Chemistry
Cube
Game

Instructions

Playing chemistry by turning cubes with different chemical species

by Markus T. Müller

For Sophie and Bärbel

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Distribution:	www.vsn-shop.ch

Content

* Games for School Box (204 Cubes)

Homepage: www.swisschemcube.ch

Abstract

The Chemistry Cube Game consists of 16 different cubes. The cubes can be turned in those directions indicated by the letters. Each allowed vertical or horizontal turn of 90° stands for a chemical reaction or a physical transition. New is especially the positioning of different chemical species of corresponding acids and bases, as well as species of reducing and oxidising agents such as metals and non-metals and their corresponding cations and anions, respectively. Other aspects such as precursors or phase transfer processes of these species are shown on the cubes.

This game focuses on one hand on the speciation of different acid and base species, and on the other hand of elementary metals (Me°) and the corresponding metal-cations (Me^{x+}) as well as of non-metals (O_2°) and their anions (O^{2-}). In addition the origin of the substances, as well as phase transitions and solubility equilibria of gases in water have been considered and are shown on the cubes so that the different turning options, that are possible, chemically make sense.

Different chapters of chemistry teaching such as salts, chemical equilibrium, acid and bases as well as redox chemistry, but also different topics of environmental chemistry can be experienced playing with the chemistry cubes.

In the first chapter the basics of salt formation, combination (to derive) of salt formulas and their ion-notation, solvation (Lösevorgänge) and crystallization can be worked out.

Another focus of the game lays in the acid and base species that are present at different pH-values. The aspect of pH and pK_a-values can be easily experienced. The titration of an acid or a base can be played as well.

The games in redox chemistry start with the formation of salts starting with the different elementary substances such as metals an non-metals. Using oxidation numbers redox reactions can be recognized and partial reactions of the oxidation and the reduction can be written down correctly.

Environmental chemistry starts with the carbon cycle and the different equilibria that have to be considered. Acidic rain are treated using the examples of sulfuric and nitric acid. Here we follow the goal, to demonstrate complex connections between different reactions and to discover their dependence of ambient conditions, such as pH-value, temperature, pressure. The nitrogen cycle, where aerobic and anaerobic conditions play a major role, combines the different aspects and themes treated before.

Five years experience using the self made prototypes of the chemistry cubes have helped to create and write down the games for the different topics. But beside this, the cubes offer the possibility to create own ideas and new plying forms in the class room.

General Information

Idea of the Games

The major idea of Chemistry Cube Game includes the different forms or species, in which a compound or a substance, such as an acid or base, or a reduction- or oxidation media can occur in the environment. In addition to these species the precursors of a compound, e.g. nitric acid, are given on some of the cubes as well. The students can play and discover with the cubes many different reactions.

Content of the school box (204 cubes)

16 different cubes (total 204 cubes for 12 students or half a class):

Anz.		Anz.		Anz.		Anz.	
24	H_2O	12	NH_3	12	H_3PO_4	12	Pb, Sn
12	H_2S	12	HNO_2	12	Na, Mg, Al	12	N_2, O_2, S
12	H_2SO_3	12	HNO_3	12	Ca, Zn, Ag,	12	F_2, Cl_2, Br_2
12	H_2SO_4	12	H_2CO_3	12	Fe, Cu	12	blank

The blank cubes can be used for own ideas and other formulas. If you mail us your ideas for additional cubes we might produce them in the next edition.

Assembling the cubes

The cubes are printed, coated, grooved, punched, glued once and flat when they are delivered. They are ready to be assembled before the first use. They have to be folded and clicked together (e.g. with a class). Once assembled, the cubes should not be opened again, otherwise the plug in tongue may break. It is recommended to glue the connecting rims to close the cubes.

Storage of Cubes and Cleaning

After assembling the cubes can be stored and sorted in stable boxes (see picture below). We recommend 2 (or 4) UTZ-boxes of 40 x 30 x 12 cm (96 cubes/box) or 40 x 30 x 6.5 cm (48 cubes/box). These storage boxes are not included in the delivery of the school box.
As the cubes are coated with a protecting film, they can be cleaned with a moist tissue.

Playing Rules

Turn the cubes in those directions that are allowed by the letters, vertically and/or horizontally. If the letters stay up side down or in a 90° angle after a turn, then this transition or reaction normally is not possible directly.

In some games the cubes have to be played like a dice to get a probability effect (e.g. salt formulas) or might be stapled to create kind of a crystal structure.

