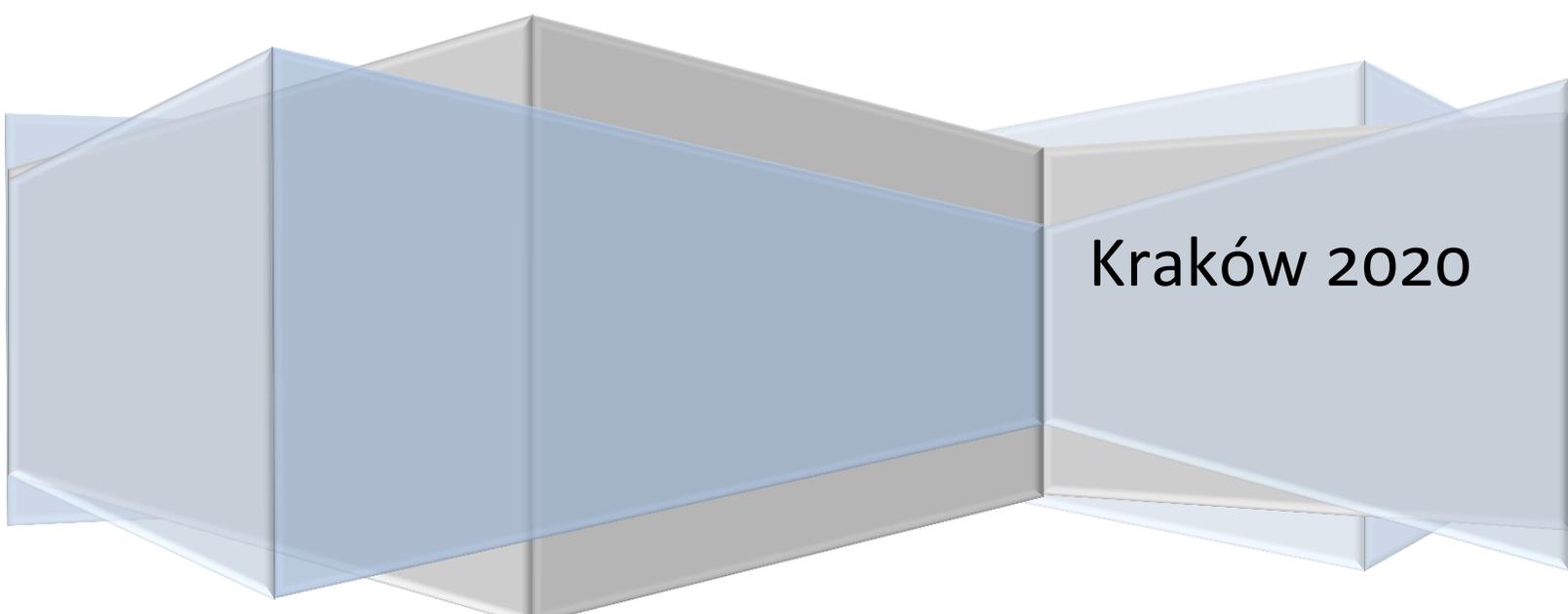


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# **General Chemistry GUIDE**

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# A. GENERAL CHEMISTRY

## 1. Atomic and molar mass, number of moles

The **mole** is a chemical (atomistic) unit of quantity of a substance. According to the definition provided by the International Union of Pure and Applied Chemistry (IUPAC) *a mole is the amount of substance of a given system which contains as many elementary entities as there are atoms in 0.012 kilogram of a sample of carbon-12 isotope*. When the mole is used, the elementary entities must be specified and may be atoms, molecules, ions, electrons, other particles, or specified groups of such particles (i.e. mole of atoms, mole of cations, mole of molecules, etc.). Thus, one mole contains as many entities as there are in 12 grams of carbon-12 (or 0.012 kilogram). The symbol for mole is "mol."

In one mole, there are  $6.022 \times 10^{23}$  entities. Let's say that clearly: one mole of anything contains  $6.022 \times 10^{23}$  entities. The last number is so important in chemistry that it has a name. It is called **Avogadro's number** ( $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$ ) and it has been very carefully measured in a number of ways over many decades.

Because atoms are too small to be weighed in units of grams on a balance the more convenient mass scale was proposed in which the mass of atoms is measured in atomic mass units. The *atomic mass unit (1amu)* is defined as *1/12 the mass of one atom of the carbon-12 isotope ( $^{12}\text{C}$ )*. By choosing this unit the atomic masses of other elements and compounds are approximately whole numbers. However, most elements in nature exist as a mixture of isotopes with different masses ( $^1\text{H}$  – protium and  $^2\text{H}$  – deuterium). Therefore, the average atomic masses are not whole numbers (see example below) and its value depends on the relative abundance of isotopes. In chemical calculus **molar mass** is the mass ( $m$ ) of a given substance (chemical element or chemical compound) divided by its amount of substance ( $n$ ).

$$M = m/n \text{ (g / mol)}$$

The molar mass is expressed in g/mol. Obviously each element has a different molar mass depending on the weight of  $6.022 \times 10^{23}$  of its atoms (1 mol). The molar mass of any element can be determined by finding the atomic mass of the element on the periodic table. For example, if the atomic mass of sulfur (S) is 32.066 atomic mass units (amu), then its molar mass is 32.066 g/mol.

Example 1.1 Determining the molar mass of a compound.

Calculate the molar mass of  $\text{Al}(\text{NO}_3)_3$ .

In a compound of  $\text{Al}(\text{NO}_3)_3$ , the molar mass of Al alone is  $M_{\text{Al}} = 26.98 \text{ g/mol}$ , the molar mass of N is  $M_{\text{N}} = 14.01 \text{ g/mol}$ , and O is  $M_{\text{O}} = 16.00 \text{ g/mol}$ .

$$M = M_{\text{Al}} + 3M_{\text{N}} + 9M_{\text{O}} = (1 \times 26.98) + (3 \times 14.01) + (9 \times 16.00) = 213.01 \text{ g/mol}$$

213.01 grams is the mass of one mole of aluminum nitrate. And thus 213.01 grams of aluminum(III) nitrate(V) contains  $6.022 \times 10^{23}$  entities of  $\text{Al}(\text{NO}_3)_3$ .

Example 1.2 How many moles of NaOH are present in 90 g of NaOH?

Since the molar mass of NaOH is 40 g/mol, we can divide the 90 g of NaOH by the molar mass (40 g/mol) to find the moles of NaOH.

$$n_{\text{NaOH}} = 90 \text{ g} / [40 \text{ g/mol}] = 2.25 \text{ mol NaOH}$$

Example 1.3 How many moles and how many atoms are contained in 10.0 g of nickel?

According to the periodic table, the atomic mass of nickel (Ni) is 58.69 amu, which means that the molar mass of nickel is 58.69 g/mol. Therefore, we can divide 10.0 g of Ni by the molar mass of Ni to find the number of moles present.

$$n_{\text{Ni}} = 10.0 \text{ g} / (58.69 \text{ g/mol}) = 0.170 \text{ mol Ni}$$

To determine the number of atoms, convert the moles of Ni to atoms using Avogadro's number:

$$0.170 \text{ moles} \times 6.022 \times 10^{23} \text{ mol}^{-1} = 1.02 \times 10^{23} \text{ atoms Ni}$$

Given a sample's mass and number of atoms moles in that sample, it is also possible to calculate the mass of a single nickel atom.

$$m_{\text{Ni}} = 10 \text{ g} / (1.02 \times 10^{23}) = 9.80 \times 10^{-23} \text{ g}$$

Example 1.4 Atomic mass of isotopic mixtures.

Natural chlorine is a mixture of  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$  isotopes. The natural concentrations (abundances) (mol.%) of these isotopes in natural chlorine are 77.5% and 22.5%, respectively. What is the atomic mass of natural chlorine?

The atomic mass of isotopic mixture equals to a weighted average of atomic masses of the individuals with abundances taken as the weights. Thus,

$$\langle M \rangle = \frac{M_{35}p_{35} + M_{37}p_{37}}{100\%},$$

where  $M_{35}$  and  $M_{37}$  stand for atomic masses of Cl-35 and Cl-37 isotopes, and  $p_{35}$  and  $p_{37}$  are abundances (in percent). Obviously  $M_{35}$  equals 35 amu and  $M_{37} = 37$  amu. Substituting the numerical values we get  $\langle M \rangle = 35.45$  amu

## 2. Concentration of substance in solution

### 2.1 Mass percent concentration

Percent composition (by mass),  $c_p$  (or weight percent, or mass-mass percent concentration,  $m/m\%$  as it is sometimes called) can be considered in two ways: (a) the parts of a solute per 100 parts of a solution or (b) the fraction of a solute in a solution multiplied by 100. Two pieces of information are needed to calculate the percent by mass of a solute in a solution: the mass of the substance, solute, ( $m_{\text{sub}}$ ) and the mass of the solution ( $m_{\text{sol}}$ ). Then, the following equation is used for calculation of the percent by mass:

$$c_p = \frac{m_{\text{sub}}}{m_{\text{sol}}} \times 100\%$$

The mass of the solution is equal to the mass of the solvent ( $m_{\text{solvent}}$ ) added to the mass of the solute ( $m_{\text{sub}}$ ). For example, if given a solution that contains 5.0 grams of a solute and 110.0 grams of solvent, then the mass percent concentration of the solute is  $c_p = [5.0 \text{ g} / (5.0 \text{ g} + 110.0 \text{ g})] \times 100\%$ , which is equal to 4.35%.

Example 2.1 Preparing solution of KCl.

What masses of potassium chloride and water are needed to make 250g of 5.00% solution?

Given are mass of the solution  $m_{\text{sol}} = 250 \text{ g}$  and mass percent concentration  $c_p = 5.00\%$ .

Calculate mass of KCl,  $m_{\text{sub}} = c_p m_{\text{sol}} / 100\% = 5.00\% \times 250 \text{ g} / 100\% = 12.5 \text{ g}$  KCl (solute). Then calculate the mass of water:  $m_{\text{solv}} = m_{\text{sol}} - m_{\text{sub}} = 250 \text{ g} - 12.5 \text{ g} = 238 \text{ g}$  H<sub>2</sub>O. To conclude, dissolving 12.5 g KCl in 238 g H<sub>2</sub>O gives a 5.00% solution.

## 2.2 Volume percent composition

For solution the percent concept can be confusing because the units used for the part and the whole are variable (solvent in mL or cm<sup>3</sup>, solute in grams). So it is common for liquid-liquid solution that the concentration is expressed as a *volume percent*,  $c_{\text{vol}}$  (v/v%). Thus,

$$c_{\text{vol}} = \frac{V_{\text{sub}}}{V_{\text{sol}}} \times 100\%$$

Example 2.2

A solution is prepared by dissolving 90 milliliters (mL = cm<sup>3</sup>) of pure hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) in enough water to make 3000 mL of solution. What is the concentration of the hydrogen peroxide solution? Assume no volume contraction effect.

Given are volume of solute  $V_{\text{sub}} = 90 \text{ mL}$ , volume of solution  $V_{\text{sol}} = 3000 \text{ mL}$ . Substituting numerical values:

$$c_{\text{vol}} = (V_{\text{sub}} / V_{\text{sol}}) \times 100\% = (90 \text{ mL} / 3000 \text{ mL}) \times 100\% = 3\%.$$

Therefore, the concentration of the hydrogen peroxide solution is 3%.

Example 2.3

Calculate the volume/volume percent solution formed by combining 25 milliliters of ethanol with enough water to make 200 milliliters of solution.

In analogy to Example 2.2.  $c_{\text{vol}} = (25 \text{ mL} / 200 \text{ mL}) \times 100\% = 12.5\%$ .

*Note, however, that reasoning showed above is true only if there is no volume contraction upon mixing two solutions. One can expect volume contraction in case of (a) strong interaction between molecules of two solutions, e.g. formation of hydrogen bonds between molecules of a solute and a solvent (for instance water and alcohols) or (b) mixing two solutions of very different densities. In such cases one must not use volumes of parts to calculate a total volume of a solution but rather calculate total mass of a solution by adding masses of parts:*

$$m_{\text{sol}} = m_{\text{sub}} + m_{\text{solv}}$$

using their given densities ( $m = dV$ )

$$m_{\text{sol}} = d_{\text{sub}} V_{\text{sub}} + d_{\text{solv}} V_{\text{solv}}$$

and next calculate volume of the solution

$$V_{\text{sol}} = m_{\text{sol}} / d_{\text{sol}}$$

*Note. In all calculations only metric system of units must be utilized. Therefore volumes must be expressed in m<sup>3</sup>, dm<sup>3</sup> or cm<sup>3</sup>. The equivalent units are 1000L (kL), L, mL, respectively.*

### 2.3 Mole fraction

In chemistry, the **mole fraction** or **molar fraction** ( $x_i$ ) is defined as the amount of  $i$ -th constituent (expressed in moles),  $n_i$ , divided by the total amount of all constituents in a mixture (expressed as a sum of moles):

$$x_i = \frac{n_i}{\sum_j n_j}$$

Note that the sum of all the mole fractions in a given mixture is equal to 1,  $\sum n_j = 1$ .

Example 2.4 Calculation of mole fraction of 2-component mixture.

0.100 mole of NaCl is dissolved into 100.0 grams of pure H<sub>2</sub>O. What is the mole fraction of NaCl?

Solution relies on calculation of number of moles of the components. For water one gets

$n_{\text{H}_2\text{O}} = 100.0 \text{ g} / 18.0 \text{ g mol}^{-1} = 5.56 \text{ mol}$  of H<sub>2</sub>O. Add that to the 0.100 mol of NaCl,  $\sum n = 5.56 \text{ mol} + 0.100 \text{ mol} = 5.66 \text{ mol}$ . Mole fraction of NaCl equals  $x_{\text{NaCl}} = 0.100 \text{ mol} / 5.66 \text{ mol} = 0.018$ . The mole fraction of the H<sub>2</sub>O is  $5.56 \text{ mol} / 5.66 \text{ mol} = 0.982 (= 1 - 0.018)$ .

Example 2.5 Mole fractions of ethanol in water.

A solution of ethanol in water contains 30% of ethanol by number of molecules. Calculate the mole fractions of ethanol and water in the solution.

A solution of ethanol in water contains 30% of ethanol by weight. Calculate the mole fractions of ethanol and water in the solution.

Molecular weight of ethanol, C<sub>2</sub>H<sub>5</sub>OH, is 46 g/mol and the molecular weight of water, H<sub>2</sub>O, is 18 g/mol. Let's assume we have 100 g of the mixture. Since, in 100 g of the mixture there are 30 g of ethanol and 70 g of water, mole fraction of ethanol

$$x_{\text{ethanol}} = (30 \text{ g} / 46 \text{ g} \times \text{mol}^{-1}) / [(30 \text{ g} / 46 \text{ g} \times \text{mol}^{-1} + (70 \text{ g} / 18 \text{ g} \times \text{mol}^{-1})] = 0.14$$

$$\text{and mole fraction of water } x_{\text{H}_2\text{O}} = (70/18) / [(30/46 + (70/18))] = 0.86 = (1 - 0.14)$$

### 2.4 Molarity - molar concentration

**Molar concentration**, also called **molarity**, is a measure of the concentration of a solute in a solution, or of any chemical species, in terms of the *number of moles of a substance in a given volume*. Concentration refers to the volume of the solution and not the volume of the solvent.

$$c_m = \frac{n}{V} \quad \left[ \frac{\text{mol}}{\text{dm}^3} \right]$$

A commonly used unit for molar concentration used in chemistry is mol/dm<sup>3</sup> (mol/L). A solution of concentration 1 mol/dm<sup>3</sup> is also denoted as 1 molar (1 M). The molar concentration (molarity) of a chemical species is symbolized either with  $c_m$  or by enclosing the formula of this species within brackets. For example, [H<sup>+</sup>] refers to molar concentration of hydrogen ions, [Br<sup>-</sup>] refers to the molar concentration of bromide ion, [NH<sub>3</sub>] refers to the molar concentration of ammonia.

*Note the concept of ionic molar concentration that is a measure of the actual number of ions (expressed as a number of moles) in a solution of volume of V. In contrast ionic activity (a) is a measure of the*

effective concentration of electrolytes that results from the charge interaction on dissociated species. The difference between ionic concentration and ionic activity is important because the molar concentration of any electrolyte will not affect the molar concentration of any other electrolyte, but ionic activities are mutually interactive. The ionic activity is related to the molarity with the following formula:  $a = f c_m$ , where  $f$  is an activity factor ( $f$  approaches a value of 1, when molarity is close to zero). For all cases discussed in this course we assume activity equal to molarity, i.e. all electrolytes are treated as highly dissolved.

Molar concentration of ions is related to the stoichiometry of an ionic solute. Consider the following equation representing complete electrolytic dissociation:  $\text{Ca}(\text{NO}_3)_{2(s)} \rightarrow \text{Ca}^{2+}_{(aq)} + 2\text{NO}_3^{-}_{(aq)}$ . Supposing that the molar concentration of calcium nitrate(V),  $\text{Ca}(\text{NO}_3)_2$ , is 0.20 M, the molar concentrations of ions follow the reaction stoichiometry so that 1 mol  $\text{Ca}(\text{NO}_3)_2$  yields 1 mol  $\text{Ca}^{2+}_{(aq)}$  and 2 mol  $\text{NO}_3^{-}_{(aq)}$ . Thus,  $[\text{Ca}^{2+}_{(aq)}] = 0.20 \text{ M}$  and  $[\text{NO}_3^{-}_{(aq)}] = 2 \times 0.20 \text{ M} = 0.40 \text{ M}$ .

