = 8.31 **J**/mol·K or **0.00831 kJ**/mol·K

     T in K = 25ºC + 273 = **298 K**

     ln(K) = ln(2.6 x 10^{130}) **= 300.**

     $\boxed{\Delta G^\circ_{rxn.} = -RT \ln(K)}$

$$= \, - \, 0.00831 \text{ \textbf{k}J/mol·K}(298 \text{ K})(\, \textbf{+ 300.})$$

$$= \, - \, 0.00831 \text{ \textbf{k}J/mol·K}(298 \text{ K})(\, \textbf{+ 300.})$$

$$= \boxed{ - \quad \textbf{743} \quad \textbf{k}J/\text{mol} \; = \; \mathbf{\Delta G^o_{rxn}}}.$$

Now solve $\boxed{\Delta G^o = \Delta H^o - T\Delta S^o}$ for ΔS^o.

$$\mathbf{\Delta S^o} \; = \; \frac{\Delta G^o - \Delta H^o}{- \, T} \; = \; \frac{- \, 743 \; kJ - (-826 \; kJ)}{-298 \text{ K}} \; = \; - \, 0.279 \text{ \textbf{k}J/K}$$

$\mathbf{\Delta S^o = } \, - \, \textbf{279 joules/K} ,$ or since one mole of product is formed, $-$ **279** joules/**mol**·K

Either J or kJ can be used in the answer unit.

4. Suggested strategy: Convert all units to SI base units: kg, m, s; cancel units that are not those units.

** *   *   *   ***

WANT: ? joules = = $? \text{ kg} \cdot \text{m}^2 \cdot \text{s}^{-2}$

DATA: 1 pascal (Pa) = 1 newton/meter^2

1 newton = $1 \text{ kg} \cdot \text{m} \cdot \text{s}^{-2}$

1 joule = $1 \text{ kg} \cdot \text{m}^2 \cdot \text{s}^{-2}$

one atm = 101 kPa

Hint: Add to the data table: 1 liter = ? dm^3, 1 atm = ? Pa

** *   *   *   ***

SOLVE: ? joule = $? \text{ kg} \cdot \text{m}^2 \cdot \text{s}^{-2}$ = 1 liter • atm

** *   *   *   ***

$$? \text{ joules} = ? \text{ kg} \cdot \text{m}^2 \cdot \text{s}^{-2} \; = \; \textbf{1} \text{ liter} \cdot \text{atm} \cdot \frac{1 \text{ dm}^3}{1 \text{ L}} \cdot \left(\frac{1 \textbf{ m}}{10 \text{ dm}} \right)^3 \cdot$$

** *   *   *   ***

$$? \text{ kg} \cdot \text{m}^2 \cdot \text{s}^{-2} = \textbf{1} \text{ L} \cdot \text{atm} \; \cdot \; \frac{1 \text{ dm}^3}{1 \text{ L}} \cdot \frac{1 \text{ m}^3}{10^3 \text{ dm}^3} \cdot \frac{101 \times 10^3 \text{ Pa}}{1 \text{ atm}} \cdot \frac{1 \text{ N} \cdot \text{m}^{-2}}{1 \text{ Pa}} \cdot \frac{1 \text{ kg} \cdot \text{m} \cdot \text{s}^{-2}}{1 \text{ N}} =$$

$$= 101 \text{ kg} \cdot \text{m}^2 \cdot \text{s}^{-2} \; = \; 101 \text{ joules}$$

This calculation verifies that $\boxed{1 \text{ L} \cdot \text{ atm} \; = \; 101 \text{ joules}}$.

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Summary: Thermodynamics

Energy and Enthalpy

1. Energy is the capacity to do work.

2. The first law of thermodynamics: Energy can neither be created nor destroyed.
    In any physical or chemical process, $\boxed{\Delta E_{universe} = E_{final} - E_{initial} = \mathbf{0}}$

3. Energy (E), heat (q), and work (w) in the SI system are measured in joules and (in chemistry) from the perspective of the system.

4. In any physical or chemical change: $\boxed{\Delta E_{system} = q + w}$

5. In the case of PV work by a gas, $\boxed{w_{system} = -\,P_{external}\,\Delta V_{system}}$

   From the perspective of the system, if a system does work on its surroundings, w is negative.