Generally, gaseous species (g) are on the top of the cube, aqueous species on the sides (aq) and solid species as well as additional information on the bottom of the cubes (e.g. carbon cube, sulfur cubes).

Color change of the font generally indicates a chemical reaction, other than proton or electron transfer. Slight change of background color indicates electron transfer (redox reaction).

It is recommended to play on a table to prevent the cubes from damage or pollution.

Using laminated reaction arrows, equlibrium arrows and/or stochiometric coefficients (1, 2, 3, 4, 5, 6) quite complex reaction-schemes can be displayed on the table (see attachement). Students also created stop motion pictures e.g. for the reactions in the environmental chapter.

Color Change of Font or Background

Color change of the font generally indicates a chemical reaction, other than proton or electron transfer.

Slight change of background color indicates an electron transfer (redox reaction).

Acid and Base Cubes

Acid (Proton H^+ donor)	Turn the cube to the left.
Base (Proton H^+ acceptor)	Turn the cube to the right.

Turning a cube displays the different species of the acid and its corresponding bases. The acidity constants, pK_a-values, can be looked up at the bottom of the cubes, below the acid species. The idea is to look it up and memorize some of the values by playing.

pK_a-Values

The acidity constants, pK_a-values, used on the cubes were taken from "Formeln, Tabellen, Begriffe" by Orell Füssli Verlag (5. Edition).

pH-Value

The pH-value, as we use it here, is defined as follows: pH = -log $c(H_3O^+(aq))$. In the attachement you find a pH-scale, that can be printed out, laminated und used for the games of chapter 2.

Redox Reactions

The cubes with 2 or 3 different colors can be used for electron transfer reactions. The following terms are used:

Reduction medium (Electron donator)	Redm
Oxidation medium (Electron acceptor)	Oxm
Oxidation:	Turn the cube to the left.
Reduction:	Turn the cube to the right.

General redox reaction scheme:

$$\text{Reduction medium} \quad \underset{\text{Reduction}}{\overset{\text{Oxidation}}{\rightleftharpoons}} \quad \text{Oxidation medium} \; + \; \text{x Electrons} \qquad E°[V]$$

Metals and Metal-Ions

The cubes for metals and their ions can be used for redox chemistry or salt formation. If you turn a cube with an uncharged metal (e.g. Magnesium: Mg°) to the left, an oxidation step (electron donation) occurs and the Magnesium-Kation (Mg^{2+}) is formed. It has to be stated, that electron donation always requires the ionization energy (IE) and that they do not occur without an adequate oxidation media, such as O_2, F_2, Cl_2, S, etc. and usually also some activation energy (E_A) to start the reaction.

Standard reduction potentials (E° [V]) and /or ionization energies (IE) have not been printed to the cubes. If needed we recommend to hand out and use separate tables.

Non-Metals and their Ions

Thr cubes for non-metals and their ions can be used for redox chemistry or salt formation. If you turn a cube with an uncharged non-metal (e.g. Oxygen: O_2°) to the right, a reduction step (electron uptake) occurs and the oxygen-anion (O^{2-}) is formed.

Standard reduction potentials (E° [V]) and /or electron affinities have not been printed to the cubes. If needed we recommend to hand out and use separate tables.

Salts and their Ion-Notation

All the cubes can be used to derive salt formulas and for learning salt names. We follow the concept to use, besides the salt formula (e.g. Na_2CO_3), always the ion notation of the salt (2 Na^+ + CO_3^{2-}), too. The ion notation and the correct salt formula can be found easily using the cubes. Salt names can be

For students it is always a challenge to distinguish between the uncharged element substance (Mg°, Al°, O_2°, Cl_2°, S°), their ions (Mg^{2+}, Al^{3+}, O^{2-}, Cl^-, S^{2-}) and their salt formulas (MgO, $MgCl_2$, Al_2O_3, ...) formed in salt formation reactions. Using the chemistry cubes they train and learn the differentiation between the different species easily.

Color of the Cubes

In the following table the color chosen for the cubes are explained .

