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## CHAPTER 4      Chemical Processes

Processes that have to do with the nature of substances are called chemical. Chemical processes are essentially of two types: Transports and reactions. Substances can wander from place to place, or they can change—in fact, they get produced or destroyed in chemical reactions. Chemical phenomena will be described with the help of two basic concepts—amount of substance and chemical potential.

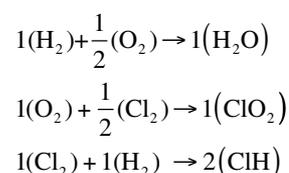
### 4.1 SOME IMPORTANT OBSERVATIONS

**Chemical reactions and amount of substances.** It is customary to consider substances as composed of the “building blocks” of matter, the elements. Consider some reactions involving any two of the three elements hydrogen, oxygen, and chlorine, each time involving two of them. If we start with a unit amount of substance of hydrogen gas having a mass of 2 grams, we find that 16 g of oxygen gas will *completely* react with the hydrogen to form water. However, exactly twice that amount of oxygen gas, i.e., oxygen with a mass of 32 g, will react completely with 35.5 g of chlorine. Finally, twice as much chlorine, i.e., 71 g, will use up 2 g of hydrogen gas. Fig. 4.1 shows these examples written in the language of chemical reaction equations.

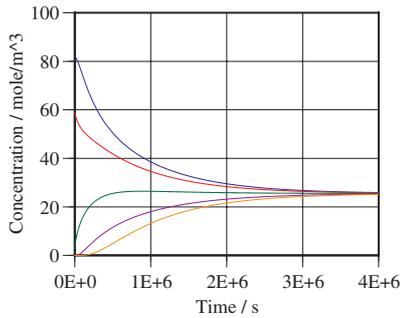
*Interpretation.* We see that the mass of a certain quantity of an element cannot serve as a natural measure of amount of substance. It appears that 71 g of chlorine are chemically equivalent to 2 g of hydrogen. Therefore, it is necessary to introduce a new measure of *amount of substance*. If we count 2 g of hydrogen gas as one unit of amount of substance, called 1 mole, the reactions tell us that 1 mole of hydrogen gas ( $H_2$ ) has a mass of 2 g, 1 mole of oxygen gas ( $O_2$ ) has a mass of 32 g, while the mass of 1 mole of chlorine ( $Cl_2$ ) is 71 g. The mass of one mole of amount of substance is called the *molar mass* of the substance.

According to the particle model of the structure of substances, equal amounts of substance correspond to equal numbers or particles.

**Pressure of dilute gases.** Substances can be brought into gaseous form. If the gas is dilute or hot enough, or both, all substances show the same behavior (*ideal gas*). If we fill such a gas into a container of given volume at a prescribed temperature, the following is observed. It takes different masses for different substances to obtain the same pressure. For example, 2 g of hydrogen gas, 71 g of chlorine, or 32 g of oxygen gas all have the same pressure if volume and temperature are the same.



**Figure 4.1:** Examples of chemical reactions written in the form of reaction equations. H, Cl, and O are the symbols for hydrogen, chlorine, and oxygen, respectively. Subscript numbers symbolize multiples of amounts of these substances.



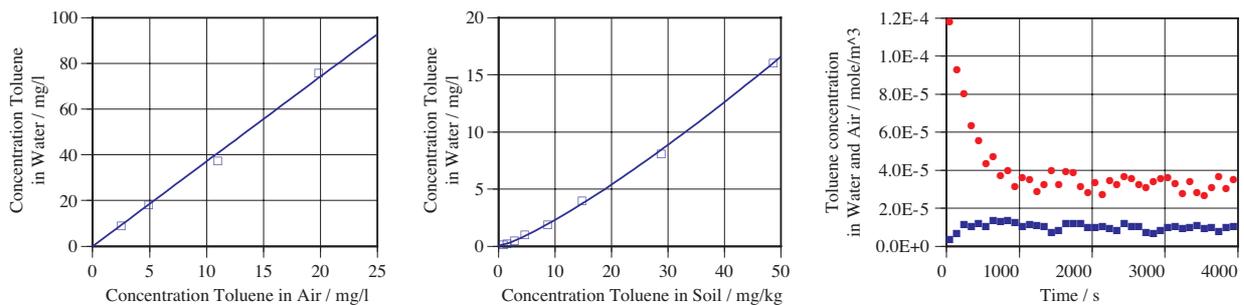
**Figure 4.2:** Simulation of concentration of salt at different heights in the cube seen in the photograph. Salt concentration is highest at the beginning in the lowest layers. In the experiment, the conductivity of the solution is measured.

*Interpretation.* According to what we know from reactions, 2 g of hydrogen gas, 71 g of chlorine, or 32 g of oxygen are equal amounts of the three substances. Therefore, the pressure of simple gases depends upon the amount of substance of the gas, not upon its mass or some other possible measure. In the particle model, it takes equal numbers of particles to get the same pressure for the same volume and temperature.

**Diffusion of salt.** If you introduce a layer of salty water in a container and make sure it rests below layers of distilled water (Fig. 4.2, top), the salt will slowly spread upward. Eventually, all the salt will be evenly distributed, meaning that the concentration of salt has become uniform throughout the body of water (Fig. 4.2, bottom). We can determine the concentration of salt indirectly by measuring the conductivity of the solution. A simulation based on actual measurements shows that it takes more than a month for about 1 g salt to spread in a cube of 1 liter of distilled water.

*Interpretation.* Salt can be dissolved in liquids such as water (common salt decomposes into  $\text{Na}^+$  and  $\text{Cl}^-$  ions, making the solution electrically conductive). If the concentration of the dissolved substance is higher in some places than in others, it migrates through the liquid to where there is less. When the concentration has become uniform throughout the solvent, the process—called *diffusion*—stops. We say that concentration differences are the driving force for diffusive transports.

**Equilibrium distributions of toluene in water and air.** In an environment that is the same everywhere (homogeneous environment), a substance diffuses and distributes evenly if we wait long enough. This is not the case if the substance can travel through different materials. For example, toluene diffuses from water into air (or vice-versa) until the concentration of toluene is about four times higher in water than in air (Fig. 4.3, left and right). If we have soil and water present that can take up toluene, final (equilibrium concentrations) are again not the same. The situation is even more complex than in the case of water and air. The relation between equilibrium concentrations in soil and water is not linear.



**Figure 4.3:** Equilibrium relations between concentrations of toluene in two different substances (air and water, left, and soil and water, center). Dynamic case (concentrations of toluene in water and air; data for soil not shown) on the right. Data courtesy J. Hosang.