The molar concentration of pure water  $[\text{H}_2\text{O}]$  is quite large compared to any possible concentrations of solutes and can be considered as constant. The molar concentration value is 55.5 M, which is obtained by division of number of grams of water in  $1 \text{ dm}^3$  (density of water is approximately equal to  $1000 \text{ g/dm}^3$ ) by the molecular weight of water,  $18 \text{ g/mol}$ .

**Example 2.6** Basic calculations of mass and molar concentrations.

Consider 11.6 g of NaCl dissolved in 100 g of water. The mass concentration is calculated as  $c_p = [11.6 \text{ g} / (11.6 \text{ g} + 100 \text{ g})] \times 100\% = 10.4 \%$ . Knowing that the density of such a solution is  $1.07 \text{ g/cm}^3$  ( $d = m/V$ ), thus its volume can be calculated as  $V = (11.6 \text{ g} + 100 \text{ g}) / (1.07 \text{ g/cm}^3) = 104.3 \text{ cm}^3 = 0.1043 \text{ dm}^3$ . The molar concentration of NaCl ( $M = 58.5 \text{ g/mol}$ ) in the solution is therefore:

$$c_m(\text{NaCl}) = n_{\text{NaCl}}/V = (11.6 \text{ g} / 58.5 \text{ g/mol}) / 0.1043 \text{ dm}^3 = 1.90 \text{ mol/dm}^3.$$

*Note. Remember to express the volume in cubic decimeters  $\text{dm}^3$  (= L).*

**Example 2.7** Preparation of a solution of given molarity.

How to prepare  $100 \text{ cm}^3$  (=  $0.1 \text{ dm}^3$ ) of a  $0.5 \text{ mol/dm}^3$  solution of  $\text{Na}_2\text{SO}_4$  in water?

The mass of salt needed is  $m_{\text{NaCl}} = n \times M = c_m \times V \times M = 0.5 \text{ mol/dm}^3 \times 0.1 \text{ dm}^3 \times 142 \text{ g/mol} = 7.1 \text{ g}$  where  $142 \text{ g/mol}$  is a molar mass of  $\text{Na}_2\text{SO}_4$ .

Thus, to create the solution,  $7.1 \text{ g Na}_2\text{SO}_4$  are placed in a volumetric flask, dissolved in some water, then followed by the addition of more water until the total volume reaches  $100 \text{ cm}^3$ .

## 2.5 Dilution of solutions and mixing solutions

To dilute a solution means to add more solvent without the addition of more solute. Of course, the resulting solution is thoroughly mixed so as to ensure that all parts of the solution are identical. The fact that the solute amount stays constant allows us to develop calculation techniques. First we note that  $n$  = constant upon adding solvent. So  $n_1 = n_2$  where 1 and 2 denote initial and final (after dilution) states, respectively. From rearranging the equation that defines molarity, we know that the moles of solute equals the molarity times the volume. So we can substitute  $c_m V$  and get  $c_{m1} V_1 = c_{m2} V_2$ .

Example 2.8 Mixing two solutions.

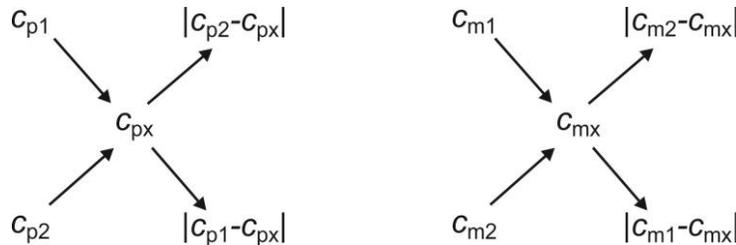
Calculate the final concentration if 2.00 dm<sup>3</sup> of 3.00 M NaCl and 2.00 dm<sup>3</sup> of 1.50 M NaCl are mixed. Assume there is no volume contraction upon mixing.

Number of moles of NaCl in both solutions are  $n_1 = (3.00 \text{ mol/dm}^3) \times (2.00 \text{ dm}^3) = 6.00 \text{ mol}$  and  $n_2 = (1.50 \text{ mol/dm}^3) \times (2.00 \text{ dm}^3) = 3.00 \text{ mol}$ . The total volume is  $2.00 \text{ dm}^3 + 2.00 \text{ dm}^3 = 4.00 \text{ dm}^3$ . Now we divide total moles by total volume to get the final answer.  $c_m = (6 \text{ mol} + 3 \text{ mol}) / 4 \text{ dm}^3 = 1.5 \text{ mol/dm}^3$ .

Alternatively we can use the following equation  $c_{m1}V_1 + c_{m2}V_2 = c_mV$ , and we have this:

$$(3.00 \text{ mol/dm}^3) \times (2.00 \text{ dm}^3) + (1.50 \text{ mol/dm}^3) \times (2.00 \text{ dm}^3) = c_m \times (4.00 \text{ dm}^3), c_m = 1.5 \text{ mol/dm}^3.$$

Having two solutions of known molar concentrations we can easily calculate the ratio of their volumes to be mixed to produce a solution of a given final molarity. Similarly, having two solutions of known mass percent concentrations we can calculate the ratio of their masses to be mixed to produce a solution of a given final mass concentration. We make use of the following schemes:



In case of mass percent concentration one gets the relation:

$$\frac{m_1}{m_2} = \frac{|c_{p2} - c_{px}|}{|c_{p1} - c_{px}|},$$

where  $c_{p1}$  and  $c_{p2}$  are mass percent concentrations of the solutions 1 and 2, respectively, while  $c_{px}$  is a mass concentration of the resulting solution.  $m_1$  and  $m_2$  denote masses of the solutions.

In case of molar concentration similar relations can be used:

$$\frac{V_1}{V_2} = \frac{|c_{m2} - c_{mx}|}{|c_{m1} - c_{mx}|},$$

where  $c_{m1}$  and  $c_{m2}$  are molarities of the solutions 1 and 2, respectively, while  $c_{mx}$  is molarity of the resulting solution, and  $V_1$  and  $V_2$  stand for volumes of the initial solutions.

Example 2.9

How to prepare 100 cm<sup>3</sup> solution of 0.45 M HCl using 0.10 M and 1.00 M solutions of hydrochloric acid?

Using one of the above relationships one gets  $V_1/V_2 = (1.00 - 0.45)/(0.45 - 0.10)$ . This constitutes one equation with two independent variables. The second equation results from the total volume of the solution to be prepared,  $V_1 + V_2 = 100 \text{ cm}^3$ .

$$V_1/V_2 = 1.57 \text{ and } V_1 + V_2 = 100 \text{ cm}^3$$

$$V_1 = 61.1 \text{ cm}^3 \text{ and } V_2 = 38.9 \text{ cm}^3.$$

One needs to mix 61.1 cm<sup>3</sup> of 0.10 M HCl with 38.9 cm<sup>3</sup> of 1.00 M HCl to produce the solution of 0.45 M.

*Note: the same calculation technique can be applied to dissolution problem. Simply, molarity (or concentration by mass) of one of the components is fixed to zero (pure water).*

## 2.6 Mass percent to molarity

One of the problems in chemical calculus is finding molarity using mass concentration and vice versa. Below there are few examples showing how to deal with this kind of calculations.

### Example 2.10

Concentrated hydrochloric acid HCl is usually available at a concentration of 37.7% by mass. What is its molar concentration? The density of the solution is  $1.19 \text{ g/cm}^3$ .

*First method.* Determine moles of HCl in 100.0 g (this is only assumed mass) of 37.7% solution in a following way:  $m_{\text{sub}} = c_p m_{\text{sol}} / 100\% = 37.7\% \times 100 \text{ g} / 100\% = 37.7 \text{ g}$  pure HCl

$$n_{\text{HCl}} = 37.7 \text{ g} / 36.5 \text{ g/mol} = 1.03 \text{ mol}$$

Determine volume of 100.0 g of the solution using its density,  $d = m_{\text{sol}}/V$ ,

$$V = 100.0 \text{ g} / 1.19 \text{ g/cm}^3 = 84.03 \text{ cm}^3 = 0.08403 \text{ dm}^3.$$

Determine molarity:

$$c_m = 1.03 \text{ mol} / 0.08403 \text{ dm}^3 = 12.3 \text{ mol/dm}^3.$$

*Second method.* Assume  $1.00 \text{ dm}^3$  of solution. Use density to get mass:

$$m_{\text{sol}} = dV = 1.19 \text{ g/cm}^3 \times 1000 \text{ cm}^3 = 1190 \text{ g}.$$

Use percent mass to get mass of HCl,  $m_{\text{sub}} = c_p m_{\text{sol}} / 100\% = 37.7\% \times 1190 \text{ g} / 100\% = 448.63 \text{ g}$

and now calculate moles:  $n_{\text{HCl}} = 448.63 \text{ g} / 36.5 \text{ g/mol} = 12.3 \text{ mol}$

Finally, determine molarity:

$$c_m = 12.3 \text{ mol} / 1.00 \text{ dm}^3 = 12.3 \text{ mol/dm}^3.$$

### Example 2.11

Concentrated nitric acid  $\text{HNO}_3$  is a solution that is 70.4% by mass. The density of this acid is  $1.42 \text{ g/cm}^3$ . What is the molarity of the acid?

Determine mass and moles of pure  $\text{HNO}_3$  in 100.0 g of 70.4% solution.

$m_{\text{sub}} = c_p m_{\text{sol}} / 100\% = 70.4\% \times 100 \text{ g} / 100\% = 70.4 \text{ g}$  of  $\text{HNO}_3$  and  $n = 70.4 \text{ g} / 63.0 \text{ g/mol} = 1.1 \text{ mol}$ , where  $M_{\text{HNO}_3} = 63.0 \text{ g/mol}$ .

Determine volume of 100.0 g of solution using its density,  $d = m_{\text{sol}}/V$ ,

$$V = 100 \text{ g} / 1.42 \text{ g/cm}^3 = 70.4 \text{ cm}^3 = 0.0704 \text{ dm}^3.$$

Determine molarity:

$$c_m = 1.1 \text{ mol} / 0.0704 \text{ dm}^3 = 15.6 \text{ mol/dm}^3.$$

In the above solution, what is the mole fraction of  $\text{HNO}_3$ ?

Let us assume 100.0 grams of the solution. Therefore 70.4 g is  $\text{HNO}_3$  and 29.6 g is  $\text{H}_2\text{O}$  (because  $c_p = 70.4\%$ ). Now the moles of each substance can be determined:  $n_{\text{HNO}_3} = 70.4 \text{ g} / 63.0 \text{ g/mol} = 1.1 \text{ mol}$ ,  $n_{\text{H}_2\text{O}} = 29.6 \text{ g} / 18.0 \text{ g/mol} = 1.6 \text{ mol}$ . Mole fraction can be calculated now in a straightforward way:  $x_{\text{HNO}_3} = 1.1 \text{ mol} / (1.1 \text{ mol} + 1.6 \text{ mol}) = 0.4$ ,  $x_{\text{H}_2\text{O}} = 1 - x_{\text{HNO}_3} = 0.6$ .

### Example 2.12

What is the density (in  $\text{g/cm}^3$ ) of a 3.60 M aqueous sulfuric acid solution that is 29.0%  $\text{H}_2\text{SO}_4$  by mass?

Instead of making assumption about mass of the solution it is possible to combine and transform formulas for concentration by mass and by mole with definition of density to get the final solution.

$$c_p = m_{\text{sub}} 100\% / m_{\text{sol}};$$

by combining  $V = n/c_m$  and  $n = m_{\text{sub}}/M$  one gets  $V = m_{\text{sub}}/M c_m$ , where  $M = 98 \text{ g/mol}$  for  $\text{H}_2\text{SO}_4$ ;

using definition of density  $d = m_{\text{sol}}/V$  and collecting all formulas together one gets

$$d = m_{\text{sol}}c_m M / m_{\text{sub}} = c_m M 100\% / c_p$$

$$d = (3.60 \text{ mol/dm}^3 \times 98 \text{ g/mol} \times 100\%) / 29.0\% = 1216.5 \text{ g/dm}^3 = 1.2165 \text{ g/cm}^3.$$

### 3. Molecular formula of compounds

#### 3.1 Inorganic acids and bases

The names of acids differentiate between (1) acids in which the  $\text{H}^+$  ion is attached to an oxygen atom of a polyatomic anion (these are called oxoacids, or occasionally oxyacids) and (2) acids in which the  $\text{H}^+$  ion is attached to some other element. In the latter case, the name of the acid begins with hydro- and ends in -ic, with the root of the name of the other element or ion in between. Recall that the name of the anion derived from this kind of acid always ends in -ide. Thus hydrogen chloride (HCl) gas dissolves in water to form hydrochloric acid (which contains  $\text{H}^+$  and  $\text{Cl}^-$  ions), hydrogen cyanide (HCN) gas forms hydrocyanic acid (which contains  $\text{H}^+$  and  $\text{CN}^-$  ions), and so forth (Table 1).

**Table 1** Nomenclature for some inorganic acids

<i>formula</i>	<i>name</i>	<i>formula</i>	<i>name</i>	<i>systematic name</i>
HF	hydrofluoric acid	$\text{HNO}_2$	nitrous acid	nitric(III) acid
HCl	hydrochloric acid	$\text{HNO}_3$	nitric acid	nitric(V) acid
HBr	hydrobromic acid	$\text{H}_2\text{SO}_3$	sulfurous acid	sulfuric(IV) acid
HI	hydroiodic acid	$\text{H}_2\text{SO}_4$	sulfuric acid	sulfuric(VI) acid
HCN	hydrocyanic acid	$\text{H}_3\text{PO}_4$	phosphoric acid	phosphoric(V) acid
$\text{H}_2\text{S}$	hydrosulfuric acid	$\text{H}_2\text{CO}_3$	carbonic acid	carbonic acid
		HClO	hypochlorous acid	chloric(I) acid
		$\text{HClO}_2$	chlorous acid	chloric(III) acid
		$\text{HClO}_3$	chloric acid	chloric(V) acid
		$\text{HClO}_4$	perchloric acid	chloric(VII) acid

If an acid contains one or more  $\text{H}^+$  ions attached to oxygen, it is a derivative of one of the common oxoanions, such as sulfate(VI) ( $\text{SO}_4^{2-}$ ) or nitrate(V) ( $\text{NO}_3^-$ ). These acids contain as many  $\text{H}^+$  ions as are necessary to balance the negative charge on the anion, resulting in a neutral species such as  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$ .

Typical inorganic bases are ionic compounds containing the hydroxide ion ( $\text{OH}^-$ ) and a metal cation such as sodium hydroxide NaOH and barium hydroxide  $\text{Ba}(\text{OH})_2$ . These have the general formula  $\text{M}(\text{OH})_n$ . It is important to recognize that alcohols, with the general formula ROH, are covalent compounds, not ionic compounds; consequently, they do not dissociate in water to form a basic solution (containing OH ions). When a base reacts with any of the acids above, it accepts a proton ( $\text{H}^+$ ). For example, the hydroxide ion ( $\text{OH}^-$ ) accepts a proton to form  $\text{H}_2\text{O}$  (neutralization reaction). Thus bases are also referred to as proton acceptors.

Concentrated aqueous solutions of ammonia ( $\text{NH}_3$ ) contain significant amounts of the hydroxide ion, even though the dissolved substance is not primarily ammonium hydroxide ( $\text{NH}_4\text{OH}$  – in fact such

compound does not exist in solutions and must not be used in chemical equations). Thus aqueous ammonia solution (in chemical reactions usually indicated as  $\text{NH}_3(\text{aq})$ ) is also a common base. Replacing a hydrogen atom of  $\text{NH}_3$  with an alkyl group results in an amine ( $\text{RNH}_2$ ), which is also a base (being and organic compounds, amine will be discussed in chapters devoted to organic chemistry of this guide).

### 3.2 Inorganic salts

Because ionic compounds do not contain discrete molecules, empirical formulas are used to indicate their compositions. All compounds, whether ionic or covalent, must be electrically neutral. Consequently, the positive and negative charges in a formula unit must exactly cancel each other. If the cation and the anion have charges of equal magnitude, such as  $\text{Na}^+$  and  $\text{Cl}^-$ , then the compound must have a 1:1 ratio of cations to anions, and the empirical formula must be  $\text{NaCl}$ . If the charges are not equal, then a cation:anion ratio other than 1:1 is needed to produce a neutral compound. In the case of  $\text{Mg}^{2+}$  and  $\text{Cl}^-$ , for example, two  $\text{Cl}^-$  ions are needed to balance the two positive charges on each  $\text{Mg}^{2+}$  ion, giving an empirical formula of  $\text{MgCl}_2$ . Similarly, the formula for the ionic compound that contains  $\text{Na}^+$  and  $\text{O}^{2-}$  ions is  $\text{Na}_2\text{O}$ .

Polyatomic ions are groups of atoms that bear a net electrical charge, although the atoms in a polyatomic ion are held together by the same covalent bonds that hold atoms together in molecules. Just as there are many more kinds of molecules than simple elements, there are many more kinds of polyatomic ions than monatomic ions. Some common examples of polyatomic ions are given in table below.