Nr		
1	H_2O	Color of water (turquis)
2	H_2S	Color of Sulfur (yellow) & Molymod color
3	H_2SO_3	
4	H_2SO_4	
5	NH_3	Color of Nitrogen in Molymod (blue)
6	HNO_2	
7	HNO_3	
8	H_2CO_3	Color of Carbon (Graphit) (grey)
9	H_3PO_4	Color of Phosphorus in Molymod (violet)
10	Na	-
10	Mg	-
10	Al	-
11	Ca	-
11	Zn	-
11	Ag	Color of Silver (Silver)
12	Fe	-
12	Cu	Color of Cupper (Cupper)
13	Pb	-
13	Sn	-
14	N_2	Color of Nitrogen in Molymod (blue)
14	O_2	Color of Oxygen in Molymod (red)
14	S	Color of Sulfur and color in Molymod (yellow)
15	F_2	Color of Fluorine-gas (slightly yellow)
15	Cl_2	Color of Chlorine-gas (slightly green-yellow)
15	Br_2	Color of Bromine-gas (orange)
16	leer	

Order Information

The cubes can be ordered as a School-Box containing 204 cubes (12 of each, for 1/2 class), as a Student Box containing 16 cubes (1 of each) or as replacement parts also individually at your local dealer (see homepage) or at the vsn-shop:

www.vsn-shop.ch

Age and Class-Level

For each game we tried to add a class level or age of the students, as suitable (green) or maybe suitable (orange). Feel free to use the games, or slightly modified versions, for younger or older students.

Age	10	11	12	13	14	15	16	17	18	>19
Class Level	4	5	6	7	8	9	10	11	12	FH
	PS	PS	PS	Sek I	Sek I	Sek I	Sek II	Sek II	Sek II	FH/HS

Teachers Role

The cubes allow the students learning by playing either following the game instructions (hand outs) or after a short introduction given by the teacher.

The teacher can act as a game leader, as a moderator or as performer of the experiment:

In e.g. the titration game the teacher can accompany the game with a real titration.

The teacher shall also decide in which form the students write down results in predefined tables or documentation forms. You will find some suggestions and tips in the different tutorials.

Role of the Students

Students can play alone, in groups or as a class with the chemistry cubes and learn by playing, note results and discuss them with one another. The games give students the opportunity to play different topics, as well as to learn and understand chemistry in a different way.

If you are setting up competitions, as suggested in some games, then students will find strategies by themselves to win against other groups.

ChemCube - Salt Formulas

4	5	6	7	8	9	10	11	12	HS

1.1 Salts, Salt Formulas, Ion Notation, Salt Names

Theory

Salts are ionic compounds. They consist of positively charged cations (+, 2+, 3+, ...) and negatively charged anions (-, 2-, 3-, ...). In the table next page you will find a list with the ion formulas, their charges and their correct names.

Salt names are set together from the name of the cations (e.g. Sodium-, Magnesium-, ...) followed by the name of the anion, usually with a salt ending (-id, -it, -at), as for example Chlor**id** (Cl^-), Sulf**id**- (S^{2-}), Sulf**it**- (SO_3^{2-}) or Sulf**at**-Ion (SO_4^{2-}).

Salts as compounds are uncharged, that means that the charges of the cations and the charges of the anions cancel each other. The ratio of cations and anions is given in the salt formula, but not in the salt name that consists only of the name of the cation and the name of the anion (1).

Example:	**x** Cations	+	**y** Anions	⟶	Salt Formula	
Formulas:	**1** Mg^{2+}	+	**2** Cl^-	⟶	$MgCl_2$	(1)
	Magnesium-Ion		Chlorid-Ion		Magnesiumchlorid	

Game 1: Chose a metal-cube (first row) and roll it until a cation lies side up. Chose and roll a non-metal cube (second row) until a anion lies up. Replenish the amount of cations (**x**) and anions (**y**) so that the charges of the ions cancel each other.

Note the ion ratio obtained - in a table as shown below - starting with the ion notation (1st step), the salt formula (2nd step) and the salt name (3rd step). Take care, that the salt name is unique. If there exists *more than one ion* of a species (e.g. Fe^{2+} and Fe^{3+}) you have to add the charge as oxidation numbers (roman numerals) to the name of the ion (Iron(II) or Iron(III)).