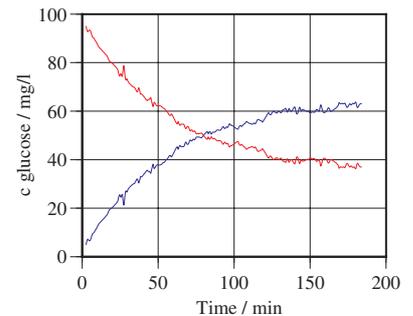
*Interpretation.* It appears that toluene “prefers” to be in water rather than in air. So, if there are equal concentrations of toluene in water and air in contact, there still is a drive of toluene to migrate into water. We can explain this by introducing the concept of chemical potential. At equal concentration, the chemical potential of toluene is lower in water than in air. The difference of the chemical potentials of toluene in water and in air is interpreted as the drive (or driving force) for the diffusion of toluene. The observation tells us that the driving force for the flow of toluene cannot be differences in its concentration; rather, it is a gradient of the chemical potential of a substance. This is reflected in the dynamical case (Fig. 4.3, right).

The difference in the relations between equilibrium concentrations for toluene in water/air and in soil/water indicate that the form of the dependence of the chemical potentials upon the concentration of toluene is different for different environments (soil is different in this respect from water or air).

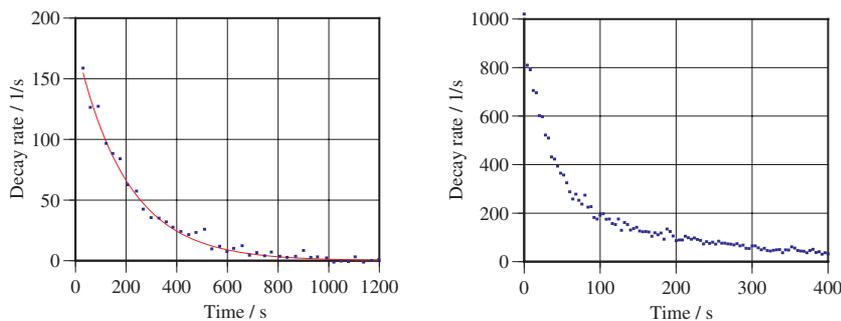
**Transformation of sugar.** Glucose exists in two different configurations (called anomers) that only differ in the spatial arrangement of the elements in its molecules (the elemental composition is the same). The configurations are called  $\alpha$ -glucose and  $\beta$ -glucose, respectively. Originally, we only have  $\alpha$ -glucose. If we dissolve it in water, part of it will change slowly into  $\beta$ -glucose (Fig. 4.4).

*Interpretation.* A configuration of glucose has a tendency or drive to change. The strength of this tendency can be expressed in terms of the chemical potential, just as we did in the case of the tendency of a substance to disperse.  $\alpha$ -glucose and  $\beta$ -glucose have different chemical potentials, and these potentials also depend upon concentration. If there is a difference in chemical potential, there is a tendency to change. Once the chemical potentials have become equal, this chemical driving force stops. The experiments shows that the chemical potentials of  $\alpha$ -glucose and  $\beta$ -glucose become equal at different concentrations. This behavior is the same as that observed for the tendency to disperse (see Fig. 4.3).

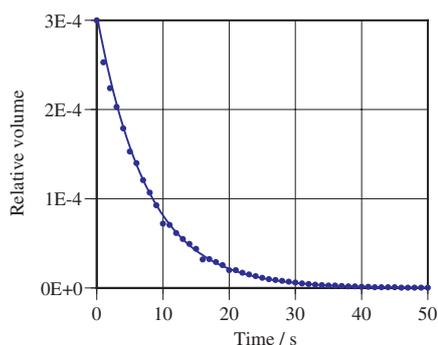
**Radioactive decay.** Nuclear reaction in general, and radioactive decay in particular, can be considered a kind of chemical reaction. Unlike in normal chemical reactions, nuclei change which normally leads to a change of the elements involved. Nuclei of a particular isotope decay until everything is gone (Fig. 4.5).



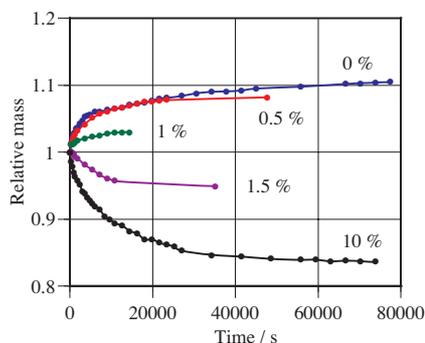
**Figure 4.4:** Concentration of  $\alpha$ -glucose (decreasing curve) and  $\beta$ -glucose in water as functions of time.  $\alpha$ -glucose decays into  $\beta$ -glucose. The concentration is determined by measuring the rotation of the plane of polarization of plane-polarized light shining through a solution of glucose. Data courtesy B. Sonnleitner.



**Figure 4.5:** Radioactive decay of a barium isotope (left) and of a mixture of two silver isotopes (right). Values represent the decay rate, the number of nuclei decaying per second. Data from E. B. Norman et al. (barium), and L. Wickham (silver).



**Figure 4.6:** The dye murexide reacts with protons in an aqueous solution and decays into colorless substances. If the concentration of protons is high, the concentration of murexide is almost perfectly an exponentially decaying function of time.



**Figure 4.7:** Relative mass of potato cores as a function of time. The cores are placed in distilled water containing different concentrations (percent by mass) of table salt. If placed in pure water, the cores grow. If more salt is dissolved, the cores grow less and less. They lose mass if the concentration of salt increases beyond a critical value.

*Interpretation.* Unstable isotopes have a high chemical potential. They decay into isotopes whose chemical potential is lower. Since radioactive processes release a lot of energy, we see that energy is involved with substances going through changes of the chemical potential. This is analogous to what we know from other types of processes such as electric or thermal.

In Fig. 4.5 (left), an exponentially decaying function has been fitted through the data points. The result of the decay of a single isotope is analogous to the draining of an oil tank or the discharging of a capacitor. Therefore, the rate at which the process runs appears to be proportional to how much of the decaying substance is present. The result of the example with silver (Fig. 4.5, right) is a little more complicated since there are two species decaying at the same time.

**Decay of murexide in an acid solution.** Murexide ( $C_8H_5N_5O_6$ ) is a dye made from uric acid which early on was made in large amounts from guano. If dissolved in water containing protons, it decays into alloxan and uramid. Murexide in water is deep purple, alloxan and uramid are colorless. By determining the absorbance of the purple solution (measuring how much light is passed through a length of this liquid), we can find the concentration of murexide. If the concentration of  $H^+$  ions is very high, the concentration of murexide is a decaying exponential function of time.

*Interpretation.* There must be a driving force for the reaction, i.e., a difference of the chemical potentials between reactants and products. Even though the result of the decay of murexide is analogous to that of radioactive decay, there is an important difference. Murexide needs a partner ( $H^+$  ions) to react, and therefore the behavior is equal to radioactive decay only if the concentration of  $H^+$  ions is constant.