**Table 2** Nomenclature for some common ions forming salts

formula	name	formula	name	formula	name
$\text{NH}_4^+$	ammonium	$\text{NO}_3^-$	nitrate(V)	$\text{HPO}_4^{2-}$	hydrogen phosphate(V)
$\text{CH}_3\text{NH}_3^+$	methylammonium	$\text{CO}_3^{2-}$	carbonate	$\text{H}_2\text{PO}_4^-$	dihydrogen phosphate(V)
$\text{OH}^-$	hydroxide	$\text{HCO}_3^-$	hydrogen carbonate, or bicarbonate	$\text{ClO}_4^-$	chlorate(VII)
$\text{O}_2^{2-}$	peroxide	$\text{SO}_3^{2-}$	sulfate(IV)	$\text{MnO}_4^-$	manganite(VII)
$\text{CN}^-$	cyanide	$\text{SO}_4^{2-}$	sulfate(VI)	$\text{CrO}_4^{2-}$	chromate(VI)
$\text{Cl}^-$	chloride	$\text{HSO}_4^-$	hydrogen sulfate(VI), or bisulfate(VI)	$\text{Cr}_2\text{O}_7^{2-}$	dichromate(VI)
$\text{NO}_2^-$	nitrate(III)	$\text{PO}_4^{3-}$	phosphate(V)	$\text{CH}_3\text{COO}^-$	acetate

The method to predict the empirical formulas for ionic compounds that contain monatomic ions can also be used for compounds that contain polyatomic ions. The overall charge on the cations must balance the overall charge on the anions in the formula unit. Thus  $\text{K}^+$  and  $\text{NO}_3^-$  ions combine in a 1:1 ratio to form  $\text{KNO}_3$  (potassium nitrate(V)). Similarly,  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  form  $\text{CaSO}_4$  (calcium sulfate(VI)). The polyatomic

ions  $\text{NH}_4^+$  and  $\text{NO}_3^-$  form  $\text{NH}_4\text{NO}_3$  (ammonium nitrate(V)). One example of a compound in which the ions have charges of different magnitudes is calcium phosphate(V), which is composed of  $\text{Ca}^{2+}$  and  $\text{PO}_4^{3-}$  ions. The compound is electrically neutral because the ions combine in a ratio of three  $\text{Ca}^{2+}$  ions ( $3(+2) = +6$ ) for every two ions ( $2(-3) = -6$ ), giving an empirical formula of  $\text{Ca}_3(\text{PO}_4)_2$ ; the parentheses around  $\text{PO}_4$  in the empirical formula indicate that it is a polyatomic ion.

Many ionic compounds occur as hydrates, compounds that contain specific ratios of loosely bound water molecules, called waters of hydration. Waters of hydration can often be removed simply by heating. For example, calcium dihydrogen phosphate(V) can form a solid that contains one molecule of water per  $\text{Ca}(\text{H}_2\text{PO}_4)_2$  unit. The empirical formula for the solid is  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$  and its name is calcium dihydrogen phosphate(V) - water 1:1. In contrast, copper(II) sulfate(VI) usually forms a blue solid that contains five waters of hydration per formula unit, with the empirical formula  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (copper(II) sulfate(VI) – water 1:5). When heated, all five water molecules are lost, giving a white solid with the empirical formula  $\text{CuSO}_4$ .

Below some examples of names of typical ionic compounds are provided according to IUPAC recommendations. When polyanions are composed of an element of a diverse valence (oxidation state), and when metal forming cations can exhibit various oxidation numbers, then the actual oxidation number are placed in parenthesis immediately after name of the respective anion and cation. However, when an element exhibit one typical oxidation state (metals of the 1<sup>st</sup> and 2<sup>nd</sup> group of periodic table, carbon in carbonates), then this figure is omitted in systematic name.

#### Example 3.1

$\text{LiCl}$	lithium chloride	$\text{Fe}_2(\text{SO}_4)_3$	iron(III) sulfate(VI)
$\text{CuCl}$	copper(I) chloride	$\text{KHSO}_3$	potassium hydrogen sulfate(IV)
$\text{Hg}_2\text{Cl}_2$	mercury(I) chloride	$\text{CrO}_3$	chromium(III) oxide
$\text{Ba}(\text{NO}_3)_2$	barium nitrate(V)	$\text{Co}(\text{NO}_3)_3$	cobalt(III) nitrate(V)
$\text{Ca}(\text{OH})_2$	calcium hydroxide	$\text{MgCO}_3$	magnesium carbonate
$\text{Fe}(\text{OH})_2$	iron(II) hydroxide	$\text{KMnO}_4$	potassium manganite(VII)
$(\text{NH}_4)_3\text{PO}_4$	ammonium phosphate(V)	$\text{MnSO}_3$	manganese(II) sulfate(IV)
$\text{Ca}(\text{H}_2\text{PO}_4)_2$	calcium dihydrogen phosphate(V)	$(\text{CH}_3\text{COO})_2\text{Ca}$	calcium acetate

### **3.3 Molecular formula form mass composition**

Molecular formula can be established based on elemental analysis. This is a chemical analysis resulting in qualitative (type of elements) and quantitative (composition expressed as weights of particular elements) data. Other method involve thermogravimetric analysis, where the composition can be calculated from the mass loss induced by thermal decomposition. More advanced analytical techniques use sophisticated spectroscopic and spectrometric measurements, such as mass spectrometry, nuclear magnetic resonance, X-ray fluorescence, etc. They are not discussed in this tutorial.

### Example 3.2

A compound consists of 16.6 wt.% Mg, 16.4 wt.% C, 1.4 wt.% H, and 65.6 wt.% O. Establish molecular formula of this compound.

Assume 100 g of the compound. Then, masses of the elements are as follow: 16.6 g Mg, 16.4 g C, 1.4 g H and 65.6 g O. By dividing the masses by molar masses one obtains number of moles, which can next be transformed into integers corresponding to molecular formula.

element	Mg	C	H	O
wt.%	16.6 wt.%	16.4 wt.%	1.4 wt.%	65.6 wt.%
mass	16.6 g	16.4 g	1.4 g	65.6 g
$m/M$	16.6 g / 24.3 $\text{gmol}^{-1}$	16.4 g / 12 $\text{gmol}^{-1}$	1.4 g / 1 $\text{gmol}^{-1}$	65.6 g / 16 $\text{gmol}^{-1}$
moles	0.68	1.37	1.4	4.1
common integer	1	2	2	6

The resulting composition is  $\text{MgC}_2\text{H}_2\text{O}_6$  which corresponds to  $\text{Mg}(\text{HCO}_3)_2$  magnesium hydrogen carbonate.

*Notice: identical weight percent composition would be obtained for any formula of the type of  $(\text{MgC}_2\text{H}_2\text{O}_6)_n$ ,  $n$  integer number. Thus, for definite determination of the molecular formula a molar weight is necessary.*

### Example 3.3

Unknown hydrate of sodium carbonate ( $\text{Na}_2\text{CO}_3 \times n\text{H}_2\text{O}$ ) was heated which resulted in 63% loss of its mass. The temperature was low enough to prevent from thermal decomposition of carbonate itself. How many moles of water are crystallized within the structure per 1 mole of sodium carbonate?

Assume a 100 g sample. 63 g of the hydrate is water ( $M = 18 \text{ g/mol}$ ), while remaining 37 g is  $\text{Na}_2\text{CO}_3$  ( $M = 106 \text{ g/mol}$ ). This information allows for calculation of moles:

$$n_{\text{water}} = 63 \text{ g} / 18 \text{ gmol}^{-1} = 3.5 \text{ mol}$$

$$n_{\text{Na}_2\text{CO}_3} = 37 \text{ g} / 106 \text{ gmol}^{-1} = 0.35 \text{ mol}$$

Number of moles per one mole of sodium carbonate is  $3.5/0.35 = 10$ . As a result, molecular formula of the hydrate is  $\text{Na}_2\text{CO}_3 \times 10\text{H}_2\text{O}$ .

### Example 3.4

Naphthalene is an organic compound that contains carbon and hydrogen only. Complete combustion of a 20.10 mg sample of naphthalene in oxygen yielded 69.00 mg of  $\text{CO}_2$  and 11.30 mg of  $\text{H}_2\text{O}$ . Determine the empirical formula of naphthalene, which molar weight is 128 g/mol.

Note that concentration of carbon that forms naphthalene can be calculated from the mass of  $\text{CO}_2$ , and hydrogen – from mass of  $\text{H}_2\text{O}$ . Masses all  $\text{CO}_2$  ( $M = 44 \text{ g/mol}$ ) and  $\text{H}_2\text{O}$  ( $M = 18 \text{ g/mol}$ ) are used for calculation of masses of carbon and hydrogen:

$$44 \text{ g } \text{CO}_2 \text{ include } 12 \text{ g C so in } 69.00 \text{ mg of } \text{CO}_2 \text{ there is } m_{\text{C}} = (12/44) \times 69.00 \text{ mg} = 18.82 \text{ mg}$$

$$18 \text{ g } \text{H}_2\text{O} \text{ include } 2 \text{ g H so in } 11.30 \text{ mg of } \text{H}_2\text{O} \text{ there is } m_{\text{H}} = (2/18) \times 11.30 \text{ mg} = 1.26 \text{ mg}$$

Those masses and the molar masses of the elements are used for calculation the empirical formula of naphthalene:

$$n_{\text{C}} = 0.01882 \text{ g} / 12 \text{ gmol}^{-1} = 0.00157 \text{ mol}$$

$$n_{\text{H}} = 0.00126 \text{ g} / 1 \text{ gmol}^{-1} = 0.00126 \text{ mol}$$

$$n_C : n_H = 1 : 0.80 = 5 : 4$$

Now by checking the molar mass of  $C_5H_4$  and with 128 g/mol (molar mass of naphthalene)  $M(C_5H_4) = 64$  g/mol one finds that calculated molecular formula must be doubled  $128/64 = 2$ . Finally, the molecular formula of naphthalene is  $C_{10}H_8$ .

#### 4. Chemical reactions and stoichiometry

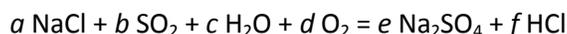
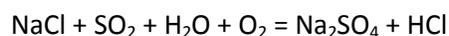
##### 4.1 Balancing chemical equation

Reaction stoichiometry allows us to determine the amount of substance that is consumed or produced by a reaction. The stoichiometric coefficients are the numbers which make the equation balanced (with respect to mass – number of atoms - and charge). The ratios obtained from the stoichiometric coefficients correspond to relative proportions of the chemicals in a given reaction. The ratios are called the mole ratio, the stoichiometric factor, or the stoichiometric ratio. The mole ratio can be used as a conversion factor between different quantities (masses, volumes, molarities).

Example 4.1 Practice in balancing chemical equations

$NH_3 + O_2 = NO + H_2O$	$4NH_3 + 5O_2 = 4NO + 6H_2O$
$C_2H_2 + O_2 = CO_2 + H_2O$	$2C_2H_2 + 5O_2 = 4CO_2 + 2H_2O$
$NO_2 + H_2O = NH_3 + O_2$	$4NO_2 + 6H_2O = 4NH_3 + 7O_2$
$CO_2 + H_2O = C_2H_5OH + O_2$	$2CO_2 + 3H_2O = C_2H_5OH + 3O_2$
$CO_2 + H_2O = C_2H_6 + O_2$	$4CO_2 + 6H_2O = 2C_2H_6 + 7O_2$
$K_4Fe(CN)_6 + H_2SO_4 + H_2O = K_2SO_4 + FeSO_4 + (NH_4)_2SO_4 + CO$	$K_4Fe(CN)_6 + 6H_2SO_4 + 6H_2O = 2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4 + 6CO$

Example 4.2



Writing down the balance conditions on each element gives:

Sodium balance:  $a = 2e$

Chlorine balance:  $a = f$

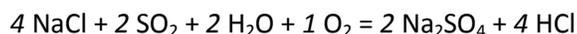
Sulfur balance:  $b = e$

Oxygen balance:  $2b + c + 2d = 4e$

Hydrogen balance:  $2c = f$

Setting  $e = 1$  arbitrarily, gives the immediate solution:  $a = 2, b = 1, c = 1, d = \frac{1}{2}, f = 2$ .

In order to clear the fraction, we multiply all the coefficients by 2 and write down the balanced equation:



##### 4.2 Typical reactions of inorganic synthesis, analysis and exchange

Most chemical reactions can be classified into one or more of five basic types: *protolytic reactions* (reactions based on proton exchange such as acid–base reactions, hydrolysis reaction), *exchange reactions* (single or multiple exchange depending on how many entities are being exchanged), *synthesis*

reactions (including condensation, addition), *analysis reactions* (decomposition, splitting, dissociation) and *oxidation-reduction reactions* (for which electrons are being exchanged). The general forms of these five kinds of reactions are summarized in table below. It is important to note, however, that many reactions can be assigned to more than one classification.

**Table 3** Basic types of chemical reactions

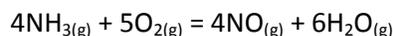
name of reaction	general form	example(s)
<i>oxidation-reduction (redox)</i>	oxidant + reductant → reduced oxidant + oxidized reductant	$2\text{KMnO}_4 + 16\text{HCl} = 2\text{KCl} + 2\text{MnCl}_2 + 8\text{H}_2\text{O} + 5\text{Cl}_2$
<i>acid-base (protolytic)</i>	acid + base → salt	$\text{NH}_3(\text{aq}) + \text{HCl}(\text{aq}) \rightarrow \text{NH}_4^+(\text{aq}) + \text{Cl}^-(\text{aq})$
<i>exchange (single and double)</i>	$\text{AB} + \text{C} \rightarrow \text{AC} + \text{B}$	$\text{CH}_3\text{Cl} + \text{OH}^- \rightarrow \text{CH}_3\text{OH} + \text{Cl}^-$
	$\text{AB} + \text{CD} \rightarrow \text{AD} + \text{CB}$	$\text{BaCl}_2(\text{aq}) + \text{Na}_2\text{SO}_4(\text{aq}) \rightarrow \text{BaSO}_4(\text{s}) + 2\text{NaCl}(\text{aq})$
<i>synthesis (condensation, addition)</i>	$\text{A} + \text{B} \rightarrow \text{AB}$	$\text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{CO}_3(\text{aq})$
		$\text{HBr} + \text{H}_2\text{C}=\text{CH}_2 \rightarrow \text{CH}_3\text{CH}_2\text{Br}$
<i>analysis (decomposition, cleavage, elimination)</i>	$\text{AB} \rightarrow \text{A} + \text{B}$	$\text{MgCO}_3(\text{s}) \rightarrow \text{MgO}(\text{s}) + \text{CO}_2(\text{g})$
		$\text{CH}_3\text{CH}_2\text{Cl} \rightarrow \text{H}_2\text{C}=\text{CH}_2 + \text{HCl}$

### 4.3 Limiting reactant

Once the balanced chemical equation is set, a limiting reactant can be identified. In a chemical reaction, the *limiting reagent is the reactant that determines how much of the products are made. The other reactants are sometimes referred to as being in excess, since there will be some leftover after the limiting reagent is completely used up.* The maximum amount of product that can be produced (calculated based on the amount of limiting reactant) is called the theoretical yield.

#### Example 4.3

A 2.00 g sample of ammonia is mixed with 4.00 g of oxygen. Which is the limiting reactant and how much excess reactant remains after the reaction has stopped? The balanced reaction equation is:



The limiting reactant can be identified by (method 1) calculating moles of reactants and comparing them with stoichiometric ratio or (method 2) by calculating how much product is produced by each reactant (note: does not matter which product is chosen, but the same product must be used for both reactants so that the amounts can be compared).

Method 1.

Number of moles of reactants:

$$n(\text{NH}_3) = 2.00 \text{ g} / 17.0 \text{ g mol}^{-1} = 0.118 \text{ mol}$$

$$n(\text{O}_2) = 4.00 \text{ g} / 32.0 \text{ g mol}^{-1} = 0.125 \text{ mol}$$

$n(\text{NH}_3)/n(\text{O}_2) = 0.944$  whereas stoichiometric ration of  $\text{NH}_3$  and  $\text{O}_2$  equals  $4/5 = 0.800$ . It means that  $\text{NH}_3$  is in excess and the limiting reactant is  $\text{O}_2$ .

Method 2.

Mass of produced NO calculated based on the masses of NH<sub>3</sub> and O<sub>2</sub> are:



$$m(\text{NO}) = [m(\text{NH}_3) \times M(\text{NO})] / M(\text{NH}_3) = 2.00 \text{ g} \times 30 \text{ gmol}^{-1} / 17 \text{ gmol}^{-1} = 3.5 \text{ g}$$



$$m(\text{NO}) = [m(\text{O}_2) \times 4M(\text{NO})] / 5M(\text{O}_2) = 4.00 \text{ g} \times 4 \times 30 \text{ gmol}^{-1} / 5 \times 32 \text{ gmol}^{-1} = 3.0 \text{ g}$$

Because mass of NO produced from a given mass of O<sub>2</sub> is smaller than the corresponding mass obtained from NH<sub>3</sub>, thus O<sub>2</sub> is a limiting reactant.

After the reaction has stopped unused NH<sub>3</sub> will remain in the reactor. This amount is equal to:



$$m(\text{NH}_3) = [m(\text{O}_2) \times 4M(\text{NH}_3)] / 5M(\text{O}_2) = 4.00 \text{ g} \times 4 \times 17 \text{ gmol}^{-1} / 5 \times 32 \text{ gmol}^{-1} = 1.7 \text{ g}$$

Excess of ammonia  $2.0 \text{ g} - 1.7 \text{ g} = 0.3 \text{ g}$  NH<sub>3</sub> remaining.