1. Ion Notation			
x Cations	**y** Anions	2. Salt Formula	3. Salt Name
1 Mg^{2+}	**2** Cl^-	$MgCl_2$	Magnesiumchlorid

Na^+	Mg^{2+}	Al^{3+}	Sn	Cu	Fe	Ca^{2+}	Zn	Ag^+
	°	°	N^{3-}	S^{2-}	O^{2-}	F^-	Cl^-	Br^-

ChemCube - Salt Formulas

1.1 Salts, Salt Formulas, Ion Notation, Salt Names (ff)

Table of Ions (**bold** printed ions should be known by heart)

Kation	***Name***	***Anion***	***Name***
Li^{+}	Lithium-	**F^{-}**	Fluoride
Na^{+}	Sodium-	**Cl^{-}**	Chloride
K^{+}	Potassium-	**Br^{-}**	Bromide
Ag^{+}	Silver-	**O^{2-}**	Oxide
Be^{2+}	Beryllium-	**S^{2-}**	Sulfide
Mg^{2+}	Magnesium-	**N^{3-}**	Nitride
Ca^{2+}	Calcium-	$(NO_2)^{-}$	Nitrite
Fe^{2+}, Fe^{3+}	Iron(II)-, Iron(III)-	**$(NO_3)^{-}$**	Nitrate
Cu^{+}, Cu^{2+}	Cupper(I)-, Cupper(II)-	**$(OH)^{-}$**	Hydroxide
Zn^{2+}	Zink-	$(CH_3COO)^{-}$	Acetate
Pb^{2+}, Pb^{4+}	Lead(II), Lead(IV)	**$(CO_3)^{2-}$**	Carbonate
Al^{3+}	Aluminium-	**$(HCO_3)^{-}$**	Hydrogencarbonate
Sn^{2+}, Sn^{4+}	Tin(II)-, Tin(IV)-	$(SO_3)^{2-}$	Sulfite
Ti^{2+}, Ti^{4+}	Titan(II)-, Titan(IV)-	**$(SO_4)^{2-}$**	Sulfate
Cr^{3+}, Cr^{6+}	Chromium(III)- / (VI)-	**$(HSO_4)^{-}$**	Hydrogensulfate
Ni^{2+}, Ni^{3+}	Nickel(II)-, Nickel(III)-	**$(PO_4)^{3-}$**	Phosphate
NH_4^{+}	Ammonium-	**$(HPO_4)^{2-}$**	Hydrogenphosphate
H_3O^{+}	Oxonium-Ion	**$(H_2PO_4)^{-}$**	Dihydrogenphosphate

Game 2: Many ions are set up as charged molecules. Chose a metal-cube (first row) and roll it until a cation lies side up. Chose and roll a cube from the lower row and combine new salts, note the salt formula and name it correctly.

Game 3: Chose a cation ***and*** an anion for your neighbour so that he/she can name the salt correctly.

Na^{+}	Mg^{2+}	Al^{3+}	Sn	Cu	Fe	Ca^{2+}	Zn	Ag^{+}
H_2CO_3	H_2SO_3	H_2SO_4	H_2S	NH_3	HNO_2	HNO_3	H_3PO_4	OH^{-}

ChemCube - Solvation of Salts

4	5	6	7	8	9	10	11	12	HS

1.2 Solvation of well soluble Salts

Theory

The solvation process of a salt - a ionic compound - in water can be described as follows:

general: Salt Formula(s) $\xrightarrow{\text{dissolve in } H_2O}$ Cations(aq) + Anions(aq)

example: NaCl(s) $\xrightarrow{\text{dissolve in } H_2O}$ Na^+(aq) + Cl^- (aq) (1)

Sodiumchloride — Sodium-Ion — Chloride-Ion

Highly and well soluble salts can be dissolved in water in bigger amounts. E.g. the maximum solubility of sodium chloride in water is 358 g/L. In such a solution about 4 to 5 water molecules account for one ion. Try to simulate this using 9 water cubes to surround a **Na^+**-cube ***and*** a **Cl^-**-cube in the 3 dimensional space.

Game: The better soluble salt wins (A: in [g/L] or B: in [mol ions/L])

Game for 3-4 students, 1 i-pad, tablet or computer with internet access.

1st player — choose a metal cube (1st row) and a non-metal cube from the 2nd or 3rd row. Note the formula and the correct name of the salt. Investigate and note the water solubility [g/L] and the molecular mass M [g/mol] of the salt formula. Check whether this salt "exists".

2nd player — choose **another cation** on a metal cube (1st row). Note the formula and name of the salt and look up water solubility [g/L] and M [g/mol]. Check whether this salt "exists". If the salt is better soluble than the first one, the 2nd player gets a point, otherwise the 1st player.

3rd player — choose **another anion** cube (2nd or 3rd row). Note the formula and name of the salt and look up water solubility [g/L] and M [g/mol]). Check whether this salt "exists". If the salt is better soluble than the last one, player 3 gets a point, otherwise player 2.

etc.

Find out: Which strategies are successful to win the game? Which rules can be derived for well soluble salts? Which ions can be used to form soluble salts?