6. In converting from PV work units to energy units: $\boxed{1 \text{ liter} \bullet \text{atm} = 101 \text{ joules}}$

7. If no subscript is given after a thermodynamic symbol, assume the subscript is *system*.

8. The definition of enthalpy (H): $\boxed{H = E + PV}$

9. $H_{final} - H_{initial} = \boxed{\Delta H = \Delta E + \Delta(PV)}$ if work is limited to PV work.

10. If external P is held constant and work is limited to PV work, ΔH measures *heat flow* into or out of the system. $\boxed{\Delta H = q}$.

Entropy

1. *Entropy* (S): Comparing two systems, in the system with higher entropy, the particles

   - are in arrangements that are more *probable*; mixed, random, or chaotic;

   - are less well ordered;

   - have more freedom of motion or positions for the particles to occupy.

   - Gas particles of a substance have higher entropy than solid particles.

   - Other variables being equal, a gas has more entropy at lower pressure and higher volume.

   - In a chemical reaction, the side of the balanced equation that has *more* gas molecules (determined by *adding* the gas particle coefficients) generally has higher entropy.

2. <u>The second law of thermodynamics</u>: A process will be spontaneous if it increases the entropy of the universe.

   $\boxed{\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} = \textbf{Positive for spontaneous change}}$

3. The *units* of ΔS, per mole, are joules per (mol·K), written as J/mol·K or J·mol^{-1}·K^{-1}.

4. Systems *tend* to go to lower enthalpy and higher entropy.

5. $\boxed{\Delta S_{surroundings} = -\dfrac{\Delta H_{sys.}}{T}}$ when P and T are constant, and T is absolute.

6. $\Delta S_{universe} = \Delta S_{system} - \dfrac{\textbf{\Delta H}_{\textbf{sys.}}}{\textbf{T}}$ = Positive for spontaneous change
   (applies *if* P and T are held constant)

Standard State ΔH and ΔS Calculations

1. <u>The third law of thermodynamics</u>: Entropy (S) of a perfect crystal of a substance at absolute zero is *zero*.

2. $\Delta H_{reaction} = \sum c_{product} \Delta H^o_{f\ product} - \sum c_{reactant} \Delta H^o_{f\ reactant}$

3. $\Delta S^o_{reaction} = \sum c_{product} S^o_{product} - \sum c_{reactant} S^o_{reactant}$

Free Energy

1. G is the symbol for free energy, also known as Gibbs free energy.

   ΔG is the energy of the system that is available to do work.

2. $\boxed{G = H - TS}$ and at constant temperature, $\boxed{\Delta G = \Delta H - T\Delta S}$.

3. When referencing a single substance, the unit of ΔG may be *joules* or *joules/mole*.

   When referencing more than one substance, the unit of ΔG is *joules* .

4. For a process at constant temperature and pressure:

   ★ if **ΔG** is *negative,* the process will be spontaneous (*go* toward the products).

   • if ΔG is *positive*, the process will go backward or not go (favors the reactants).

   ★ if ΔG is *zero*, no net change occurs (the process is at equilibrium).

6. At the T and P of a phase change in a closed system, equilibrium exists between the phases, and ΔG = 0 .

7. When trying to shift a reaction direction, to make the entropy change more important, raise the temperature.

8. For calculations reversing, multiplying, or adding reaction equations with ΔG° values attached, follow the rules for ΔH.

9. ΔG^o_{rxn} can be calculated by the summation method using

   $$\Delta G^o_{rxn} = \sum c_{product} \Delta G^o_{f\ product} - \sum c_{reactant} \Delta G^o_{f\ reactant}$$

Free Energy, *Q*, and *K*

1. $\boxed{\Delta G_{rxn.} = \Delta G^o_{rxn.} + RT \ln(Q)}$

2. In problems that mix *joules* and *R*, use $\boxed{R = 8.31\ \textbf{J}/\text{mol·K}\ \ or\ \ 0.00831\ \textbf{kJ}/\text{mol·K}}$

3. When *K* or *Q* are calculated, gas pressures must be converted to atmospheres, concentrations must be in moles/liter, and units are omitted. For solids, solvents, and pure liquids, pressures and concentrations = 1

4. $\boxed{\Delta G^o_{rxn.} = -RT \ln(K)}$

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