#### 4.4 Reaction yield

The *theoretical (maximum) yield* is the maximum amount of product which can be expected from a reaction based on the amount of limiting reagent. In practice, however, the maximum yield is hardly achieved for many reasons. Despite how nice and tidy a balanced reaction appears, reactants can also react in unexpected and undesirable ways such as doing an entirely different reaction - sometimes called a side reaction - to give by-products. The *actual yield* may change based on factors such as the relative stability of reactants and products, the purity of the chemicals used, etc. This is why the actual yield using percent yield, which is defined as the percentage of the theoretical yield, is calculated to characterize the efficiency of a chemical reaction. The *percent yield* is determined using the following equation:

$$Y = \frac{Y_{\text{actual}}}{Y_{\text{theoretical}}} \times 100\%$$

As a measure of theoretical and actual yields the amount (masses, volumes, moles) of a selected product is used.

#### Example 4.4

The reaction between barium chloride and silver(I) nitrate(V) is performed with 1.56 g of BaCl<sub>2</sub> and 1.75 g of AgNO<sub>3</sub>. 1.41 g of desired product, AgCl, was isolated. Calculate the percent yield of the reaction.

Balanced reaction equation:  $\text{BaCl}_{2(\text{aq})} + 2\text{AgNO}_{3(\text{aq})} = 2\text{AgCl}_{(\text{s})} + \text{Ba}(\text{NO}_3)_{2(\text{aq})}$ .

Given data:  $m(\text{BaCl}_2) = 1.56 \text{ g}$ ,  $M(\text{BaCl}_2) = 208.20 \text{ g/mol}$ ,  $m(\text{AgNO}_3) = 1.75 \text{ g}$ ,  $M(\text{AgNO}_3) = 169.90 \text{ g/mol}$ ,  $m(\text{AgCl}) = Y_{\text{actual}} = 1.41 \text{ g}$ ,  $M(\text{AgCl}) = 143.35 \text{ g/mol}$

Checking for limiting reactant.

$$n(\text{BaCl}_2) = 1.56 \text{ g} / 208.20 \text{ gmol}^{-1} = 0.0075 \text{ mol}$$

$$n(\text{AgNO}_3) = 1.75 \text{ g} / 169.90 \text{ g mol}^{-1} = 0.0103 \text{ mol}$$

Because molar ration between  $\text{BaCl}_2$  and  $\text{AgNO}_3$  is 1:2 (see reaction equation), so the limiting agent is  $\text{AgNO}_3$  and yield calculation must involve this reactant only.

Calculation of theoretical yield (theoretical mass of  $\text{AgCl}$ ):



$$Y_{\text{theoretical}} = [\text{M}(\text{AgCl}) \times m(\text{AgNO}_3)] / \text{M}(\text{AgNO}_3) = (143.35 \times 1.75 \text{ g}) / 169.90 = 1.48 \text{ g}$$

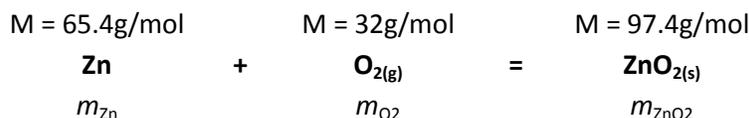
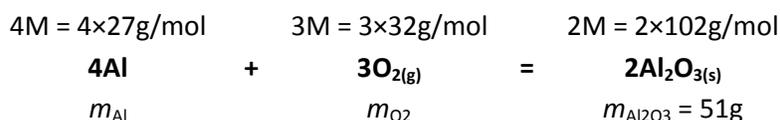
$$\text{The percent yield } Y = (Y_{\text{actual}}/Y_{\text{theoretical}}) \times 100\% = (1.41\text{g}/1.48\text{g}) \times 100\% = 95.3\%$$

#### 4.5 Reactions with chemical mixtures

##### Example 4.5

By oxidation of 100 g of aluminum and zinc alloy one obtains 51 g of  $\text{Al}_2\text{O}_3$  and some amount of  $\text{ZnO}$ . Calculate the composition (weight percent) of the alloy.

Balanced chemical reactions:



We obtain two algebraic equations with two variables:

$$4 \times 27\text{g/mol} \times 51\text{g} = 2 \times 102\text{g/mol} \times m_{Al} \text{ and } m_{Al} + m_{Zn} = 100\text{g}$$

Solving for  $m_{Al}$  and  $m_{Zn}$  one gets  $m_{Al} = 27\text{g}$  and  $m_{Zn} = 73\text{g}$

The composition of the alloy is 27 wt.% Al and 73 wt.% Zn.

##### Example 4.6

Now assume the same amount of alloy (100 g) which is completely oxidized with 62.9 g of oxygen. Calculate the composition of the alloy.

Again, we can write down two algebraic equations by making use of two chemical equations. The two variable are  $m_{Zn} = 100 - m_{Al}$  and  $m_2 = 62.9 - m_1$  ( $m_1$  and  $m_2$  are masses of  $\text{O}_2$  consumed by Al and Zn, respectively).

$$4 \times 27\text{g/mol} \times m_1 = 3 \times 32\text{g/mol} \times m_{Al} \text{ and } 65.4\text{g/mol} \times (62.9\text{g} - m_1) = 32\text{g/mol} \times (100\text{g} - m_{Al})$$

Solving for  $m_{Al}$  and  $m_1$  one gets:

$$m_{Al} = 35.0\text{g} \text{ and } m_1 = 31.1\text{g}$$

$$\text{and next } m_{Zn} = 100\text{g} - 35.0\text{g} = 65.0\text{g} \text{ and } m_2 = 62.9\text{g} - 31.1\text{g} = 31.8\text{g}$$

The composition of the alloy is 35 wt.% Al and 65 wt.% Zn.

## 5. Ideal gas laws

### 5.1 Standard and normal conditions

**Standard conditions** for gases are commonly used to define temperature and pressure which is important for the measurements of chemical and physical processes involving gas-phase substances. Standard temperature and pressure, is defined by IUPAC, are *temperature, 273.15 K (0 °C) and pressure of  $10^5$  Pa (pascals)*. IUPAC recommends that the former use of the pressure of 1 atm as standard pressure (equivalent to  $1.01325 \times 10^5$  Pa) should be discontinued. Normal temperature and pressure conditions are defined as 293.15 K (20 °C) and 1 atm (101325 Pa). Standard volume of 1 mole of an ideal gas at STP is 22.4 liters.

Pressure, one of the parameter of gas state, is defined as a force acting on an unitary area:

$$p = F/A \text{ [N/m}^2 \text{ = Pa].}$$

Below you can find variety of units characteristic of pressure and conversion conditions between them.

**Table 4** Pressure and units

Unit	Symbol	Conversions
pascal	Pa	1 Pa = 1 N/m <sup>2</sup>
psi	psi	lb/in <sup>2</sup>
atmosphere	atm	1 atm = 101325 Pa = 14.7 lb/in <sup>2</sup>
bar	bar	1 bar = 100000 Pa
torr	torr	760 torr = 1 atm
millimeters of mercury	mm Hg	1 mm Hg = 1 torr

Most behaviors of a pure gas-phase sample can be related to just four physical properties. Physical properties of a gas state can be categorized as being either *intensive or extensive quantities*, according to how the property changes when the size (or extent) of the system (gas sample) changes. According to IUPAC, *an intensive property is one whose magnitude is independent of the size of the system. An extensive property is one whose magnitude is additive for subsystems.*

**Table 5** Parameters of gas state

Property	Symbol	Unit	Type
pressure	$p$	Pa	intensive
volume	$V$	m <sup>3</sup>	extensive
temperature	$T$	K	intensive
moles	$n$	mol	extensive

### 5.2 Ideal gas law (Clapeyron's equation)

A molecular model of gases relies on few simple observations. Namely, gases are easy to expand which is a consequence of lack of strong attraction between gas molecules. Gases are easy to compress which means that gas molecules don't strongly repel each other. Gases have densities that are about 1/1000 of solid or liquid densities - molecules are much farther apart in gases than in liquids and solids. Gases

completely fill their containers because their molecules are in constant motion. And finally hot gases leak through holes faster than cold gases, which means that the hotter the gas, the faster the molecules are moving.

An **ideal gas** is defined as one in which all collisions between atoms or molecules are perfectly elastic and in which there are no intermolecular attractive forces. One can visualize it as a collection of perfectly hard spheres (without volume) which collide but which otherwise do not interact with each other. In such a gas, all the internal energy is in the form of kinetic energy and any change in internal energy is accompanied by a change in temperature. Obviously an ideal gas is only a mathematical concept, a model for real gases.

An ideal gas can be characterized by three state variables: absolute pressure ( $p$ ), volume ( $V$ ), and absolute temperature ( $T$ ). The relationship between them may be deduced from kinetic theory and is called the ideal gas law (Clapeyron's equation)

$$pV = nRT$$

where  $n$  = number of moles,  $R = 8.314 \text{ J}/(\text{mol}\times\text{K})$  is called universal gas constant which is related to other universal constants by the relationship  $R = kN_A$  ( $k = 1.38066\times 10^{-23} \text{ J}/\text{K}$  is called Boltzmann constant,  $N_A = 6.022\times 10^{23} \text{ mol}^{-1}$  is Avogadro's number).

*Notice: 1 Joule = 1 N×m = 1 (N/m<sup>2</sup>)×(m<sup>3</sup>) = 1 Pa×m<sup>3</sup>.*

Any equation that relates  $p$ ,  $V$ ,  $T$ , and  $n$  (state variables) for a sample is called an equation of state. The Clapeyron's equation is obeyed exactly only by an ideal gas. Whereas for real gases experiments show  $pV = nRT$  is an approximate equation.

Here are some useful hints how to apply the ideal gas law for:

- estimating a property from constant values of the other three properties (make a  $pVnT$  table, convert to units consistent with  $R$  (m<sup>3</sup>, K, mol, Pa), solve  $pV = nRT$  for the unknown property);
- finding how one property changes when some of the other three properties change (make a  $pVnT$  table with rows for initial (denoted as 1) and final (denoted as 2) conditions, convert inconsistent units (always use K, not °C), note that  $R = pV/nT = \text{constants}$ , eliminate constant values from  $p_1V_1/n_1T_1 = p_2V_2/n_2T_2$ , solve the resulting equation for the unknown property.

**Example 5.1 Molar volume ( $V_m$ ) is a volume of 1 mole of a pure substance at a given conditions.**

Molar volume is not constant and depends on the conditions (state parameters).

Calculate with ideal gas equation the volume of 1 mole of an ideal gas at 0°C and 1 atmosphere pressure.

First, we have to get the units right. 0°C is 273 K so  $T = 273 \text{ K}$ , 1 atm = 101325 Pa,  $p = 101325 \text{ Pa}$ .  $n = 1 \text{ mol}$ , and, finally,  $R = 8.314 \text{ J}/(\text{mol}\times\text{K})$ .

Slotting all of this into the ideal gas equation and then rearranging it gives:

$$V_m = nRT/p = (1 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 273 \text{ K}) / 101325 \text{ Pa} = 0.0224 \text{ m}^3 = 22.4 \text{ dm}^3.$$

The molar volume of an ideal gas is therefore  $V_m = 22.4 \text{ dm}^3$  (in fact at standard conditions,  $p = 10^5 \text{ Pa}$ , and consequently the molar volume is a bit bigger and equals 22.7 dm<sup>3</sup>).

### Example 5.2

What volume is needed to store 0.050 moles of helium gas at 202.6 kPa and 400 K?

$$p = 202.6 \text{ kPa} = 202600 \text{ Pa}, n = 0.050 \text{ mol}, T = 400 \text{ K}$$

$$V = nRT/p = (0.050 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 400 \text{ K}) / 202600 \text{ Pa} = 8.2 \times 10^{-4} \text{ m}^3 = 0.82 \text{ dm}^3.$$

### Example 5.3

To what temperature does a 250 mL cylinder containing 0.40 g helium gas need to be cooled in order for the pressure to be 253.25 kPa?

Given data:  $p = 253.25 \text{ kPa} = 253250 \text{ Pa}$ ,  $V = 250 \text{ mL} = 250 \text{ cm}^3 = 2.50 \times 10^{-4} \text{ m}^3$ ,  $n = 0.40 \text{ g} / 4.00 \text{ g mol}^{-1} = 0.10 \text{ mol}$  ( $M_{\text{He}} = 4.00 \text{ g mol}^{-1}$ ).

$$T = pV/nR = (253250 \text{ Pa} \times 2.50 \times 10^{-4} \text{ m}^3) / (0.10 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1}) = 76.15 \text{ K}$$

### Example 5.4

At standard conditions, a 5.00 dm<sup>3</sup> flask filled with air has a mass of 543.251 g. The air in the flask is replaced with another gas and the mass of the flask is 565.687 g. The density of air is 1.29 g/dm<sup>3</sup>. What is the gas that replaced the air?

Mass of air in flask is  $m_{\text{air}} = 1.29 \text{ g/dm}^3 \times 5.00 \text{ dm}^3 = 6.45 \text{ g}$ . So mass of empty flask is  $543.251 \text{ g} - 6.45 \text{ g} = 536.801 \text{ g}$ .

Mass of unknown gas is  $m_x = 565.687 \text{ g} - 536.801 \text{ g} = 28.886 \text{ g}$

Number of moles of the unknown gas can be calculated by using ideal gas equation  $pV = nRT$

$$p = 10^5 \text{ Pa}, T = 273 \text{ K}$$

$$n = pV/RT = (10^5 \text{ Pa} \times 0.005 \text{ m}^3) / (8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 273 \text{ K}) = 0.220 \text{ mol}$$

Now the molar mass of unknown gas can be calculated:

$M_x = m_x/n = 28.886 \text{ g} / 0.220 \text{ mol} = 131.3 \text{ g/mol}$ . Based on the data in periodic table the unknown gas could be xenon.

## 5.3 Density of gas phase

The ideal gas law allows for finding the relative formula for molar mass of a gas from its density. The assumption is that the real gas behaves as an ideal gas which is a bit tricky. The inherent inconsistency can be accepted from the point of view of general chemistry calculus but it must be realized that this type of calculation is only approximate.

Let us consider a sample of ethane (C<sub>2</sub>H<sub>6</sub>), organic gas, enclosed in a flask. The density of ethane is 1.264 g/dm<sup>3</sup> at 20 °C. The pressure indicated by a manometer mounted on top of the flask is 1 atmosphere. Calculate the molar mass of ethane.

Starting from ideal gas equation  $pV = nRT$ , we define number of moles  $n = m/M$  and recollect definition of density  $d = m/V$ . Slotting all of this into the ideal gas equation:

$$pV = nRT = (m/M)RT$$

$$pVM = mRT$$

$$pM = (m/V)RT$$

$$pM = dRT.$$

Again, before we do calculation, one must get the awkward units sorted out. The volume of 1 dm<sup>3</sup> has to be converted to cubic meters, by dividing by 1000. We have a volume of 0.001 m<sup>3</sup>. Thus, the density value  $d = 1.264 \text{ g/dm}^3 = 1264 \text{ g/m}^3$ . A pressure of 1 atmosphere is 101325 Pa. The temperature is 293 K.

$$M = dRT/p = 1264 \text{ g/m}^3 \times 8.314 \text{ J/(mol K)} \times 293 \text{ K} / 101325 \text{ Pa} = 30.4 \text{ g/mol}$$

The obtained value of molecular weight compares well with the one obtained from periodic table data ( $M = 2 \times 12 \text{ g/mol} + 6 \times 1 \text{ g/mol} = 30 \text{ g/mol}$ ).

#### Example 5.5

An air sample containing only nitrogen and oxygen gases has a density of 1.3393 g/dm<sup>3</sup> at 1 atmosphere pressure and 0 °C. Find the weight and mole percentages of nitrogen and oxygen in the sample.

From the density  $d$  of air we can evaluate an average molar mass,  $pM = dRT$ .

Given data:  $d = 1.3393 \text{ g/dm}^3 = 1339.3 \text{ g/m}^3$ ,  $T = 273 \text{ K}$ ,  $p = 1 \text{ atm} = 101325 \text{ Pa}$

$$M = dRT/p = (1339.3 \text{ g/m}^3 \times 8.314 \text{ J/molK} \times 273 \text{ K}) / 101325 \text{ Pa} = 30.0 \text{ g/mol}$$

Assume that we have 1.0 mol of gas, and  $x$  mol of which is nitrogen ( $M = 28 \text{ g/mol}$ ), then  $(1 - x)$  is the amount of oxygen ( $M = 32 \text{ g/mol}$ ). The average molar mass is the mole weighted average, and thus,

$$28.0x + 32.0(1 - x) = 30.0$$

$$x = 0.50 \text{ mol of N}_2, \text{ and } 1.0 - 0.50 = 0.50 \text{ mol O}_2$$

Now, to find the weight percentage, find the amounts of N<sub>2</sub> and O<sub>2</sub> in 1.0 mol (30.0 g) of the mixture.

$$m_{\text{N}_2} = 0.5 \text{ mol} \times 28.0 \text{ g/mol} = 14.0 \text{ g}$$

$$m_{\text{O}_2} = 0.5 \text{ mol} \times 32.0 \text{ g/mol} = 16.0 \text{ g}$$

Percentage of nitrogen equals  $(14.0 \text{ g} / 30.0 \text{ g}) \times 100\% = 46.7\%$  and percentage of oxygen equals  $(16.0 \text{ g} / 30.0 \text{ g}) \times 100\% = 53.3\%$

Alternatively one can find the density of pure nitrogen and oxygen first and evaluate the fraction from the density as shown below.