**Soaking potato cores in water.** Spherical potato cores of roughly the same size are soaked in distilled water, and in water with some dissolved table salt. In the course of time, the mass of the potato cores changes (Fig. 4.7). If there is only water, or water with a low concentration of salt, the cores grow. If the salt concentration is above a certain value, the cores lose mass. At a certain concentration (called isotonic), the mass does not change. If sugar is used instead of water, it is found that it is isotonic if the molality (concentration measured as amount of substance per kilogram of solvent) is about twice that of salt.

*Interpretation.* Since the mass of the cores changes, substances must be flowing into or out of the cores. We have already seen that substances such as salt can diffuse through materials. However, this case is different. Take the example with pure water (0% salt in Fig. 4.7). The core is taking up substance, but the only substance present outside is water. Therefore, water is flowing into the potato. Even if a little salt is present in the solution, the potato takes up water. If the concentration of salt is larger than a certain critical value, the potato core loses water. (This last point is not so clear; we would have to prove more carefully that there are no other substances—such as minerals—being washed out of the core.)

Commonly we say that water flows from point of high pressure to points of low pressure. Take the case of a core in pure water. If we adhere to this interpretation,

we must conclude that the pressure of the water inside the potato core is lower than the pressure outside. The core consists mostly of water with different substances dissolved in it. This indicates that the pressure of water is lower when substances are dissolved in it.

If we accept this conclusion, we can explain the other observations as well. If salt is introduced in the water outside, its pressure decreases. Therefore, the pressure difference of the water outside and inside the core becomes smaller, letting less water migrate into the potato. Finally, at a certain concentration, the water pressure inside and outside is equal. With still more salt dissolved outside, water will actually flow from the core into the solution surrounding it.

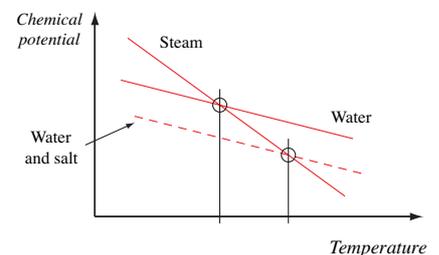
This transport of water is called *osmosis*. Osmosis is water transport across selectively permeable membranes (such as the potato cell walls) between different watery solutions. Pressure is an indication of the chemical potential of a liquid. Solutes (dissolved substances) decrease the pressure and therefore the chemical potential of water. If the concentration of amount of substance of solutes is higher in a batch of water, and lower in another, water flows from where there is less solute to where there is more.

Observing that isotonic solutions of salt or sugar are obtained if the molar concentration is the same (except for a factor of 2)—and not if the concentration by mass is made equal—again shows that amount of substance counts, not mass. In fact, the factor 2 is the result of the dissociation of table salt into  $\text{Na}^+$  and  $\text{Cl}^-$  ions, making twice as many particles per mole as in the case of sugar.

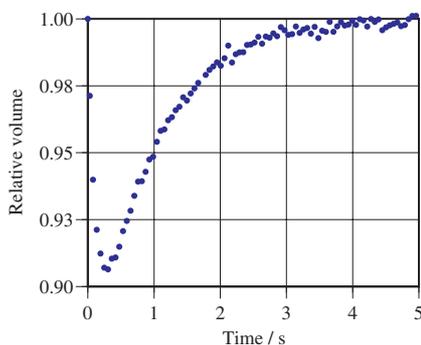
**Salt changes melting and boiling temperatures of water.** Water freezes at  $0^\circ\text{C}$  and boils at  $100^\circ\text{C}$  (at an air pressure of 1 bar). Phase changes can be looked upon as chemical processes just like all the other phenomena considered so far. It is observed that adding salt to water lowers the freezing point, and it raises the boiling point.

*Interpretation.* Phase changes can be interpreted as follows. Take ice, water, and steam in an environment of  $25^\circ\text{C}$  and a pressure of 1 bar. We know that ice will melt and steam will condense. This means that under these conditions (temperature and pressure) the chemical potential of water is lowest. That's why both ice and steam change into water. Now consider ice and water at  $-10^\circ\text{C}$ : Water will freeze, its chemical potential is now higher than that of ice. Apparently, the chemical potentials of ice, water, and steam change with temperature in such a way that the potentials of ice and water become equal at  $0^\circ\text{C}$ , and those of water and steam are equal at  $100^\circ\text{C}$ .

Now consider adding salt to water and try to boil it. The boiling point will be raised (the more salt, the bigger the change). Take water at  $100^\circ\text{C}$ : It is ready to boil. If we add salt, its pressure, and therefore its chemical potential, are lowered (Fig. 4.8). Since the conditions for steam have not been changed, its chemical potential is now higher, meaning steam will condense, and water will not boil any longer at  $100^\circ\text{C}$ . Put differently, steam (water) flows into the salty water, diluting it, like in osmosis. We have to raise the temperature of the salt water to balance the chemical potentials



**Figure 4.8:** The chemical potentials of steam and water decrease with temperature. At low temperature, the potential of steam is higher than that of water. The potentials are equal at  $100^\circ\text{C}$ . If we add salt to water, the solute lowers the pressure (and therefore the chemical potential) of water. A new (higher) boiling point is established.



**Figure 4.9:** Red blood cells first shrink when a solute is introduced in an isotonic watery solution. Then they slowly regain their original size. Data by Macey and Oster.

**Table 4.1: Heating Values of Fuels**

Fuel	Formula	Higher Heating Value / kJ/kg <sup>a</sup>
Carbon	C	32,800
Hydrogen	H <sub>2</sub>	141,800
Methane	CH <sub>4</sub>	55,530
Methanol	CH <sub>4</sub> O	22,660
Ethanol	C <sub>2</sub> H <sub>6</sub> O	29,670
Propane	C <sub>3</sub> H <sub>8</sub>	50,330
Gasoline	C <sub>n</sub> H <sub>1.87n</sub>	47,300
Natural Gas	C <sub>n</sub> H <sub>3.8n</sub> N <sub>0.1n</sub>	50,000

a. For liquid water in products (the Lower Heating Value is defined for gaseous water in products).

of steam and water again.

**Blood cells in a solution.** Red blood cells are placed into an isotonic watery solution. Nothing should happen. If we now introduce a solute that can cross the cell membranes in the bath, the cells shrink rapidly at first by about 10%. Then they slowly regain their original volumes (Fig. 4.9).

*Interpretation.* The added solute raises the concentration of dissolved substances in the bath relative to the inside of the cells. Two things happen: The solute will travel into the cell (diffusion), and water will flow out of the cell into the bath (osmosis). Since only the amount of water in a cell effectively determines its volume, the volume of the cells shrinks (Fig. 4.9).

At a certain point, the flow of water stops (the chemical potentials of water inside and outside have become equal). However, the permeable solute continues to diffuse (it only reacts to gradients of its own species, not to total dissolved substance like water). Since the concentration of solutes continues to grow inside the cells, water changes its direction of flow. The cells grow (Fig. 4.9).