Challenge: Ask another group for a challenge and try to beat them!

Na°	Mg°	Al°	Sn°	Cu°	Fe°	Ca°	Zn°	Ag°
	°	°	N_2°	S°	O_2°	F_2°	Cl_2°	Br_2°
H_2CO_3	H_2SO_3	H_2SO_4	H_2S	NH_3	HNO_2	HNO_3	H_3PO_4	OH^-

ChemCube - Solvation of Salts

4	5	6	7	8	9	10	11	12	HS

1.3 Solvation of hardly soluble Salts

Theory

Hardly soluble salts do only partially dissolve in water so that a significant sediment of salt remains. Between the sedimented salt and the dissolved ions the solubility equilibrium arises that can be described by a double arrow (equilibrium arrow) and the constant called solubility product K_L.

General: Salt formula(s) $\underset{}{\overset{K_L}{\rightleftharpoons}}$ Cation(aq) + Anion(aq)

Example: AgCl(s) $\overset{K_L}{\rightleftharpoons}$ Ag^{+}(aq) + Cl^{-} (aq) (1)

Silver(I)chloride — Silver-Ion — Chloride-Ion

This equilibrium constant can be mathematically described with the solubility product (2), where the concentrations of the dissolved ions are multiplied with one another:

Definition K_L: $$K_L(AgCl) = c(Ag^{+}(aq)) * c(Cl^{-}(aq)) = 2\cdot10^{-10}\ \frac{mol^2}{L^2} \qquad (2)$$

The solubility product is constant for a certain temperature. In the table next page pK_L-values are given for different hardly soluble salts and a way to estimate equilibrium concentration EEC.

Game: The harder soluble salt wins

Game for 3-4 Schüler/innen, 1 i-pad, tablet, or pc with internet access

1st player... choose a metal cube (1st row) and a non-metal cube from the 2nd or 3rd row. Note the formula and name of the salt, look up water solubility [g/L], molecular mass (M [g/mol]) and/or determine the estimated equilibrium concentration **EEC** in [mol/L] from pK_L-values.

2nd player ... choose another **cation** on a metal cube (1st row). Note formula and name of the salt, look up water solubility [g/L], molecular mass (M [g/mol]) and determine the EEC in [mol/L]. If the salt is ***less soluble*** (lower EEC) than the first one, player 2 gets a point, otherwise player 1.

3rd player ... choose another **anion** (2nd or 3rd row). Note formula and name of the salt, look up water solubility [g/L] and its molecular Mass (M [g/mol]). If the salt is ***less soluble*** (lower EEC) than the last one, player 3 gets a point, otherwise player 2.

Na°	Mg°	Al°	Sn°	Cu°	Fe°	Ca°	Zn°	Ag°
	°	°	N_2°	S°	O_2°	F_2°	Cl_2°	Br_2°
H_2CO_3	H_2SO_3	H_2SO_4	H_2S	NH_3	HNO_2	HNO_3	H_3PO_4	OH^-

Table: Solubility product (pK_L-values) of different hardly soluble salts.

Source: "Formelsammlung" by Urs Wuthier, Switzerland.

	pK_L
AgBr	12.1
$AgBrO_3$	4.2
Ag_2CO_3	11.2
AgCl	9.8
Ag_2CrO_4	11.0
$Ag_2Cr_2O_7$	6.7
AgI	15.8
$AgIO_3$	8.0
AgOH	7.8
Ag_2S	48.8
AgSCN	11.9
$Al(OH)_3$	32.3
$BaCO_3$	8.1
BaC_2O_4	6.8
$BaCrO_4$	9.7
BaF_2	5.8
$Ba(IO_3)_2$	9.2
$BaSO_4$	10.0
$CaCO_3$	8.1
CaC_2O_4	8.6
CaF_2	10.4
$Ca(IO_3)_2$	6.2
$CaSO_4$	4.6
CdC_2O_4	7.8
$Cd(OH)_2$	13.9
CdS	28.4
CoS	25.5
CuBr	7.4
CuI	11.3
Cu_2S	46.7
CuSCN	10.8
CuC_2O_4	7.5
$Cu(IO_3)_2$	6.9
$Cu(OH)_2$	19.8
CuS	44.1