At given conditions molar volume equals 22.4 dm<sup>3</sup>, so

$$d(\text{N}_2) = M/V_m = (28.0 \text{ g/mol}) / (22.4 \text{ dm}^3) = 1.25 \text{ g/dm}^3$$

$$d(\text{O}_2) = (32.0 \text{ g/mol}) / (22.4 \text{ dm}^3) = 1.4286 \text{ g/dm}^3$$

Now density of air is the mole weighted average of individual densities of nitrogen and oxygen:

$$d = 1.3393 \text{ g/dm}^3 = x 1.25 \text{ g/dm}^3 + (1 - x) 1.4286 \text{ g/dm}^3$$

Solving for  $x$  gives  $x = 0.50$  (same result as above).

#### Example 5.6 Pressure of a gas mixture

Find the volume when 7.00 g of O<sub>2</sub> and 1.50 g of Cl<sub>2</sub> are mixed in a container with a pressure of 482 atm and at a temperature of 22 °C.

Note that if we assume that both gases (O<sub>2</sub> and Cl<sub>2</sub>) obey ideal gas law, so it is enough to calculate total moles of gas phase and apply Clapeyron's equation  $pV = n_{\text{total}}RT$ .

Given data:  $p = 482 \text{ atm} = 482 \times 101325 \text{ Pa} = 48838650 \text{ Pa}$ ,  $T = (22+273)\text{K} = 295\text{K}$ ,  $m_{\text{Cl}_2} = 1.50 \text{ g}$ ,  $m_{\text{O}_2} = 7.00 \text{ g}$ .

The total moles of the mixed gases are

$$n_{\text{total}} = n_{\text{O}_2} + n_{\text{Cl}_2} = (7.0 \text{ g} / 32.0 \text{ g mol}^{-1}) + (1.5 \text{ g} / 71.0 \text{ g mol}^{-1}) = 0.22 \text{ mol} + 0.02 \text{ mol} = 0.24 \text{ mol}$$

Plug in all data in the ideal gas equation.

$$V = n_{\text{total}}RT/p = (0.24 \text{ mol} \times 8.314 \text{ J/(mol K)} \times 295 \text{ K}) / 48838650 \text{ Pa} = 1.21 \times 10^{-5} \text{ m}^3 = 0.0121 \text{ dm}^3 = 12.1 \text{ cm}^3$$

### 5.4 Isothermal, isobaric and isochoric transformation of gases

There's another useful way to write the ideal gas law. If the number of moles  $n$  of the gas doesn't change, then the quantity  $nR$  is constant for a gas. This happens frequently since the gas under consideration is often in a sealed container. So, after rearranging the ideal gas law we get,

$$nR = pV/T = \text{constant}$$

This shows that, as long as the number of moles (i.e. molecules) of a gas remains the same, the quantity  $pV/T$  is constant for a gas regardless of the process through which the gas is taken. In other words, if a gas starts in the initial state  $i$  (with some value of pressure  $p_i$ ,  $V_i$ ,  $T_i$ ) and is altered to the final state  $f$  (with  $p_f$ ,  $V_f$  and temperature  $T_f$ ), then regardless of the details of the process we know the following relationship holds.

$$p_i V_i / T_i = p_f V_f / T_f$$

This formula is particularly useful when describing an ideal gas that changes from one state to another. Since this formula does not use any gas constants, we can use whichever units we want, but we must be consistent between the two sides (e.g. if we use  $\text{cm}^3$  for  $V_i$ , we'll have to use  $\text{cm}^3$  for  $V_f$ ).

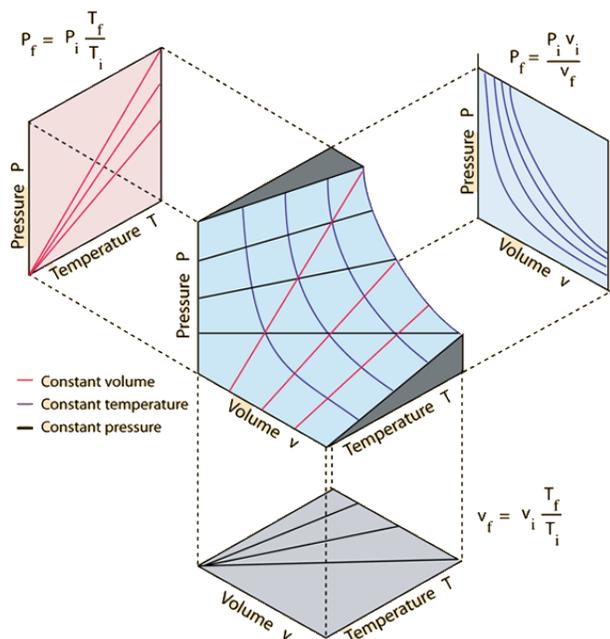
In addition, in frequent cases of transformation of a gas sample from one state to the other, selected state parameter holds constant. If this parameter is temperature,  $T = \text{const.}$ , then this transformation is called *isothermal*. For  $p = \text{const.}$ , we deal with *isobaric* transformation, while for  $V = \text{const.}$ , the process is called *isochoric*. For those particular cases the above relationship becomes even simpler:

$$p_i V_i = p_f V_f \text{ (so called Boyle's law), } T = \text{const.}$$

$$V_i / T_i = V_f / T_f \text{ (so called Charles's law), } p = \text{const.}$$

$$p_i / T_i = p_f / T_f \text{ (so called Gay-Lussac's law), } V = \text{const.}$$

as depicted below in figure.



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### Example 5.7

If the initial volume was 500 mL at a pressure of 760 torr, when the volume is compressed to 450 mL, what is the pressure?

We assume that gas compression was carried out at constant temperature, and thus  $p_1V_1 = p_2V_2$

$$(760 \text{ torr}) \times (500 \text{ mL}) = p_2 \times (450 \text{ mL})$$

$$p_2 = 760 \text{ torr} \times 500 \text{ mL} / 450 \text{ mL} = 844 \text{ torr}$$

## 5.5 Partial pressure

Dalton's law of pressures states that the *total pressure* ( $p_{total}$ ) of a mixture of nonreacting gases is the sum of their individual partial pressures ( $p_i$ ).

$$p_{total} = \sum_i p_i$$

or

$$p_{total} = \sum_i \frac{n_i RT}{V} = \frac{RT}{V} \sum_i n_i$$

So partial pressure is a pressure exerted by one gaseous component in a mixture. Note that the pressure in a flask containing a mixture of 0.20 mole O<sub>2</sub> and 0.80 mole N<sub>2</sub> would be the same as in the same flask holding 1 mole of O<sub>2</sub> alone.

It results from the above formula that there is a simple relationship between partial pressure and molar fraction of any component of gas mixture:

$$p_i = x_i p_{total}$$

Partial pressures are useful when gases are collected by bubbling through water. The gas collected is saturated in water vapor which contributes to the total number of moles of gas in the container.

### Example 5.8

A sample of H<sub>2</sub> was prepared in the laboratory by the reaction  $\text{Mg}_{(s)} + 2\text{HCl}_{(aq)} = \text{MgCl}_{2(aq)} + \text{H}_{2(g)}$ . 456 mL of gas was collected at 22.0 °C. The total pressure in the flask was 742 torr. How many moles of H<sub>2</sub> were collected if the vapor pressure of H<sub>2</sub>O at 22.0 °C is 19.8 torr?

$$p_{total} = p_{\text{H}_2} + p_{\text{H}_2\text{O}}$$

$$p_{\text{H}_2} = 742 \text{ torr} - 19.8 \text{ torr} = 722.2 \text{ torr}$$

Pressure must be converted to metric-based unit (see Table 1),  $p_{\text{H}_2} = 722.2/760 \text{ atm} = 0.9503 \text{ atm} = 101325 \times 0.9503 \text{ Pa} = 96289.1 \text{ Pa}$

$$n_{\text{H}_2} = pV/RT = (96289.1 \text{ Pa} \times 456 \times 10^{-6} \text{ m}^3) / (8.314 \text{ J}/(\text{mol K}) \times 295 \text{ K}) = 0.0179 \text{ mol}$$

### Example 5.9

A 3.00 L container is filled with Ne at 1.50 atm at 27 °C. A 0.748 g sample of CO<sub>2</sub> vapor is then added. What is the partial pressure of CO<sub>2</sub> and Ne? What is the total pressure in the container?

Given data:  $p = 1.50 \text{ atm} = 151987.5 \text{ Pa}$ ,  $V = 3.00 \text{ L} = 3.00 \text{ dm}^3 = 0.003 \text{ m}^3$ ,  $T = (27 + 273)\text{K} = 300 \text{ K}$

$$n_{\text{Ne}} = pV/RT = (151987.5 \text{ Pa} \times 0.003 \text{ m}^3) / (8.314 \text{ J}/(\text{mol K}) \times 300 \text{ K}) = 0.183 \text{ mol}$$

$$n_{\text{CO}_2} = 0.748 \text{ g} / 44 \text{ gmol}^{-1} = 0.017 \text{ mol}$$

Because the pressure of the container before the CO<sub>2</sub> was added contained only Ne, that is in fact partial pressure of Ne,  $p_{\text{Ne}} = 1.50 \text{ atm} = 151987.5 \text{ Pa}$ .

To find other pressures we make use of molar fractions:

$$n_{\text{total}} = n_{\text{Ne}} + n_{\text{CO}_2} = 0.183 \text{ mol} + 0.017 \text{ mol} = 0.200 \text{ mol}$$

$$x_{\text{Ne}} = n_{\text{Ne}}/n_{\text{total}} = 0.183 / 0.200 = 0.915$$

$$x_{\text{CO}_2} = 1 - 0.915 = 0.085$$

Since  $p_{\text{Ne}} = x_{\text{Ne}}p_{\text{total}}$  we get total pressure  $p_{\text{total}} = p_{\text{Ne}}/x_{\text{Ne}} = 1.5 \text{ atm} / 0.915 = 1.64 \text{ atm}$

Partial pressure of CO<sub>2</sub> is  $p_{\text{CO}_2} = p_{\text{total}} - p_{\text{Ne}} = 1.64 \text{ atm} - 1.50 \text{ atm} = 0.14 \text{ atm}$

### Example 5.10

Air is approximately 79% N<sub>2</sub> and 21% O<sub>2</sub> by mass. What is the mole fraction and pressure of O<sub>2</sub> in air?

Mass percent composition of air is equivalent to say that a sample of air (100 g) is composed of 79 g N<sub>2</sub> and 21 g O<sub>2</sub>. That allows for calculation of moles:

$$n_{\text{N}_2} = 79 \text{ g} / 28 \text{ gmol}^{-1} = 2.82 \text{ mol} \text{ and } n_{\text{O}_2} = 21 \text{ g} / 32 \text{ gmol}^{-1} = 0.66 \text{ mol}$$

Resulting molar fractions are equal to:

$$x_{\text{N}_2} = 2.82/(2.82 + 0.66) = 0.81 \text{ and } x_{\text{O}_2} = 0.66/(2.82 + 0.66) = 0.19$$

Because these calculations are related to air we may assume the normal pressure of air equal 1 atm. The pressure of O<sub>2</sub> in air is

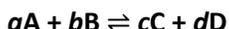
$$p_{\text{O}_2} = p_{\text{air}}x_{\text{O}_2} = 1 \text{ atm} \times 0.19 = 0.19 \text{ atm}$$

## 6. Chemical equilibrium

### 6.1 Equilibrium constant

**Chemical equilibrium** is a dynamic process consisting of forward and reverse reactions that proceed at equal rates. At equilibrium, the composition of the system no longer changes with time. The composition of an equilibrium mixture is independent of the direction from which equilibrium is approached.

For any reversible reaction of the general form



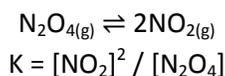
where A and B are reactants, C and D are products, and  $a$ ,  $b$ ,  $c$ , and  $d$  are the stoichiometric coefficients in the balanced chemical equation for the reaction, *the ratio of the product of the equilibrium concentrations of the products (raised to their coefficients in the balanced chemical equation) to the product of the equilibrium concentrations of the reactants (raised to their coefficients in the balanced chemical equation) is always a constant under a given set of conditions*. These conditions are constant temperature and pressure. This relationship is known as **the law of mass action** and can be stated as follows:

$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

where K is the equilibrium constant for the reaction. Note that K is unitless quantity as all the concentrations appearing the formula above are divided by unitary molar concentration:  $[X] = c_x/c^\circ$ , where  $c^\circ = 1 \text{ mol/dm}^3$ .

Example 6.1 Decomposition of  $\text{N}_2\text{O}_{4(g)}$  into  $\text{NO}_{2(g)}$

The reaction of decomposition of  $\text{N}_2\text{O}_{4(g)}$  reached an equilibrium state after some time at 25 °C. Check that equilibrium constant does not depend on the composition of gas mixture.



Initial concentrations		Equilibrium concentrations		$K = [\text{NO}_2]_{\text{eq}}^2 / [\text{N}_2\text{O}_4]_{\text{eq}}$
$[\text{N}_2\text{O}_4]_0 / \text{M}$	$[\text{NO}_2]_0 / \text{M}$	$[\text{N}_2\text{O}_4]_{\text{eq}} / \text{M}$	$[\text{NO}_2]_{\text{eq}} / \text{M}$	
0.0500	0.0000	0.0417	0.0163	$6.54 \times 10^{-3}$
0.0000	0.1000	0.0417	0.0163	$6.54 \times 10^{-3}$
0.0750	0.0000	0.0647	0.0206	$6.56 \times 10^{-3}$
0.0250	0.0750	0.0532	0.0186	$6.50 \times 10^{-3}$

Example 6.2

A 1.00 mol sample of NOCl was placed in a 2.00 dm<sup>3</sup> reactor and heated to 227 °C until the system reached equilibrium. The contents of the reactor were then analyzed and found to contain 0.056 mol of Cl<sub>2</sub>. Calculate K at this temperature. The equation for the decomposition of NOCl to NO and Cl<sub>2</sub> is as follows:  $2\text{NOCl}_{(g)} \rightleftharpoons 2\text{NO}_{(g)} + \text{Cl}_{2(g)}$ .

At initial stage, concentration of NOCl was  $[\text{NOCl}]_0 = 1.00 \text{ mol} / 2.00 \text{ dm}^3 = 0.500\text{M}$  and initial concentration of NO and Cl<sub>2</sub> were  $[\text{NO}]_0 = [\text{Cl}_2]_0 = 0$ .

At equilibrium,  $[\text{Cl}_2]_{\text{eq}} = 0.056 \text{ mol} / 2.00 \text{ dm}^3 = 0.028\text{M}$  (which is a change in concentration of chlorine). Reaction stoichiometry gives additional constraints on particular concentrations.

And so according to the coefficients in the balanced chemical equation, 2 mol of NO are produced for every 1 mol of Cl<sub>2</sub>, so the change in the NO concentration is twice of that of Cl<sub>2</sub>,  $[\text{NO}]_{\text{eq}} = 2[\text{Cl}_2]_{\text{eq}} = 0.056\text{M}$ .

Similarly, 2 mol of NOCl are consumed for every 1 mol of Cl<sub>2</sub> produced, so the change in the NOCl concentration is  $2[\text{Cl}_2]_{\text{eq}} = 0.056\text{M}$ . Because initial concentration  $[\text{NOCl}]_0 = 0.500\text{M}$  so at equilibrium  $[\text{NOCl}]_{\text{eq}} = 0.500\text{M} - 0.056\text{M} = 0.444\text{M}$ .

$$K = \frac{[\text{NO}]^2 [\text{Cl}_2]}{[\text{NOCl}]^2} = \frac{0.056 \times (0.028)^2}{(0.444)^2} = 4.5 \times 10^{-4}$$

## 7. Acid-base equilibria in aqueous solution

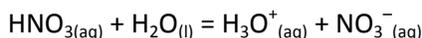
### 7.1 Electrolytic dissociation of weak acids and bases

According to Arrhenius definition *acid is any neutral species that can increase the concentration of H<sup>+</sup> in aqueous solution and an Arrhenius base is any neutral species that can increase the concentration of OH<sup>-</sup> in aqueous solution*. A major limitation of Arrhenius theory is that we can only describe acid-base behavior in water. A step forward toward more general theory, which applies to a broader range of chemical reactions, is definition of Brønsted and Lowry.

The Brønsted-Lowry theory describes acid-base interactions in terms of proton transfer between chemical species. **A Brønsted-Lowry acid is any species that can donate a proton, H<sup>+</sup>, and a base is any**

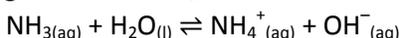
**species that can accept a proton.** In terms of chemical structure, this means that any Brønsted-Lowry acid must contain a hydrogen that can dissociate as  $H^+$ . In order to accept a proton, a Brønsted-Lowry base must have at least one lone pair of electrons to form a new bond with a proton.

In the reaction between nitric acid and water, nitric acid,  $HNO_3$ , donates a proton to water, thereby acting as a Brønsted acid:



Subscript (aq) denotes aqueous solution, (l) liquid phase.  $H_3O^+$  is called hydronium cation produced by the protonation of water. So water acts as a Brønsted-Lowry base, and  $HNO_3$  is a Brønsted-Lowry acid.

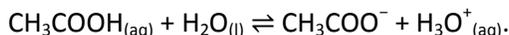
Let's now look at a reaction involving ammonia,  $NH_3$ , in water:



In this reaction, water is donating one of its protons to ammonia. After losing a proton, water becomes hydroxide anion,  $OH^-$ . Since water is a proton donor in this reaction, it is acting as a Brønsted-Lowry acid. Ammonia accepts a proton from water to form an ammonium cation,  $NH_4^+$ . Therefore, ammonia is acting as a Brønsted-Lowry base.