**Burning hydrogen.** Burning fuels is a chemical reaction that proceeds voluntarily (they have to be ignited, but than the run by themselves). Take the example of burning hydrogen with oxygen which produces water. Depending on the type of fuel, a certain amount of heat is produced per mole of fuel.

*Interpretation.* A mixture of 1 mole of hydrogen gas and 0.5 moles of oxygen gas has a higher chemical potential than one mole of water which results from the reaction. The starting substances “run downhill” (down a gradient of chemical potential) in the reaction and therefore release a certain quantity of energy. In burning, the energy is used to produce entropy. The entropy—and therefore the energy—available for heating other substances is given by the entropy produced and the change of entropy of the species taking part in the reaction (normally, products have more or less entropy than the reactants).

The entropy produced can be used to determine the amount of energy released per mole of hydrogen. This then allows us to determine the chemical potential difference between reactants and products.

**Batteries and fuel cells.** Batteries and fuel cells are devices that allow us to use voluntary chemical reactions to set up a voltage and drive an electric current. The open circuit voltage of electrochemical cells are between about 1 and 4 Volts.

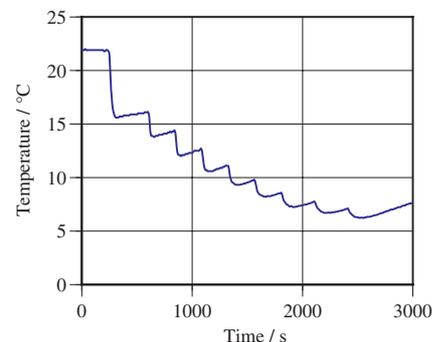
*Interpretation.* Voluntary chemical reactions release energy. In electrochemical cells, the energy is used not to produce entropy but to pump electric charge (in reality, a part of the energy released is always used for entropy production: processes are not ideal). The power of the electric process depends upon the electric current and the voltage set up. Analogously, the power of the chemical process depends upon the chemical driving force and the rate of the reaction. By measuring the electric quantities and the rate of reaction, the chemical driving force can be inferred. For example, results for a fuel cell that uses hydrogen and oxygen yield the same value for the chemical driving force as measurements on burning hydrogen.

**Citric acid and baking soda.** A small amount of water (about 50 g) is put in a paper cup. Then some 15 g of citric acid ( $\text{H}_3\text{C}_6\text{H}_5\text{O}_7$ ) are dissolved in it. It is observed that the temperature of the solution decreases from  $22^\circ\text{C}$  to about  $15^\circ\text{C}$  (Fig. 4.10). Then, baking soda ( $\text{NaHCO}_3$ ) is added six times (2 g each time). There is a strong reaction, gas is produced, and the temperature of the solution decreases again every single time. In between, the temperature increases slowly.

*Interpretation.* The dissolution of citric acid in water is like a chemical reaction: We go from a solid substance to an aqueous form (dissolved in water). Dissolved citric acid contains more entropy than the solid form. This entropy is taken from the water, making the solution colder.

The reaction of citric acid with baking soda clearly releases energy which must produce entropy. Still, the temperature of the solution continues to fall. We conclude that the product of this reaction (sodium citrate, carbon dioxide, and water) take much more entropy than can be produced in the reaction running by itself. The water of the solution must provide the entropy. Therefore, its temperature drops.

Each time the temperature decreases, the form of the data taken indicates that the reaction proceeds quickly at first and then slows down. This is what has been observed before in reactions. In between adding the substances and letting them react, the temperature increases because of the warmer environment.



**Figure 4.10:** Temperature of water in a cup (first horizontal), during and after dissolving citric acid (first drop), and during and after adding baking soda six times.

## 4.2 AMOUNT OF SUBSTANCE

In everyday life we are accustomed to measure quantities of substances in terms of their weight or mass, or by their volumes. It is important to realize that chemical processes cannot be explained on the basis of such measures.

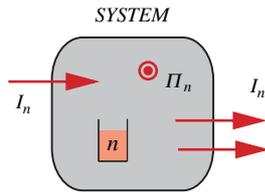
### 4.2.1 Amount of substance and particles

There is a picture that sheds additional light on the concept of amount of substance. We think of the elements as composed of *particles*, so called atoms (examples: H, Cl, O...). Atoms can combine to molecules (examples:  $\text{H}_2\text{O}$ ,  $\text{ClO}_2$ ...). Now, we have equal amounts of substance of different substances if they have the same number of particles. 1 mole—the unit of amount of substance—corresponds to  $N_o = 6 \cdot 10^{23}$  particles. This number is called Avogadro constant.

### 4.2.2 Balance of amount of substance

**Law of balance for systems with transports.** If only transports are allowed, the amount of substance  $n$  stored in a system changes because of flow of amount of substance  $I_n$  only. The sum of all flows determines the rate of change of  $n$ :

$$\dot{n} = I_{n,net} \quad (4.1)$$



**Figure 4.11:** Graphical representation of the general law of balance of amount of substance. Substances can be transported, and they can be produced or destroyed.

**Law of balance for reactions.** Reactions lead to the destruction or production of chemical species. A process of production (or destruction) is described in terms of a production rate (analogous to the production rate of entropy in thermal processes). The rate at which the amount of a certain substance changes is determined by the sum of all production rates:

$$\dot{n} = \Pi_{n,net} \quad (4.2)$$

**General law of balance.** If both transports and reactions are allowed, the rate of change of the amount of substance is determined by the sum of all flows and all production rates (Fig. 4.11). A substance can be transported in two ways. It can diffuse through some material, and it can be carried by a fluid (if it is dissolved in this fluid). The latter process is called convection. Therefore we have

$$\dot{n} = I_{n,net,cond} + I_{n,net,conv} + \Pi_{n,net} \quad (4.3)$$

### 4.2.3 Molar quantities

Quantities that are stored in materials or that are otherwise substancelike—such as entropy, mass, charge, volume—can be referred to the amount of substance of the body. We use small letters with an overstrike to denote the molar quantities. Here are molar entropy and molar volume:

$$\bar{s} = S/n, \quad \bar{v} = V/n \quad (4.4)$$

The well known molar mass is defined analogously:

$$M_o = m/n \quad (4.5)$$

### 4.2.4 Different measures of concentration

Concentration measure are used to express indirectly amounts of substance of a particular species—the solute—dissolved in a solvent. There are many different measures called *concentration*.