In the two previous reactions, we see water behaving both as a Brønsted-Lowry base—in the reaction with nitric acid—and as a Brønsted-Lowry acid—in the reaction with ammonia. Because of its ability to both accept and donate protons, water is known as an amphoteric or amphiprotic substance, meaning that it can act as either a Brønsted-Lowry acid or a Brønsted-Lowry base.

*A strong acid is a species that dissociates completely into its constituent ions in aqueous solution.* Nitric acid is an example of a strong acid. It dissociates completely in water to form hydronium  $H_3O^+$  and nitrate  $NO_3^-$  ions. After the reaction occurs, there are no undissociated  $HNO_3$  molecules in solution. By contrast, *a weak acid does not dissociate completely into its constituent ions.* An example of a weak acid is acetic acid,  $CH_3COOH$ . Acetic acid dissociates partially in water to form hydronium and acetate ions,  $CH_3COO^-$ :

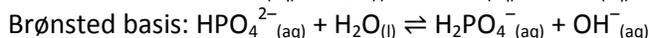
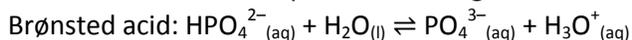


Notice that in this reaction, we have arrows pointing in both directions:  $\rightleftharpoons$ . This indicates that dissociation of acetic acid is a dynamic equilibrium where there will be a significant concentration of acetic acid molecules that are present as neutral  $CH_3COOH$  molecules as well as in the form of the dissociated ions,  $H^+$  and  $CH_3COO^-$ .

Similar distinction between strong and weak electrolytes holds for bases. A strong base is a base that ionizes completely in aqueous solution. An example of a strong base is sodium hydroxide,  $NaOH$ . In water, sodium hydroxide dissociates completely to give sodium cations and hydroxide ions. On the contrary, some of the ammonia molecules accept a proton from water to form ammonium ions and hydroxide ions. A dynamic equilibrium results, in which ammonia molecules are continually exchanging protons with water, and ammonium ions are continually donating the protons back to hydroxide. The major species in solution is non-ionized ammonia,  $NH_3$ , because ammonia will only deprotonate water to a small extent being weak basis.

Example 7.1 Reactions of hydrogen phosphate(V) anion.

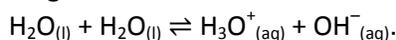
Write down chemical equilibria showing that  $\text{HPO}_4^{2-}$  anion can act as Brønsted acid or basis.



Which of the above equilibria dictates pH of the solution depends on the equilibrium constants of both reactions.

## 7.2 Auto-ionisation of water and pH scale

Water is one of the most common solvents for acid-base reactions. As pointed out above, water is also amphoteric, capable of acting as either a Brønsted-Lowry acid or base. Water molecules exchange protons with one another to a very small extent. This process is called the *autoionization*, or self-ionization, of water. The proton exchange can be written as the following balanced equation



For any sample of pure water, the molar concentrations of hydronium,  $\text{H}_3\text{O}^+$  and hydroxide,  $\text{OH}^-$ , must be equal  $[\text{H}_3\text{O}^+] = [\text{OH}^-]$ . Note that autoionization is readily reversible. Because water is a weak acid and a weak base, the hydronium and hydroxide ions exist in very, very small concentrations relative to that of non-ionized water. These concentration can be obtained from examining the equilibrium constant for this reaction (also called the autoionization constant), which has the special symbol  $K_w$ .

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

Note that when writing equilibrium expressions, the concentrations of water is not included, because undissociated molecules are in great majority and the concentration of water is practically constant. For pure water at 25 °C  $K_w$  value equals  $10^{-14}$ . Therefore, we can calculate the concentration of hydronium ions in pure water:

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] \text{ and } K_w = [\text{H}_3\text{O}^+]^2 \text{ it results in } [\text{H}_3\text{O}^+] = 10^{-7} \text{ and } [\text{OH}^-] = 10^{-7} \text{ at } 25 \text{ }^\circ\text{C}.$$

By taking the negative logarithm of both sides of  $K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$ , we get the following:

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

and by introducing the **pH scale defined as  $-\log[\text{H}_3\text{O}^+] = \text{pH}$  (in a similar way  $-\log[\text{OH}^-] = \text{pOH}$ )** we get:

$$14 = \text{pH} + \text{pOH}$$

Therefore, the sum of pH and pOH will always be 14 for any aqueous solution at 25 °C. Keep in mind that this relationship will not hold true at other temperatures, because  $K_w$  is temperature dependent.

The **pH scale** is a negative logarithmic scale. The logarithmic part means that pH changes by 1 unit for every factor of 10 change in concentration of  $\text{H}^+$ . The negative sign in front of the log tells us that there is an inverse relationship between pH and  $[\text{H}^+]$ : when pH increases,  $[\text{H}^+]$  decreases, and vice versa. At 25 °C, for a neutral solution,  $\text{pH} = 7$ , acidic solutions have  $\text{pH} < 7$ , while basic solutions have  $\text{pH} > 7$ .

Example 7.2

If the  $\text{p}K_w$  of a sample of pure water at 0 °C 14.9, what is the pH of pure water at this temperature?

$$\text{p}K_w = 14.9 \text{ so } K_w = 10^{-14.9} = [\text{H}_3\text{O}^+]^2$$

$$[\text{H}_3\text{O}^+] = 10^{-7.45} \text{ and } \text{pH} = 7.45$$

### Example 7.3

100 cm<sup>3</sup> of a sodium hydroxide solution with a pH of 10 was diluted by adding water to get a total volume of 1.0 dm<sup>3</sup>. What is the pH of the diluted solution?

Using the relationship  $\text{pOH} = 14 - \text{pH} = 14 - 10 = 4$ ,

concentration of hydroxides is calculated as:  $-\log[\text{OH}^-] = 4$ ,  $[\text{OH}^-] = 10^{-4}$ .

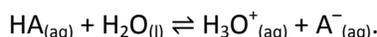
Moles of OH<sup>-</sup> are  $n_{\text{OH}^-} = [\text{OH}^-]V_0 = 10^{-4} \text{ mol/dm}^3 \times 0.1 \text{ dm}^3 = 10^{-5} \text{ mol}$

And after dilution  $[\text{OH}^-] = n_{\text{OH}^-}/V_1 = 10^{-5} \text{ mol} / 1 \text{ dm}^3 = 10^{-5}$

$\text{pOH} = -\log(10^{-5}) = 5$ .

### 7.3 Dissociation degree and dissociation constants

The strength of a weak acid depends on how much it dissociates: the more it dissociates, the stronger the acid. In order to quantify the relative strengths of weak acids, the **acid dissociation constant**  $K_a$ , the equilibrium constant for the acid dissociation reaction, is used. For a generic monoprotic weak acid HA, the dissociation reaction in water can be written as follows:



Based on this reaction, we can write expression for equilibrium constant  $K_a$  at a constant temperature

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

where  $[\text{H}_3\text{O}^+]$  and  $[\text{A}^-]$  are molar (unitless) concentrations of dissociated species at state, and  $[\text{HA}]$  is equilibrium concentration of undissociated species. The equilibrium expression is a ratio of products to reactants. The more HA dissociates into H<sup>+</sup> and the conjugate base A<sup>-</sup>, the stronger the acid, and the larger the value of  $K_a$ . Since pH is related to  $[\text{H}_3\text{O}^+]$  the pH of the solution will be a function of  $K_a$  as well as the concentration of the acid: the pH decreases as the concentration of the acid and/or  $K_a$  increase. Alternatively,  $K_a$  values can also be tabulated as a logarithmic products  $\text{p}K_a = -\log K_a$ .

**Table 6** Acid and basis dissociation constants for selected weak electrolytes

name	formula	$K_a$ at 25 °C	$\text{p}K_a$
Acetic acid	CH <sub>3</sub> COOH	$1.8 \times 10^{-5}$	4.74
Formic acid	HCOOH	$1.8 \times 10^{-4}$	3.74
Phosphoric(V) acid	H <sub>3</sub> PO <sub>4</sub>	0.007	2.15
	H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	$6.3 \times 10^{-8}$	7.20
	HPO <sub>4</sub> <sup>2-</sup>	$4.5 \times 10^{-13}$	12.35
		$K_b$ at 25 °C	$\text{p}K_b$
Ammonia	NH <sub>3</sub>	$1.8 \times 10^{-5}$	4.74
Ethylamine	C <sub>2</sub> H <sub>5</sub> NH <sub>2</sub>	$5.6 \times 10^{-4}$	3.25
Aniline	C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	$3.8 \times 10^{-10}$	9.42

Other way to quantify how much a weak acid has dissociated in solution is to calculate the dissociation degree (percent dissociation). The **dissociation degree**  $\alpha$  is defined as

$$\alpha = \frac{[\text{dissociated species}]}{[\text{all species}]}$$

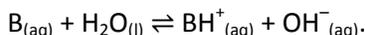
and for weak acid HA can be calculated as  $\alpha = [\text{H}_3\text{O}^+]/c_0 = [\text{H}_3\text{O}^+]/[\text{HA} + \text{H}_3\text{O}^+]$ , where  $c_0$  is analytical molar concentration of HA acid.

The equilibrium concentrations for a solution of weak acid HA are  $[H_3O^+] = \alpha c_0 = [A^-]$ , and  $[HA] = c_0 - \alpha c_0$ . Substituting the bracket concentrations into the  $K_a$  formula one gets:

$$K_a = \frac{\alpha^2 c_0}{1 - \alpha},$$

the formula showing a relationship between  $\alpha$  and  $K_a$ . It is now clear that  $\alpha$  must depend on  $c_0$  (dissociation degree must increase with dilution to keep  $K_a$  constant).

The **base dissociation constant** (also called the base ionization constant)  $K_b$  is defined in a similar way to  $K_a$ . The electrolytic dissociation reaction for a generic weak base B in water is:



In this reaction, the base accepts a proton from water to form hydroxide and the conjugate acid,  $BH^+$ . The expression for equilibrium constant  $K_b$  is as follows:

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

Obviously similar definition of dissociation degree and relationship between  $K_b$  and  $\alpha$  as for weak acids are valid for weak bases.

#### Example 7.4 Calculation of pH of strong and weak bases

Calculate pH values for two solutions: 0.1M NaOH and 0.1M  $NH_3$ .

NaOH is a strong electrolyte and  $[NaOH] = [OH^-]$ . This is not true for  $NH_{3(aq)}$ .

NaOH		$NH_{3(aq)}$	
$[NaOH] = [OH^-]$	$c_0 = [NaOH] = 0.1$	$c_0 \neq [NH_3] \neq [OH^-]$	$c_0 = 0.1$
		$K_b = [OH^-]^2 / (c_0 - [OH^-])$	$K_b = 1.8 \times 10^{-5}$
$[OH^-] = 0.1$		$[OH^-] = 0.0013$	
$pOH = -\log(0.1) = 1$		$pOH = -\log(0.0013) = 2.9$	
$pH = 14 - pOH = 13$		$pH = 14 - pOH = 11.1$	

Note that solving equation  $K_b = [OH^-]^2 / (c_0 - [OH^-])$  involves quadratic equation. However, in some cases you may simplify the problem. If a value of  $c_0/K_b$  is bigger than approximately 400 ( $c_0/K_b > 400$ ), you can safely assume that  $c_0 \gg [OH^-]$ , and you get  $K_b = [OH^-]^2 / c_0$  which gives  $[OH^-] = \sqrt{c_0 K_b}$ . Similar assumption you can make for  $\alpha$  which is small enough with respect to 1 ( $\alpha \ll 1$ ) and  $K_b = \alpha^2 c_0$ .

### 7.4 Buffer solutions

**Buffers** are solutions that maintain a relatively constant pH when small amounts of strong acid or base is added. They therefore protect, or "buffer," other molecules in solution from the effects of the added acid or base. Buffers contain either a weak acid (HA) and its conjugate base ( $A^-$ ) (salt of this weak acid) or a weak base (B) and its conjugate acid ( $BH^+$ ) (salt of this weak base), and they are critically important for the proper functioning of biological systems. In fact, every biological fluid is buffered to maintain its physiological pH.

The pH of a buffer can be calculated from the concentrations of the weak acid and the weak base used to prepare it, the concentration of the conjugate base and conjugate acid, and the  $pK_a$  or  $pK_b$  of the weak acid or weak base. The following formulas are used for calculations pH value of an acidic buffer:

$$pH = pK_a + \log \frac{c_{salt}}{c_{acid}},$$

and a basic buffer:

$$pH = 14 - pK_b + \log \frac{c_{base}}{c_{salt}}.$$

Note that  $c_{acid}$ ,  $c_{salt}$  and  $c_{base}$  are molar concentration calculated for the total volume of buffer (not analytical concentrations designated on the laboratory flask labels). Because moles are proportional to molar concentrations, and volume is common for salt-acid (base-salt) pairs the following equations can be rewritten by substituting  $c$  with  $n$  (moles):

$$pH = pK_a + \log \frac{n_{salt}}{n_{acid}} \text{ and } pH = 14 - pK_b + \log \frac{n_{base}}{n_{salt}}$$

#### Example 7.5

Calculate pH of the solution obtained by mixing of  $50 \text{ cm}^3$   $0.10\text{M}$   $\text{NH}_3$  with  $150 \text{ cm}^3$   $0.60\text{M}$   $\text{NH}_4\text{Cl}$ .

Calculate moles of the buffer components:

$$\text{Base: } n_{base} = 0.1 \text{ mol/dm}^3 \times 0.05 \text{ dm}^3 = 0.005 \text{ mol}$$

$$\text{Salt: } n_{salt} = 0.60 \text{ mol/dm}^3 \times 0.15 \text{ dm}^3 = 0.09 \text{ mol}$$

$$V = 50 \text{ cm}^3 + 150 \text{ cm}^3 = 200 \text{ cm}^3 = 0.2 \text{ dm}^3 \text{ and } c_{base} = n_{base}/V, c_{salt} = n_{salt}/V$$

$$pK_b = 4.74$$

$$pH = 14 - 4.74 + \log(0.005/0.09) = 8.00$$

(compare strong change in pH with respect to the solution of ammonia, Example 7.4)

### 7.5 Poorly soluble electrolytes – solubility product

Solubilities are most fundamentally expressed in molar (mol per  $\text{dm}^3$  of solution) units. But for practical use in preparing stock solutions, chemistry handbooks usually express solubilities in terms of grams-per- $100 \text{ cm}^3$  of water at a given temperature. When quantitative data are lacking, the designations “soluble”, “insoluble”, “slightly soluble”, and “highly soluble” are used. There is no agreed-on standard for these classifications. However, *some salts and similar compounds (such as some metal hydroxides) dissociate completely when they dissolve, but the extent to which they dissolve is so limited that the resulting solutions exhibit only very weak ionic conductivities. In these salts, which otherwise act as strong electrolytes, we can treat the dissolution-dissociation process as a true equilibrium.* Using silver(I) chromate(VI) as an example, its dissolution process in water can be quantified.



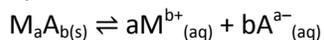
When this process reaches equilibrium (which requires that some solid be present), we can write the equilibrium constant:

$$K = \frac{[\text{Ag}^+]^2 [\text{CrO}_4^{2-}]}{[\text{Ag}_2\text{CrO}_4]}.$$

But because concentration of solid substance in its separate phase is constant, this concentration do not appear in equilibrium expressions, the equilibrium constant for this process is

$$K_s = [Ag^+]^2 [CrO_4^{2-}]$$

and it is known as a **solubility product**. For this particular case  $K_s = 2.76 \times 10^{-12}$ . In a more general case of a salt of  $M_aA_b$  stoichiometry, the electrolytic dissociation reaction is:



and the resulting formula for the solubility product would be  $K_s = [M^{b+}]^a [A^{a-}]^b$ .

An expression such as  $[Ag^+]^2 [CrO_4^{2-}]$  is known generally as an ion product (reaction quotient) — this one being the ion product for silver chromate. An ion product can in principle have any positive value, depending on the concentrations of the ions involved. Only in the special case when its value is identical with  $K_s$  does it become the solubility product. A solution in which this is the case is said to be *saturated*. Thus when  $[Ag^+]^2 [CrO_4^{2-}] = 2.76 \times 10^{-12}$  at the temperature and pressure at which this value  $K_s$  applies, we say that the “solution is saturated in silver chromate”. A solution must be saturated to be in equilibrium with the solid. True chemical equilibrium can only occur when all components are simultaneously present. That’s why a solubility system can be in equilibrium only when some of the solid is in contact with a saturated solution of its ions.

If the ion product is smaller than the solubility product, the system is not in equilibrium and no solid can be present. Such a solution is said to be *undersaturated*. A *supersaturated* solution is one in which the ion product exceeds the solubility product. A supersaturated solution is not at equilibrium, and no solid can ordinarily be present in such a solution. If some of the solid is added, the excess ions precipitate out and until solubility equilibrium is achieved.

#### Example 7.6

A sample of groundwater that has drained out of a layer of gypsum ( $CaSO_4$ ,  $K_s = 4.9 \times 10^{-5}$ ) is found to be  $8.4 \times 10^{-5}$  M in  $Ca^{2+}$  and  $7.2 \times 10^{-5}$  M in  $SO_4^{2-}$ . What is the equilibrium state of this solution with respect to gypsum?