**Mass fraction.** This is defined as the mass of the solute ( $s$ ) of a species divided by the total mass of the solution (solvent  $f$  and solutes  $s$ ):

$$x = m_s / (m_f + m_s) \quad (4.6)$$

**Molar (or mole) fraction.** The ratio of the amount of substance of a species  $i$  and the total amount of substance of the solution:

$$\chi = n_s / (n_f + n_s) \quad (4.7)$$

**Mass-volume fraction.** This is the ratio of the mass of the solute and the volume of the

total solution (even though it looks suspiciously like the standard density, it should not be confused with this concept):

$$z = m_s / V_{\text{solution}} \quad (4.8)$$

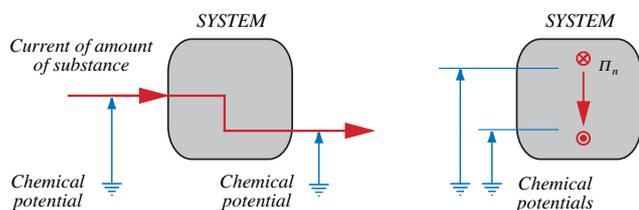
**Molar concentration (molarity, unit M = mole/liter).** This is the standard measure of concentration used in much of the following. It is defined as the amount of substance (dissolved) divided by the total volume of the solution:

$$c = n_s / V_{\text{solution}} \quad (4.9)$$

**Molality and molinity.** These terms denote the ratio of amount of substance to the mass of the solvent (molality) or the total mass of the solution (molinity). An example is given in Fig. 4.3 (center).

### 4.3 CHEMICAL POTENTIAL AND CHEMICAL DRIVING FORCE

The chemical potential measures the tendency of substances to change or to migrate. It is analogous to pressure, electrical potential, or temperature (Fig. 4.12).



**Figure 4.12:** Process diagram for flows of amount of substance. (left) or production and destruction of species (right). The chemical potential is like the level of a substance. Differences of chemical potentials denote driving forces of the transport of a species.

#### 4.3.1 Chemical potentials

Every substance can be assigned a chemical potential. Since the potential depends upon many factors, values are listed for standard conditions (25°C, pressure of 1 bar, concentration of 1 M, etc.).

The chemical potential is absolute. However, to simplify handling of the values, the chemical potentials of the elements—from which the substances are made—are assigned a value of zero in their most stable configuration. Therefore the chemical potential of a compound basically measures how much energy is needed to make the substance from the elements (if its chemical potential is positive) or how much energy is released when it is formed (if its potential is negative).

**Table 4.2: Chemical potential of substances**

Formula	Substance	Chemical potential/ kJ/ mole <sup>a</sup>
C (s) <sup>b</sup>	Carbon	0
C <sub>2</sub> H <sub>2</sub> (g)	Ethyne	209.20
CH <sub>4</sub> (g)	Methane	– 50.89
CH <sub>4</sub> O (l)	Methanol	– 166.35
C <sub>7</sub> H <sub>8</sub>	Toluene (g) Toluene (l)	122.39 110.61
Cl <sup>–</sup> (aq)	Chlorine ion	– 131.26
CO <sub>2</sub> (g) CO <sub>2</sub> (aq)	C. dioxide	– 394.40 – 385.99
FeS (s)	Iron sulfide	– 100.47
H <sub>2</sub> (g)	Hydrogen	0
H <sub>2</sub> O (g) H <sub>2</sub> O (l) H <sub>2</sub> O (s)	Water	– 228.60 – 237.18 – 236.59
MgS (s)	Magnesium sulfide	– 341.72
NH <sub>3</sub> (g)	Ammonia	– 16.40
Na <sup>+</sup> (aq)	Sodium ion	– 261.89
NaCl (s)	Table salt	– 384.03
O <sub>2</sub> (g) O <sub>2</sub> (aq)	Oxygen	0 16.44
ZnS (s)	Zinc sulfide	– 201.29

a. At standard conditions: 298.15 K, 101,325 Pa, pure or 1 mole/l.

b. (s) solid, (l) liquid, (g) gaseous, (aq) aqueous

The chemical potential is given the unit Gibbs (Joule/mole, see Table 4.2 for examples). Differences in chemical potentials between substances indicate a driving force for a reaction, while differences of the potential of a substance in different environments measures a drive of the substance to migrate (see Section 4.3.3).

### 4.3.2 Dependence of chemical potentials on other factors

Chemical potentials of substances depends upon many factors such as temperature (steam condenses at room temperature), concentration (water migrates from a piece of fresh bread to a dry piece in the same bag), pressure (water flows from points of high to low pressure, chemical reactions are influenced by pressure changes).

**Temperature dependence of the chemical potential.** If changes are not too great, one can always approximate the dependence of the chemical potential by a linear expression:

$$\mu(T, p_{ref}) = \mu(T_{ref}, p_{ref}) + \alpha_{\mu} (T - T_{ref}) \quad (4.10)$$

*ref* refers to a reference state. It can be proved that the temperature coefficient  $\alpha_{\mu}$  is equal to the negative molar entropy (entropy per amount of substance) of the substance:

$$\alpha_{\mu} = -\bar{s} \quad (4.11)$$

Some temperature coefficients of the chemical potential are listed in Table 4.3.

**Pressure dependence of the chemical potential.** As in the case of temperature, the chemical potential can be approximated by a linear relation:

$$\mu(T_{ref}, p) = \mu(T_{ref}, p_{ref}) + \beta_{\mu} (p - p_{ref}) \quad (4.12)$$

The pressure coefficient  $\beta_{\mu}$  of the chemical potential is equal to the molar volume of the substance:

$$\beta_{\mu} = \bar{v} \quad (4.13)$$

Some values of the pressure coefficient are listed in Table 4.3. For *incompressible fluids* such as water we therefore have

$$\mu(T, p) = \mu(T, p_{ref}) + (p - p_{ref})\bar{v} \quad (4.14)$$

In the case of the *ideal gas*, the chemical potential depends upon the pressure as follows:

$$\mu(T, p) = \mu(T, p_{ref}) + RT \ln \left( \frac{p}{p_{ref}} \right) \quad (4.15)$$

Table 4.3: Temperature and pressure coefficients of the chemical potential of substances<sup>a</sup>

Substance	$\alpha_{\mu} / \text{G/K}$	$\beta_{\mu} / \mu\text{G/Pa}$
C (s) <sup>b</sup>	- 5.69	5.4
C2H2 (g)	- 200.83	
CH4 (g)	- 186.10	24465
C7H8 (g)	- 319.70	
C7H8 (l)	- 219.00	
CO2 (g)	- 213.68	24465
CO2 (aq)	- 113.00	
CaCO3 (s)	- 92.88	36.92
Cl- (aq)	- 56.48	18.0
Fe (s)	- 27.3	7.1
Fe2O3	- 87.4	30.4
H2 (g)	-131	24465
H2O (g)	- 188.72	24465
H2O (l)	- 69.91	18.07
H2O (s)	- 44.77	19.73
Na+ (aq)	- 58.99	- 1.6
NaCl (s)	- 72.13	27.02
O2 (g)	- 205.02	24465
PbSO4 (s)	- 148.57	48.2
SiO2 (s)	- 41.46	22.6
ZnS (s)	- 57.74	23.89

a. At standard conditions: 298.15 K, 101,325 Pa, pure or 1 mole/l.