$CaSO_{4(s)} \rightleftharpoons Ca^{2+}_{(aq)} + SO_4^{2-}_{(aq)}$  and the ion product  $Q = [Ca^{2+}][SO_4^{2-}] = (8.4 \times 10^{-5})(7.2 \times 10^{-5}) = 6.0 \times 10^{-4}$ . Because  $Q$  exceeds  $K_s$ , so the ratio  $K_s/Q > 1$  and the solution is supersaturated in  $CaSO_4$  (solid can be precipitated).

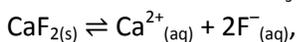
The molar solubility of a solid is expressed as the concentration of the “dissolved solid” in a saturated solution. Depending on the stoichiometry of a solid, the solubility would be connected to the concentration of ions in a various way. In the case of  $Ag_2CrO_4$ , for a saturated solution, we have  $[Ag^+] = 2S$  and  $[CrO_4^{2-}] = S$ .

Substituting this into the solubility product equation:  $(2S)^2(S) = K_s$ .

$$S = (K_s/4)^{1/3} = (2.76 \times 10^{-12})^{1/3} = 8.8 \times 10^{-5}$$

#### Example 7.7

The solubility of  $CaF_2$  (molar mass 78.1 g/mol) at 18°C is reported to be 1.6 mg per 100 cm<sup>3</sup> of water. Calculate the value of  $K_s$  under these conditions.



$$K_s = [Ca^{2+}][F^-]^2 = (S)(2S)^2 = 4S^3$$

S – molar concentration, so moles must be calculated first.

$$n\text{CaF}_2 = m/M = 0.0016 \text{ g} / (78.1 \text{ g/mol}) = 2.05 \times 10^{-5} \text{ mol.}$$

$$S = n\text{CaF}_2/V = 2.05 \times 10^{-5} \text{ mol} / 0.1 \text{ dm}^3 = 2.05 \times 10^{-4} \text{ M}$$

$$K_s = 4(2.05 \times 10^{-4})^3 = 3.44 \times 10^{-11}.$$

## 8. Oxidation-reduction reactions

### 8.1 Oxidation numbers – balancing redox equations

The concept of the **oxidation numbers** (or **oxidation states**) allows for keeping track of how many electrons an atom/ion has. *Oxidation numbers* do not always correspond to the real charges that atoms acquire, they are rather hypothetical charges resulting from the assumption that all bonds in a molecule are purely ionic. Oxidation numbers are usually written with the sign (+plus or –minus) first, then the magnitude (in Roman numerals). The following guidelines help to determine oxidation numbers of atoms in molecules and ions:

1. atoms in their elemental state or atoms in molecules of elements have an oxidation number of 0 (e.g. Fe, O<sub>2</sub>, C);
2. monatomic ions have an oxidation number equal to their charge (e.g. Fe<sup>2+</sup> oxidation number +II);
3. the more electronegative element in a substance is given a negative oxidation state, the less electronegative one is given a positive oxidation state (e.g. in a compound composed of nitrogen and oxygen, negative oxidation number is assigned to oxygen, positive oxidation number – to nitrogen); remember that fluorine is the most electronegative element with oxygen second;
4. in compounds, all atoms are assigned an oxidation number so that the sum of the oxidation numbers on all the atoms in the species equals the charge on the species (in a neutral compound is zero);
5. some elements almost always have the same oxidation states in their compounds, these are listed in a table below.

**Table 7** Rules for establishing oxidation state of selected elements

element	usual oxidation state	exceptions
group 1 metals	always +I	
group 2 metals	always +II	
oxygen	usually –II	hydrogen peroxide (H <sub>2</sub> O <sub>2</sub> ) – each H has an oxidation state of +I, each O have an oxidation state of –I F <sub>2</sub> O – F is more electronegative and has an oxidation state of –I, O has an oxidation state of +II
hydrogen	usually +I	metal hydrides (e.g. NaH) – H is present as a hydride ion, H <sup>–</sup> , oxidation number -I

Below you can find few examples of the oxidation numbers of atoms in more complex compounds.

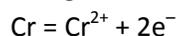
Example 8.1

compound	oxidation number				
CrCl <sub>3</sub>	Cr +III	Cl -I			
Cr(H <sub>2</sub> O) <sub>6</sub> <sup>3+</sup>	Cr +III	H +I	O -II		
CuSO <sub>4</sub>	Cu +II	S +VI	O -II		
MnO <sub>4</sub> <sup>-</sup>	Mn +VII	O -II			
MnO <sub>4</sub> <sup>2-</sup>	Mn +VI	O -II			
NaClO	Na +I	Cl +I	O -II		
Fe(HSO <sub>3</sub> ) <sub>2</sub>	Fe +II	S +IV	H +I	O -II	

Oxidation states are used in naming compounds according to IUPAC rules. It is usual to come across names like iron(II) sulphate and iron(III) chloride. The (II) and (III) are the oxidation states of the iron in the two compounds: +II and +III, respectively. That tells you that they contain Fe<sup>2+</sup> and Fe<sup>3+</sup> ions. This can also be extended to the negative ion. Iron(II) sulphate(VI) is FeSO<sub>4</sub>. There is also a compound FeSO<sub>3</sub> with the name of iron(II) sulphate(IV). The names reflect the oxidation states of the S in the two compounds.

Oxidation states are also used for identification of what's been oxidized and what's been reduced. Reactions that leads to a change of the oxidation numbers of atoms are called **redox (reduction oxidation reactions)** and are connected with electron transfer between reactants. Oxidation states simplify the whole process of working out what is being oxidized and what is being reduced in redox reactions. *Oxidation process is loss of electrons while reduction process is gain of electrons.*

Some illustrative examples of redox process can be followed based on chromium chemistry. Chromium forms a number of different ions - for example, Cr<sup>2+</sup> and Cr<sup>3+</sup>. Such cations might be produced from chromium metal (oxidation number 0), by oxidizing the metal by removing two electrons:



The chromium is now said to be in an oxidation state of +II. Removal of another electron gives the Cr<sup>3+</sup>:



The chromium now has an oxidation state of +III. The oxidation states of +IV and +V are only realized in few compounds, but +VI oxidation state is more common and stable for chromium. The following reaction shows oxidation of chromium(+III) to chromium(+VI):



The chromium is now in an oxidation state of +VI ( $2n - 7 \times (-2) = -2$ ,  $n = 6$ ). Every time chromium was oxidized by removing another electron from it, its oxidation state increases by 1.

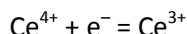
*Oxidation state shows the total number of electrons which have been removed from an element (a positive oxidation state) or added to an element (a negative oxidation state) to get to its present state. Oxidation process is loss of electrons and it is featured with an increase of the oxidation number. On the contrary, reduction is gain of electrons which involves a decrease of the oxidation number. **Oxidant** (oxidizing agent) is the one to be reduced and **reductant** (reducing agent) is the one to be oxidized in due course of redox reaction.*

In the following example one reactant plays simultaneously two roles of an oxidant and a reductant. The reaction between chlorine and cold dilute sodium hydroxide solution is  $2\text{NaOH} + \text{Cl}_2 = \text{NaCl} + \text{NaClO} + \text{H}_2\text{O}$ . Obviously the chlorine has changed oxidation state because it has ended up in compounds starting from the original element. However, checking all the oxidation states shows that the chlorine is the only thing to have changed oxidation state. It has been both oxidized or reduced. One atom has been reduced because its oxidation state has fallen. The other has been oxidized. This is a good example of a *disproportionation reaction*. A disproportionation reaction is one in which a single substance is both oxidized and reduced.

Finally, oxidation states are helpful in work out reacting proportions – balancing redox equations. Note that each time an oxidation state changes by one unit, one electron has been transferred. If one substance's oxidation state in a reaction falls by 2, that means that it has gained 2 electrons. Something else in the reaction must be losing those electrons. Any oxidation state fall by one substance must be accompanied by an equal oxidation state increase by something else. The following example shows how to balance an ionic redox reaction equation.

#### Example 8.2

Ions containing cerium in the +IV oxidation state are oxidizing agents (the simplest example is  $\text{Ce}^{4+}$ ). They can oxidize ions containing molybdenum from the +II to the +VI oxidation state (from  $\text{Mo}^{2+}$  to  $\text{MoO}_4^{2-}$ ). In the process the cerium is reduced to the +III oxidation state ( $\text{Ce}^{3+}$ ). What are the reacting proportions? Cerium is reduced from +IV to +III (it involves transfer of one electron):



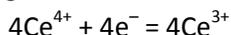
Molybdenum is oxidized from +II to +VI (it involves transfer of four electrons):



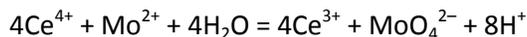
The above equation has to be augmented with additional reactants so that mass balance and charge balance are fulfilled.



Now, number of lost and gained electrons must be equal so the reduction equation must be multiplied by 4 to compensate the electrons appearing in the oxidation equation.



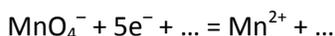
The reduction equation and oxidation equation can now be summed up side by side to get the total balanced redox equation.



#### Example 8.3

A solution of potassium manganate(VII),  $\text{KMnO}_4$ , acidified with dilute sulphuric(VI) acid oxidizes iron(II) ions to iron(III) ions. In the process, the manganate(VII) ions are reduced to manganese(II) ions. Use oxidation states to work out the equation for the reaction.

Reduction of manganate(VII) to manganese(II) ions involves gain of 5 electrons (the oxidation state of manganese has fallen by 5):



Now one will have to make guesses as to how to balance the remaining atoms and the charges. In this case, for example, it is quite likely that the oxygen will end up in water. The charge can be balanced with  $H^+$  because reaction need acidic solution.



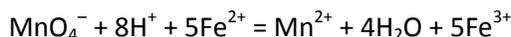
Every iron(II) ion that reacts, increases its oxidation state by 1.



Now, number of lost and gained electrons must be equal. That means that there must be five iron(II) ions reacting for every one manganate(VII) ion.



The reduction equation and oxidation equation can now be summed up side by side to get the total balanced redox equation.



## 8.2 Redox potentials and electrochemical series of metals

**Reduction potential** (also known as redox potential, oxidation-reduction potential) *is a measure of the tendency of a chemical species to acquire electrons and thereby be reduced.* Reduction potential is measured in volts (V), or millivolts (mV). Each species has its own intrinsic reduction potential; the more positive the potential, the greater the species' affinity for electrons and tendency to be reduced.

In aqueous solutions, reduction potential is a measure of the tendency of the solution to either gain or lose electrons when it is subject to change by introduction of a new species. A solution with a higher (more positive) reduction potential than the new species will have a tendency to gain electrons from the new species (i.e. to be reduced by oxidizing the new species) and a solution with a lower (more negative) reduction potential will have a tendency to lose electrons to the new species (i.e. to be oxidized by reducing the new species). Because the absolute potentials are difficult to accurately measure, reduction potentials are defined relative to a reference electrode. Reduction potentials of aqueous solutions are determined by measuring the potential difference between an inert sensing electrode (e.g. Pt wire) in contact with the solution and a stable reference electrode connected to the solution by a salt bridge.

The sensing electrode acts as a platform (electric contact) for electron transfer to or from the reference electrode. It is typically platinum, although gold and graphite can be used as well. The reference electrode consists of a redox system of known potential. The standard hydrogen electrode is the reference from which all standard redox potentials are determined and has been assigned an arbitrary potential of 0.0 mV. The redox equation is  $1/2H_{2(g)} + H_2O = H_3O^+_{(aq)} + e^-$ .

The standard reduction potential ( $E^\circ$ ) of an electrode is measured under standard conditions: 25°C, a molarity of 1M for each ion participating in the reaction, a partial pressure of  $10^5$  Pa for each gas that is part of the reaction, and metals in their pure state. The standard reduction potential is defined relative to a standard hydrogen electrode reference electrode, which is arbitrarily given a potential of 0.00 volts. Any system (electrode) or environment that accepts electrons from a standard hydrogen electrode is an electrode that is defined as having a positive redox potential; any system donating electrons to the

hydrogen electrode is defined as having a negative redox potential. Based on the  $E^\circ$  values the relative reactivities of different electrodes can be compared to predict the direction of electron flow. A higher positive  $E^\circ$  means there is a greater tendency for reduction to occur, while a lower one means there is a greater tendency for oxidation to occur. A number of examples of redox electrodes and the associated standard potentials are listed below.

**Table 8** Selected electrodes and their standard reduction potentials

half-reaction	$E^\circ / \text{V}$
$\text{F}_{2(\text{g})} + 2\text{e}^- = 2\text{F}^-$	+ 2.87
$\text{Ce}^{4+} + \text{e}^- = \text{Ce}^{3+}$	+ 1.61
$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- = \text{Mn}^{2+} + 4\text{H}_2\text{O}$	+ 1.51
$\text{Cl}_{2(\text{g})} + 2\text{e}^- = 2\text{Cl}^-$	+ 1.36
$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- = 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	+ 1.33
$\text{O}_{2(\text{g})} + 4\text{H}^+ + 4\text{e}^- = 2\text{H}_2\text{O}$	+ 1.229
$\text{Pt}^{2+} + 2\text{e}^- = \text{Pt}_{(\text{s})}$	+ 1.188
$\text{Br}_{2(\text{aq})} + 2\text{e}^- = 2\text{Br}^-$	+ 1.087
$\text{NO}_3^-_{(\text{aq})} + 4\text{H}^+ + 3\text{e}^- = \text{NO}_{(\text{g})} + 2\text{H}_2\text{O}$	+ 0.958
$\text{Ag}^+ + \text{e}^- = \text{Ag}_{(\text{s})}$	+ 0.780
$\text{Fe}^{3+} + \text{e}^- = \text{Fe}^{2+}$	+ 0.773
$\text{O}_{2(\text{g})} + 2\text{H}^+ + 2\text{e}^- = \text{H}_2\text{O}_{2(\text{aq})}$	+ 0.70
$\text{Cu}^{2+} + 2\text{e}^- = \text{Cu}_{(\text{s})}$	+ 0.337
$2\text{H}^+ + 2\text{e}^- = \text{H}_{2(\text{g})}$	0.000
$\text{Ni}^{2+} + 2\text{e}^- = \text{Ni}_{(\text{s})}$	-0.25
$\text{PbSO}_{4(\text{s})} + 2\text{e}^- = \text{Pb}_{(\text{s})} + \text{SO}_4^{2-}_{(\text{aq})}$	-0.36
$\text{Cr}^{3+} + \text{e}^- = \text{Cr}^{2+}$	-0.42
$\text{Fe}^{2+} + 2\text{e}^- = \text{Fe}_{(\text{s})}$	-0.44
$\text{Zn}^{2+} + 2\text{e}^- = \text{Zn}_{(\text{s})}$	-0.763
$2\text{H}_2\text{O} + 2\text{e}^- = \text{H}_{2(\text{g})} + 2\text{OH}^-$	-0.828
$\text{Al}^{3+} + 3\text{e}^- = \text{Al}_{(\text{s})}$	-1.662
$\text{Mg}^{2+} + 2\text{e}^- = \text{Mg}_{(\text{s})}$	-2.372
$\text{Na}^+ + \text{e}^- = \text{Na}_{(\text{s})}$	-2.71

(s) denotes solid

Some immediate conclusions can be withdrawn from such a table of standard potentials.

1. During reaction with strong acids noble metals (the ones with positive values of  $E^\circ$ ) do not evolve hydrogen. On the contrary, they reduce anions produced from acids to respective oxides (e.g.  $\text{NO}_3^-$  to  $\text{NO}$  or  $\text{NO}_2$ ). Non-noble metals (the ones with negative values of  $E^\circ$ ) evolve hydrogen from acids.
2. A nonmetal higher in the series (having high value of reduction potential) will displace another nonmetal with lower reduction potential. The nonmetal's which possess high positive reduction potentials have the tendency to accept electrons readily. These electrons are provided by the

ions of the nonmetal having low value of reduction potential. Thus,  $F_2$  can displace chlorine from chlorides,  $Cl_2$  can displace bromine and iodine from bromides and iodides, etc.

3. The metal having low standard reduction potential will displace the metal from its salt's solution which has higher value of standard reduction potential.
4. Based on the  $E^\circ$  values one may check whether a given redox reaction is feasible and spontaneous and what is direction of electrons flow (which electrode play role of an anode and which is a cathode) – see next chapter for more detail.

The potentials of each of electrodes changes with molarity (or partial pressure when in gas phase) of the involved individuals. This relationship is known as the **Nernst equation** that relates the reduction potential of an electrode to the standard electrode potential, temperature, and concentrations of the chemical species undergoing reduction and oxidation.

$$E_{red-ox} = E_{red-ox}^\circ + \frac{RT}{nF} \ln \frac{[ox]}{[red]}$$

$E_{red-ox}$  is potential of an electrode composed of reduced (red) and oxidized (ox) species,  $E^\circ$  is a standard potential (as above),  $R$  – gas constant (8.314 J/(mol K)),  $T$  – temperature (in K),  $n$  is a number of electrons appearing in the half-reaction, and  $F$  – Faraday constant equal to the charge of one mole of electrons ( $F = 96485$  C/mol).  $[ox]$  denotes molarity of the oxidized species, while  $[red]$  – molarity of the reduced species.