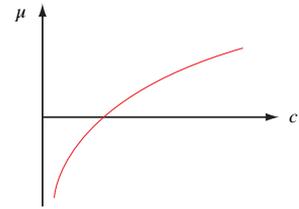
b. (s) solid, (l) liquid, (g) gaseous, (aq) aqueous

**Concentration dependence of the chemical potential.** In the case of solutions that are not too strong, the (partial) pressure of the dissolved substance in the solution obeys the equation of state of the ideal gas.

$$\begin{aligned} p_g V &= nRT && \text{ideal gas} \\ p_s &= RcT && \text{solute of dilute solution} \\ p_w &= p_a - p_s && \text{solvent (water)} \end{aligned} \quad (4.16)$$

Therefore, Equ. 4.15 holds as well for the pressure  $p_s$  of a solute. Since the concentration of the solute is proportional to the pressure, the same form must hold for the concentration dependence of the dissolved substance (Fig. 4.13):

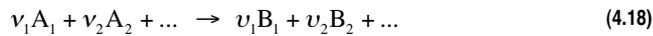
$$\mu(T, c) = \mu(T, c_{ref}) + RT \ln \left( \frac{c}{c_{ref}} \right) \quad (4.17)$$



**Figure 4.13:** The chemical potential of a dilute substance (solute in solution, ideal gas) depends logarithmically upon its concentration.

### 4.3.3 Driving force of a reaction

Consider a chemical reaction involving several reactants ( $A_i$ ) and several product substances ( $B_j$ ) such as



Each of the substances has its own chemical potential (dependent upon conditions). Figuratively speaking, the substances on one side of the reaction equation “band together against” the other side. This means that we have to add up the chemical potentials on each side to obtain its strength or drive to change (the stoichiometric coefficients have to be used as factors). Finally, the difference of the sum of the potentials on each side provides the proper measure of the chemical driving force of the reaction:

$$[\Delta\mu]_{\text{Reaction}} = v_1 \mu_{B1} + v_2 \mu_{B2} + \dots - (v_1 \mu_{A1} + v_2 \mu_{A2} + \dots) \quad (4.19)$$

If  $[\Delta\mu]_{\text{Reaction}} < 0$ , the reaction proceeds from left to right. If  $[\Delta\mu]_{\text{Reaction}} > 0$ , it proceeds in the opposite direction.  $\mathcal{A}_{\text{Reaction}} = -[\Delta\mu]_{\text{Reaction}}$  is called the *chemical tension* or *driving force* (compare to electric voltage).

### 4.3.4 Chemical equilibrium

Typical reactions run and then stop; the same holds for transports of substances. When they are finished, equilibrium has been established (analogous to equilibrium in communicating containers, or in thermal equilibrium for bodies in thermal contact). For chemical reactions, the condition of equilibrium is

$$[\Delta\mu]_{\text{Reaction}} = 0 \quad (4.20)$$

If the substances A and B in a simple reaction  $A \leftrightarrow B$  are dissolved in solvents, or if they are gases, their chemical potentials depend logarithmically upon concentration. Therefore, the equilibrium condition leads to

$$0 = \mu_A^0 - \mu_B^0 + RT \ln\left(\frac{c_A^{eq}}{c_A^0}\right) - RT \ln\left(\frac{c_B^{eq}}{c_B^0}\right)$$

The index 0 refers to standard conditions, *eq* stands for equilibrium. Let us define the equilibrium constant  $\mathcal{K}$  of this reaction:

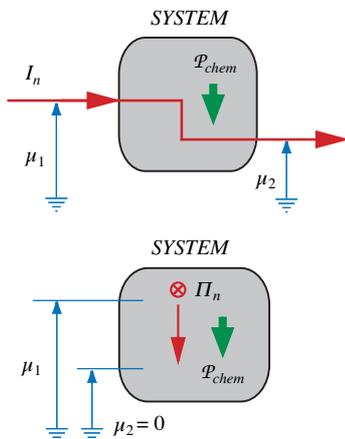
$$RT \ln(\mathcal{K}) = \mu_B^0 - \mu_A^0 = [\Delta\mu]_{Reaction}^0 \quad (4.21)$$

which yields

$$\frac{c_A^{eq}}{c_A^0} \frac{c_B^0}{c_B^{eq}} = \mathcal{K} \quad (4.22)$$

Analogous results are obtained for more general equations (stoichiometric coefficients in the reaction equation appear as powers of the concentrations in Equ. 4.22; this is why the standard concentrations—which are equal—do not always cancel in this equation, and that is why they are left in Equ. 4.22). Since a transport of a substance from environment A to environment B can be interpreted as a reaction of the form  $A \leftrightarrow B$ , the result also applies to diffusion.

Processes can be started on either side of equilibrium, meaning that a reaction can run in both directions of a reaction equation (Fig. 4.4). If they appear to run only in one direction, it is because equilibrium is obtained only when one species is almost completely consumed (as in radioactive decay, Fig. 4.5, in the decay of murexide, Fig. 4.6, or in the reaction of hydrogen and oxygen forming water). Reactions can be driven away from equilibrium by “intervention” (a battery can be recharged by applying an electric voltage from outside).



**Figure 4.14:** When a substance is flowing from higher to lower chemical potential, or if a substance is consumed in a chemical reaction, energy is released.

## 4.4 ENERGY IN CHEMICAL PROCESSES

Energy plays the same role in chemical processes as in all other phenomena studied so far. It is released when a substance “runs downhill,” used or bound when a substance is produced or pumped, and it is transported into and out of systems together with currents of substance. It can be stored in systems together with substances.

### 4.4.1 Releasing energy in chemical processes

When a substance flows from higher to lower chemical potential, energy is released (Fig. 4.14). The same is true when a substance is consumed. In the reverse process, energy is bound. The rate at which energy is released is called *chemical power*:

$$\mathcal{P}_{chem} = -\Delta\mu I_n \quad , \quad \mathcal{P}_{chem} = -\mu \Pi_{A_i} \quad (4.23)$$

### 4.4.2 Power of chemical reactions

In a chemical reaction, several different species are involved. Some of them are consumed (releasing energy), others are produced (requiring energy). Overall, the chemical driving force and one of the production rates determine the power of the process:

$$\mathcal{P}_{reaction} = \frac{1}{\nu_i} [\Delta\mu]_{reaction} \Pi_{A_i} \quad (4.24)$$

### 4.4.3 Energy transport

Chemical substances can be transported. When they enter (or leave) a system at a certain value of the chemical potential, there is an associated energy current:

$$I_w = \mu I_n \quad (4.25)$$

### 4.4.4 Entropy Production in Chemical Processes

The energy released in chemical processes is often dissipated (another important use of energy in chemical reactions is for electrical processes; see Section 4.7). If it is dissipated, entropy is produced at a rate that depends upon the power of the chemical process, and the temperature at which entropy production takes place (see Fig. 4.15).

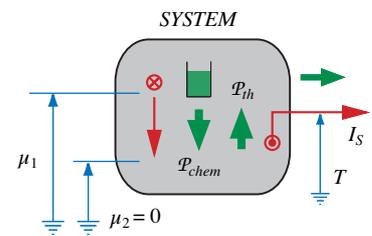


Figure 4.15: Entropy is produced in dissipative chemical processes (this is the most typical chemical process).

## 4.5 TRANSPORT OF SUBSTANCES

Substances can flow—or be transported—in two different ways. First, they can migrate by themselves *through* materials. This is called diffusion. Second, they can be transported *with* other materials, such as water, where they are contained.

### 4.5.1 Diffusion

Imagine particles with a density  $c$  in an environment (such as a liquid solvent). The current of amount of substance due to diffusion of these particles is equal to the product of cross section  $A$ , concentration  $c$ , and drift speed  $v_d$  (Fig. 4.16). The drift speed is modeled as the result of a chemical driving force  $\Delta\mu = \mu(x_2) - \mu(x_1)$ . If we take the resulting speed to be proportional to the driving force per unit distance (with a factor called the diffusion constant  $D$ ), we get

$$I_n = -ADc \Delta\mu/\Delta x \quad (4.26)$$

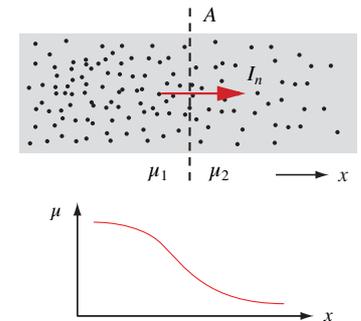


Figure 4.16: Substances diffuse from places where the chemical potential is high (due to high concentration) to places where the potential is lower.

$\Delta\mu/\Delta x$  is called the gradient of the chemical potential. The minus sign indicates that the flow is positive in the direction of decreasing chemical potential of the diffusing substance.

If the chemical potential of the substance depends logarithmically upon the concentration  $c$ , small differences of  $m$  are equal to  $\Delta c/c$ . If we introduce the current density  $j_n = I_n/A$ , diffusive currents are given by

$$j_n = -D \frac{dc}{dx} \quad (4.27)$$

The term  $dc/dx$  is called the *concentration gradient*. It can be replaced by  $\Delta c/\Delta x$  for intervals where  $c$  changes linearly with position. Note that Equ. 4.27 is analogous to Ohm's law (Chapter 2) or Fourier's law (Chapter 3).

#### 4.5.2 Transport between different environments

Substances flow from one environment into another as long as there is a difference of the chemical potentials of the substance in these environments. If the substance is dissolved, its chemical potential depends logarithmically upon its concentration. Therefore

$$\Delta\mu_{Transport} = \mu_B^{eq} - \mu_A^{eq} + RT \ln\left(\frac{c_B}{c_B^{eq}}\right) - RT \ln\left(\frac{c_A}{c_A^{eq}}\right) \quad (4.28)$$

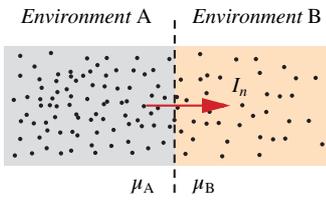
The condition of equilibrium has been chosen as the reference point for calculating the chemical potential. A and B refer to the substance in environments A and B. The difference of chemical potentials in equilibrium must be zero. For small deviations from equilibrium, the difference of the logarithms becomes

$$\Delta\mu_{Transport} = -RT \ln\left(\frac{c_A}{c_A^{eq}} \frac{c_B^{eq}}{c_B}\right) \approx -RT \left(1 - \frac{c_A}{c_A^{eq}} \frac{c_B^{eq}}{c_B}\right)$$

Since the current of amount of substance is taken to be proportional to the difference of the chemical potentials and to the concentration of the substance in the originating environment A, we have

$$\begin{aligned} I_n &= -Ak' c_A \Delta\mu_{Transport} = Ak' c_A RT \left(1 - \frac{c_A^{eq}}{c_A} \frac{c_B}{c_B^{eq}}\right) \\ &= Ak \left(c_A - \frac{c_A^{eq}}{c_B^{eq}} c_B\right) \end{aligned}$$

The observations on the migration of toluene in water and air (Fig. 4.3, right) demonstrate that there is a simple relation between concentrations in the two environ-



**Figure 4.17:** Diffusive transport of a substance from one environment into another (such as from water to air, or from soil to water) is caused by a chemical potential difference.

ments in equilibrium:

$$c_A^{eq} / c_B^{eq} = \mathcal{K} \quad (4.29)$$

Therefore, the constitutive law for transport from A to B can be written as

$$I_n = -Ak(c_A - \mathcal{K}c_B) \quad (4.30)$$

$Ak$  may be interpreted as a kind of conductance. The expression in Equ. 4.30 can be generalized to one where the equilibrium relation is not constant, such as for toluene in water and soil (Fig. 4.3, center). For this example, the term in parentheses in Equ. 4.30 would change to  $c_w - \mathcal{K}c_s^\alpha$ .

### 4.5.3 Convective transports

Convection means transport of a substance with a fluid it is stored in. The current of amount of substance must therefore depend upon the volume current of the fluid and the concentration of the substance in this fluid:

$$I_n = cI_{V,fluid} \quad (4.31)$$

### 4.5.4 Dynamical models

Dynamical models are obtained by introducing the flows of a species into its law of balance. Take the example of flow of a species from environment A to B (Equ. 4.30):

$$\frac{dn_A}{dt} = -Ak(c_A - \mathcal{K}c_B)$$

$n_A$  symbolizes the amount of substance of this species in environment A. If the volume of this environment is  $V_A$ , we have

$$\frac{dc_A}{dt} = -\frac{1}{V_A} Ak(c_A - \mathcal{K}c_B) \quad (4.32)$$

as the differential equation for the molar concentration of the species in volume  $V_A$ .

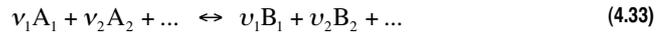
## 4.6 KINETICS OF CHEMICAL REACTIONS

To describe the dynamics of chemical reactions, we need to be able to express the *production rates* of the species in the equations of balance. The rates are called *reaction rates*. The most important factor affecting these rates are the chemical potentials which depend upon concentrations (naturally, there are many other factors such as pressure and temperature affecting the potentials; however, we will only in-

investigate the role of concentrations of gases or dissolved substances). Apart from the chemical potentials (here: the concentrations), there are parameters facilitating a reaction such as the mobility of the particles. These factors will be considered constant, simply depending upon conditions of the environment of the reaction substances.