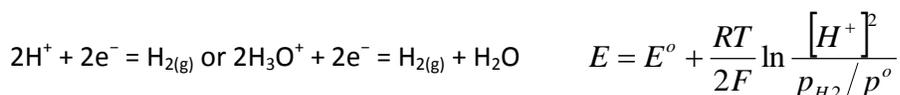
Example 8.4 Nernst potentials of electrodes



*Note: above potential is dependent on pH, protons are oxidized form of hydrogen and  $H^+$  is situated on the left-hand side of the equation (the same as  $MnO_4^-$ ) that is why  $[H^+]$  appears in the nominator to the power 8 (stoichiometric coefficient of  $H^+$  is 8).*



*Note: the reduced form is  $Cu_{(s)}$  – separate solid phase for which concentration of Cu is constant. That is way potential does not depend on  $[Cu]$ .*



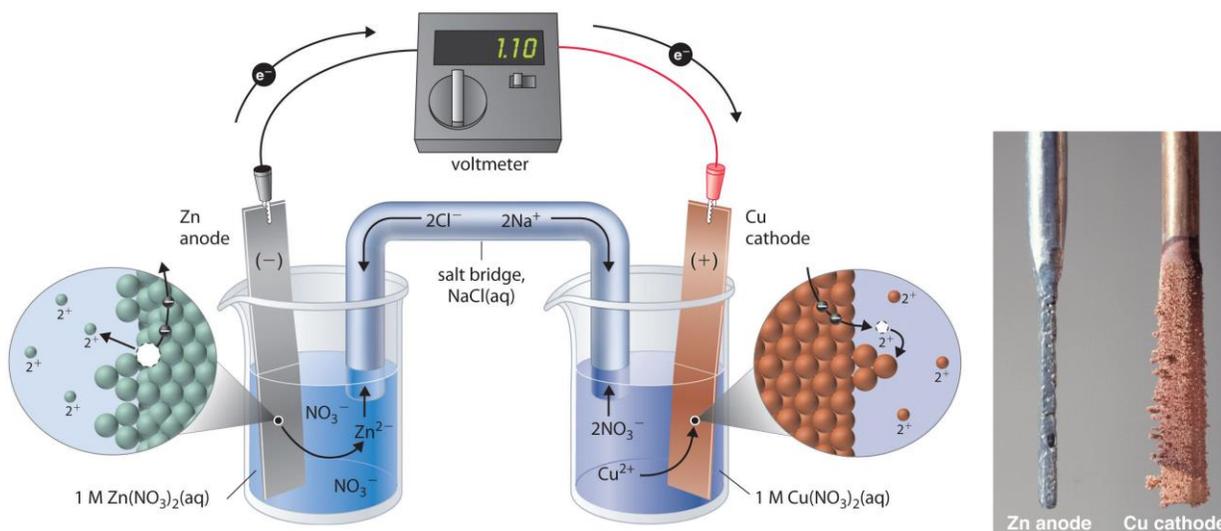
*Note: the reduced form is gaseous hydrogen, which form a separate phase. Potential depend on the partial pressure of hydrogen ( $p_{H_2}$ ),  $p^\circ$  is a standard pressure.*



### 8.3 Cell potentials

Using standard electrode potentials it is possible to predict direction of a given redox reaction. For instance, why can  $\text{Cu}^{2+}$  oxidize zinc, but  $\text{Zn}^{2+}$  cannot oxidize Cu?  $E^\circ$  values of the involved electrodes ( $\text{Cu}^{2+}|\text{Cu}$  and  $\text{Zn}^{2+}|\text{Zn}$ ) provide an indication of the relative strengths of oxidizing agents and reducing agents. The value of  $E^\circ$  for reaction  $\text{Cu}^{2+}_{(\text{aq})} + 2\text{e}^- = \text{Cu}_{(\text{s})}$  is +0.337 V. For the second reaction  $\text{Zn}^{2+}_{(\text{aq})} + 2\text{e}^- = \text{Zn}_{(\text{s})}$  is -0.763 V. Thus, *copper electrode exhibit high tendency for reduction (greater  $E^\circ$  value), while at the same time zinc electrode will undergo oxidation (smaller  $E^\circ$  value)*. As a consequence, the overall reaction will be  $\text{Cu}^{2+}_{(\text{aq})} + \text{Zn}_{(\text{s})} = \text{Cu}_{(\text{s})} + \text{Zn}^{2+}_{(\text{aq})}$ .

The two electrodes ( $\text{Cu}^{2+}|\text{Cu}$  and  $\text{Zn}^{2+}|\text{Zn}$ ) can be combined in one facility called voltaic cell. The scheme of such cell is shown below. The copper electrode plays a role of a **cathode**, *where electrons are consumed in the reduction process*, while the zinc electrode is an **anode**, *here electrons are liberated in due course of oxidation process*.



**Figure 1** Schematic illustration of copper-zinc galvanic cell. A galvanic cell can be constructed by inserting a copper strip into a beaker that contains an aqueous 1 M solution of  $\text{Cu}^{2+}$  ions and a zinc strip into a different beaker that contains an aqueous 1 M solution of  $\text{Zn}^{2+}$  ions. The two metal strips are connected by a wire that allows electricity to flow, and the beakers are connected by a salt bridge. When the switch is closed to complete the circuit, the zinc electrode (the anode) is spontaneously oxidized to  $\text{Zn}^{2+}$  ions in the left compartment, while  $\text{Cu}^{2+}$  ions are simultaneously reduced to copper metal at the copper electrode (the cathode). On the right-hand side the picture of the strips after reaction are shown. As the reaction progresses, the Zn anode loses mass as it dissolves to give  $\text{Zn}^{2+}_{(\text{aq})}$  ions, while the Cu cathode gains mass as  $\text{Cu}^{2+}_{(\text{aq})}$  ions are reduced to copper metal that is deposited on the cathode. (reference: Principles of General Chemistry (v. 1.0), (<http://2012books.lardbucket.org/>))

Copper and zinc have sufficiently different electrode potentials so as to produce a measurable potential difference between the electrodes. This potential difference (voltage) is called **standard cell potential**  $E^\circ_{\text{cell}}$  and can be calculated as a difference between potentials of cathode and anode:

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}, \quad (E^\circ_{\text{cathode}} > E^\circ_{\text{anode}}).$$

The calculated value is  $E^\circ_{\text{cell}} = 0.337 \text{ V} - (-0.763 \text{ V}) = 1.100 \text{ V}$ . Note however, that when a voltaic cell works under non-standard conditions ( $T$  and  $p$  vary from standard values or concentrations of electrolytes are different from 1M) one must use Nernst equation (given above) for the two half-reactions (two electrodes) to calculate their potentials and then calculate cell potential:

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}, \quad (E_{\text{cathode}} > E_{\text{anode}}).$$

Galvanic cells are schematically described by a series of symbols forming so called a cell diagram. The identity of the electrodes and the chemical contents of the compartments are indicated by their chemical formulas, with the *anode written on the far left and the cathode on the far right*. Phase boundaries are shown by single vertical lines, and the salt bridge, which has two phase boundaries, by a double vertical line. Thus, the cell diagram for the zinc – copper cell shown above is written as follows:



where molarity stands for the actual molar concentrations of  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$  cations.

The maximum amount of work that can be produced by an electrochemical cell ( $W_{\text{max}}$ ) is equal to the product of the cell potential ( $E_{\text{cell}}$ ) and the total charge transferred during the reaction ( $nF$ ):

$$W_{\text{max}} = nFE_{\text{cell}}$$

In standard conditions this amount of work corresponds to the change of standard free-enthalpy  $\Delta G^\circ$

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

Recall that for a given reaction, the standard free-enthalpy change and the equilibrium constant are related by the following equation:

$$\Delta G^\circ = -RT \ln K$$

Given the relationship between the standard free-enthalpy change and the standard cell potential, we can write

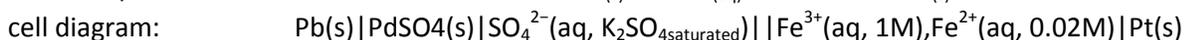
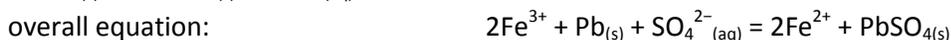
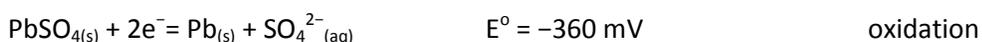
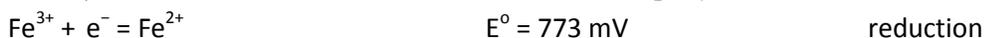
$$nFE^\circ_{\text{cell}} = RT \ln K$$

and calculate indirectly equilibrium constant  $K$  from the measurement of standard cell potential.

### Example 8.5

Construct a voltaic cell using iron(III)/iron(II) electrode and lead - sulfate(VI) electrode. Starting from proper half-reaction write down and balance overall reaction equation, write down a cell diagram and calculate standard cell potential (temperature 25 °C).

Calculate change of cell potential when molar concentration in iron electrode are  $[\text{Fe}^{3+}] = 1\text{M}$  and  $[\text{Fe}^{2+}] = 0.02\text{M}$ , whereas in lead electrode we have saturated  $\text{K}_2\text{SO}_4$  solution.



$$E^\circ_{\text{cell}} = E^\circ_{\text{Fe}^{3+}|\text{Fe}^{2+}} - E^\circ_{\text{Pb}|\text{PbSO}_4} = 773 \text{ mV} - (-360 \text{ mV}) = 1133 \text{ mV} = 1.133 \text{ V}$$

$nFE_{\text{cell}}^{\circ} = RT \ln K$  where  $n = 2$

$\ln K = (2 \times 96485 \text{ C/mol} \times 1.133 \text{ V}) / (8.314 \text{ J/(mol K)} \times 298 \text{ K}) = 88.2$

$K = \exp(88.2) = 2 \times 10^{38}$

For  $[\text{Fe}^{3+}] = 1\text{M}$  and  $[\text{Fe}^{2+}] = 0.02\text{M}$  Nernst potential equals

$$E = E^{\circ} + \frac{RT}{F} \ln \left[ \frac{\text{Fe}^{3+}}{\text{Fe}^{2+}} \right] = 0.773\text{V} + \frac{8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}} \times 298\text{K}}{96485 \frac{\text{C}}{\text{mol}}} \ln \frac{1}{0.02} = 0.873\text{V}$$

Note that the  $\text{Pb(s)}|\text{PbSO}_4(\text{s})|\text{SO}_4^{2-}$  electrode is composed of saturated solution,  $[\text{SO}_4^{2-}] = \text{const.}$ , so its potential is constant and equals  $E^{\circ}$ .

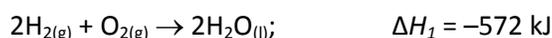
$E_{\text{cell}} = E_{\text{Fe}^{3+}|\text{Fe}^{2+}} - E_{\text{Pb}|\text{PbSO}_4} = 873 \text{ mV} - (-360 \text{ mV}) = 1233 \text{ mV} = 1.233 \text{ V}$

## 9. Thermochemistry

### 9.1 Calculations based on Hess law

The heat that flows across the boundaries of a system undergoing a change (chemical reaction or physical process) is a fundamental property that characterizes the process. If the process is a chemical reaction carried out at constant pressure, the heat can be predicted from the difference between the **enthalpies  $\Delta H$**  of the products and reactants.

In order to define the thermochemical properties of a process, it is first necessary to write a *thermochemical equation* that defines the actual change taking place, both in terms of the formulas of the substances involved and their physical states (temperature, pressure, and phase). The following points are important when writing thermochemical equations. Any thermodynamic quantity such as  $\Delta H$  that is associated with a thermochemical equation always refers to the number of moles of substances explicitly shown in the equation. Thus for the synthesis of water we can write



or



Thermochemical equations for reactions taking place in solution must also specify the concentrations of the dissolved species. Since most thermochemical equations are written for the standard conditions of 298 K and  $10^5$  Pa pressure, we can leave these quantities out if these conditions apply both before and after the reaction. If, under these same conditions, the substance is in its preferred (most stable) physical state and in separate phases, then the substance is said to be in its standard state. A thermochemical quantity such as  $\Delta H$  that refers to reactants and products in their standard states is denoted by  $\Delta H^{\circ}$ .

The enthalpy change for a chemical reaction is the difference

$$\Delta H = H_{\text{products}} - H_{\text{reactants}}$$

If a reaction represents the formation of one mole of the compound from its elements in their standard states, as in  $\text{H}_{2(\text{g})} + \frac{1}{2} \text{O}_{2(\text{g})} \rightarrow \text{H}_2\text{O}_{(\text{l})}$ ,  $\Delta H = -286 \text{ kJ}$ , then we can arbitrarily set the enthalpy of the elements to zero and write  $\Delta H^{\circ} = \sum \Delta_f H^{\circ}_{\text{products}} - \sum \Delta_f H^{\circ}_{\text{reactants}} = -286 \text{ kJ} - 0 = -286 \text{ kJ mol}^{-1}$ ,

which defines the **standard enthalpy of formation**  $\Delta_f H^\circ$  of water at 298K. In general,

$$\Delta H^\circ = \sum n \Delta_f H^\circ_{\text{products}} - \sum n \Delta_f H^\circ_{\text{reactants}},$$

where  $n$  is reaction stoichiometry coefficient. The *standard enthalpy of formation of a compound is defined as the heat associated with the formation of one mole of the compound from its elements in their standard states*. The negative sign indicates that the reaction is *exothermic*: the enthalpy of the product is smaller than that of the reactants.

When, instead of enthalpies of formation, the *standard enthalpies of combustion*  $\Delta_{\text{comb}} H^\circ$  (total combustion of 1 mole of substance in  $\text{O}_2$ ) are considered, the following equation can be used for assessing a standard enthalpy of reaction:

$$\Delta H^\circ = \sum n \Delta_{\text{comb}} H^\circ_{\text{reactants}} - \sum n \Delta_{\text{comb}} H^\circ_{\text{products}}.$$

### Example 9.1

Given the enthalpies (kJ) of formation  $\text{H}_2\text{O}$  (−285.8),  $\text{H}_2\text{S}$  (−20.6), and  $\text{SO}_2$  (−296.8). Calculate the enthalpy change for the reaction  $2\text{H}_2\text{S} + \text{SO}_2 \rightarrow 3\text{S} + 2\text{H}_2\text{O}$

Enthalpy of formation of elements is zero. Thus:

$$\begin{aligned} \Delta H^\circ &= \sum n \Delta_f H^\circ_{\text{products}} - \sum n \Delta_f H^\circ_{\text{reactants}} = 2\Delta_f H^\circ_{\text{H}_2\text{O}} - 2\Delta_f H^\circ_{\text{H}_2\text{S}} - \Delta_f H^\circ_{\text{SO}_2} = 2(-285.8) \text{ kJ} - 2(-20.6) \text{ kJ} - (-296.8) \text{ kJ} \\ &= -233.6 \text{ kJ} \end{aligned}$$

Two or more chemical equations can be combined algebraically to give a new equation. It was observed that the heats associated with those chemical reactions can be combined in the same way to yield the heat of the resulting reaction. For example, the standard enthalpy changes for the oxidation of graphite and diamond can be combined to obtain  $\Delta H^\circ$  for the transformation between these two forms of solid carbon, a reaction that is difficult to be studied experimentally.



Subtraction of the second reaction from the first (i.e., writing the second equation in reverse and adding it to the first one) yields



This principle, known as **Hess' law** of independent heat summation is a direct consequence of the *enthalpy being a state function (enthalpy is a state function because its change depends only on the final and initial state of the system; state functions do not depend on the path by which the system arrived at its present state)*. Hess' law is one of the most powerful tools of chemistry, for it allows the change in the enthalpy (and in other thermodynamic functions) of huge numbers of chemical reactions to be predicted from a relatively small base of experimental data.

### Example 9.2 Hess' law

Use the following heat of formation/combustion information to estimate the standard heat of formation of methane  $\text{CH}_{4(\text{g})}$ .





The standard heat of formation of methane is defined by the reaction



The task is thus to combine the top three equations in such a way that they add up to (4).

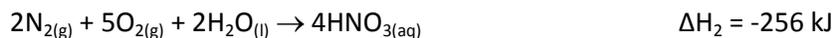
Note that when any equation is reversed, the sign of  $\Delta H^\circ$  must also be reversed, when multiplied by a number, the  $\Delta H^\circ$  value must also be multiplied by the same number.

The combustion of methane (3), is the only equation that contains the  $\text{CH}_4$  term, so it needs to be written in reverse so that  $\text{CH}_4$  appears as the product ( $-\Delta H_3^\circ$ ). Since  $\text{H}_2\text{O}$  does not appear in the net reaction (4), add two times (2) to cancel these out ( $2\Delta H_2^\circ$ ). Finally, get rid of the remaining  $\text{O}_2$  and  $\text{CO}_2$  by adding (1). This also adds a needed  $\text{C}_{(\text{graphite})}$  ( $\Delta H_1^\circ$ ).

$$\Delta H_4^\circ = -\Delta H_3^\circ + 2\Delta H_2^\circ + \Delta H_1^\circ = 890 \text{ kJ mol}^{-1} + 2(-286 \text{ kJ mol}^{-1}) - 393 \text{ kJ mol}^{-1} = -75 \text{ kJ mol}^{-1}$$

### Example 9.3

Given the following information:



calculate the enthalpy change for the reaction below:



First equation – reverse and multiply by 3/2 (this gives me  $3\text{NO}_2$  as well as the  $3\text{NO}$  which will be necessary to get one  $\text{NO}$  in the final answer).

Second equation – divide by 2 (this gives two nitric acid in the final answer).

Third equation – reverse to cancel  $2\text{NO}$  as well as nitrogen.

$$\Delta H_4 = -3/2 \Delta H_1 + 1/2 \Delta H_2 - \Delta H_3 = +174 + (-128) - (+183) = -137 \text{ kJ}$$