#### 4.6.1 Relations between production rates in chemical reactions

A chemical reaction such as in Equ. 4.33 can run in both directions, depending upon which side of the final equilibrium conditions the reactants and products are on. When the chemical driving force is positive, the reaction is assumed to go from left to right:



There is a production (or destruction) rate for every species taking part in the reaction. These are not independent. In fact, there is a single reaction rate which can be taken to be one of the production rates. All the other rates depend upon this single rate:

$$\Pi_{A1} = \frac{v_2}{v_1} \Pi_{A2} = \dots = -\frac{v_1}{v_1} \Pi_{B1} = -\frac{v_2}{v_1} \Pi_{B2} = \dots \quad (4.34)$$

#### 4.6.2 Reaction rates for simple reactions

The expressions for production or reaction rates are derived just as the flow of a species from one environment into another was determined (Section 4.5.2). For a simple reaction  $A \leftrightarrow B$  (such as the decay of  $\alpha$ -glucose) we have:

$$\Pi_A = -k' c_A [\Delta\mu]_{Reaction} \quad (4.35)$$

which, when linearized and introduced in the equation of balance Equ. 4.2, yields

$$\frac{dc_A}{dt} = -k(c_A - \mathcal{K}c_B) \quad (4.36)$$

A chemical reaction involving two species on either side of the reaction such as the decay of murexide, i.e.,  $A + B \leftrightarrow C + D$ , leads to

$$\frac{dc_A}{dt} = -k(c_A c_B - \mathcal{K}c_C c_D) \quad (4.37)$$

$\mathcal{K}$  is the equilibrium constant for the reaction, and  $k$  depends upon circumstances. It is important to note that Equ. 4.36 and Equ. 4.37 are two of the simplest possible results for the form of reaction equations. As long as reactions lead to equilibria of the form derived in Equ. 4.22 (which itself is just a simple example of its kind), we

can expect reaction equations like the ones derived here. In general, however, reactions are much more complex. Often, reactions proceed in several steps from the reactants to the products, where the intermediate reactions might not be known. Therefore, reaction rates often involve powers of the concentrations of the species in the reaction equations. These powers, along with the reaction constants  $k$ , have to be treated as unknowns, to be determined by comparing models and experimental data.

One more point is of interest here. The form of the reaction equations was derived by assuming a linear reaction law involving the chemical driving force. Then, the logarithmic dependence of the chemical potentials upon concentrations was introduced, and it was assumed that the reactions proceed not too far from equilibrium. Especially the last point is not satisfied in general in real cases. However, it is found that forms such as Equ. 4.36 or Equ. 4.37 work well for conditions far from equilibrium. This means that reaction rates depend in a more complicated way upon the chemical driving force than was assumed here, and the typical linear approaches have to be generalized.

## 4.7 ELECTROCHEMICAL PROCESSES

So far, we have considered the chemical aspects of chemical processes only (with the exception of the question of entropy production, Section 4.4.4). We know from experience, however, that chemical processes can be related to other phenomena as well. In particular, since substances may be ionized, phenomena involving substances often involve electricity as well. Moreover, since substances have mass, chemical and gravitational processes can be coupled as well.

### 4.7.1 The electrochemical potential

Consider a current of ions having a certain chemical potential and an electric potential. The energy current associated with this flow is the sum of the chemical and the electric energy current:  $I_W = \mu I_n + \varphi I_Q$ . Since the substance is ionized, charge and amount of substance are coupled by

$$I_Q = \frac{ze}{N_o} I_n = z\mathcal{F} I_n \quad (4.38)$$

$\mathcal{F} = e/N_o$  is called Faraday constant ( $\mathcal{F} = 96487 \text{ C/mole}$ ),  $e = 1.6 \cdot 10^{-19} \text{ C}$  is the charge of a singly charged particle (the elementary charge),  $N_o$  is Avogadro's constant, and  $z$  is the charge number indicating how many times the particle is ionized (typically,  $z = \pm 1$  or  $\pm 2$ ). Now, introduce this expression for  $I_Q$  in the expression for  $I_W$ :

$$I_W = \mu I_n + \varphi z \mathcal{F} I_n = (\mu + \varphi z \mathcal{F}) I_n$$

The terms in parentheses are called the electrochemical potential:

$$\mu_{EC} = \mu + \varphi z \mathcal{F} \quad (4.39)$$

If ions are flowing (and undergoing reactions), we can consider differences of the electrochemical potential as the *combined driving force* acting on a substance.

### 4.7.2 Electrochemical cells

In an electrochemical cell (a fuel cell or a battery), chemical reactions that run by themselves release energy which is used to drive an electric current through a voltage. Put differently, a voltage is established by the chemical reactions. If the process could proceed reversibly, the balance of power would lead to

$$\frac{1}{\nu_1} [\Delta\mu]_{\text{Reaction}} \Pi_{A1} = U z \mathcal{F} \Pi_{A1}$$

$U$  is the open circuit voltage established by the cell. The reaction rate and the electric current are related by Equ. 4.38 (where  $z$  is the number of electrons involved in the reaction). Therefore, we have

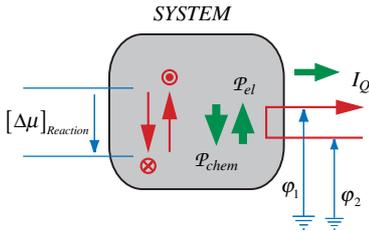
$$U_{OC} = \frac{[\Delta\mu]_{\text{Reaction}}}{\nu_1 z \mathcal{F}} \quad (4.40)$$

### 4.7.3 Ion transfer through membranes

Many important biological functions—including those of nerve cells and the conduction of nerve signals—involve the (selective) transfer of ions across membranes of cells. Having different ions at different concentrations across membranes establishes an electric membrane potential. An important relation for calculating such membrane potentials has to do with the equilibrium of different species of ions on either side of the membrane. If a species is in equilibrium, its electrochemical potential difference must be zero (not the chemical potential difference, or the electrical potential difference!). Since the chemical potential of ions in and around cells is given by the logarithm of the concentrations, the condition of equilibrium leads to

$$\Delta\varphi_{iN} = -\frac{RT}{z\mathcal{F}} \ln\left(\frac{c_{i1}}{c_{i2}}\right) \quad (4.41)$$

for this species. This voltage is called the Nernst potential if substance  $i$ . 1 and 2 denote the outside and the inside of the membrane. Note that if different dissolved ionic substances are present, the real electric potential difference across a membrane will likely be different; species  $i$  will not be in equilibrium. Still, the Nernst potential will be calculated by Equ. 4.41.



**Figure 4.18:** Process diagram of an electrochemical pump (a battery or similar device). Energy is released in a chemical reaction. The energy is used to drive an electric current.