	pK_L
FeC_2O_4	6.7
$Fe(OH)_2$	13.8
FeS	18.4
$Fe(OH)_3$	36.0
HgBr	20.9
HgCl	17.7
HgI	27.9
HgS	52.4
$MgCO_3$	4.6
MgC_2O_4	4.1
MgF_2	8.2
$MgNH_4PO_4$	12.6
$Mg(OH)_2$	10.9
$Mn(OH)_2$	13.4
MnS	14.9
$NiCO_3$	6.9
$Ni(OH)_2$	14.0
NiS	23.9
$PbCO_3$	13.5
PbC_2O_4	10.6
$PbCrO_4$	13.8
PbF_2	7.5
PbI_2	7.9
$Pb(IO_3)_2$	12.6
Pb(OH)	15.6
PbS	27.5
$PbSO_4$	8.0
SnS	28.0
$SrCO_3$	8.8
SrC_2O_4	7.3
SrF_2	8.6
$SrSO_4$	6.4
$ZnCO_3$	10.2
ZnC_2O_4	8.9
$Zn(OH)_2$	13.7
ZnS	22.9

Def: $pK_L = -\log K_L$ $\quad K_L = 10^{-pK_L}$

The equilibrium constant - solvation product - is defined:

$$AgCl(s) \rightleftarrows Ag^+(aq) + Cl^-(aq)$$

$$K_L(AgCl) = c(Ag^+(aq)) \ * \ c(Cl^-(aq))$$
$$= 2 \cdot 10^{-10} \ \frac{mol^2}{L^2}$$

The **E**stimated **E**quilibrium **C**oncentration (EEC) of the soluble ions can be calculated:

$$c(Ag^+(aq)) = c(Cl^-(aq)) = \sqrt[2]{K_L} = GGK$$

EEC for salts of 2 ions (AgCl, $CaSO_4$, ...):

$$EEC = \sqrt[2]{K_L \frac{mol^2}{L^2}} = 10^{-\frac{pK_L}{2}} \ \frac{mol}{L}$$

EEC for salts of 3 ions (CaF_2, $Fe(OH)_2$, ...)

$$EEC = \sqrt[3]{K_L \frac{mol^3}{L^3}} = 10^{-\frac{pK_L}{3}} \ \frac{mol}{L}$$

EEC for salts of 4 ions ($Al(OH)_3$, $Fe(OH)_3$, ...)

$$EEC = \sqrt[4]{K_L \frac{mol^4}{L^4}} = 10^{-\frac{pK_L}{4}} \ \frac{mol}{L}$$

ChemCube - Crystallize Salts

4	5	6	7	8	9	10	11	12	HS

1.4 Crystallization of Salts

Theory

Salts can crystallize (or fall out) if the water (or solvent) evaporates or is vaporized.

General: Cation(aq) + Anion(aq) $\xrightarrow{\text{crystallize}}$ Salt formula(s)

Bsp: $Na^+(aq)$ + Cl^- (aq) $\xrightarrow{\text{crystallize}}$ NaCl(s) (1)

Natrium-Ion, Chlorid-Ion, Natriumchlorid

You can also precipitate a salt by adding a counter ion that forms with a present ion a badly soluble salt according to pK_L-values. It is e.g. possible to precipitate chloride ions $Cl^-(aq)$ in a dilute sodium chloride solution (or in tap water) by adding silver(I) ions $Ag^+(aq)$ (2). With this method it is possible to crystallize, sediment, filter and eliminate chloride ions as precipitate of a hardly soluble salt from the solution.

Bsp: $Ag^+(aq)$ + Cl^- (aq) $\overset{K_L}{\rightleftharpoons}$ AgCl(s) $\downarrow$ (2)

Silber-Ion, Chlorid-Ion, Silber(I)chlorid precipitates

Game: Crystallization of Salts - Ion Detection (3 students)

Player 1 choose a cube and a **ion** that should be precipitated.

Player 2 & 3* are looking for a **counter ion** that forms with the **given ion** a badly soluble salt (time: 30 Sek) change roles clockwise! play 3 rounds of 3 games Discuss results after every round.

*Variation: Player 2 with i-Pad or tablet / Player 3 only with table of pK_L-values.

Results (look up with i-Pad / Tablet ***or*** calculate the **estimated equilibrium concentration EEC** from the pK_L-values p. 14)

Points:

Player 2 and 3 find ***no counter ion***. --> player 1 gets 2 points

Only one player (2 or 3) finds ***a counter ion*** and gets 2 point.

If players 2 & 3 find the **same counter ion**, they share these 2 points: 1 point each.

If players 2 & 3 find **different counter ions** then the better one with lower EEC gets 2 points, the other one gets 1 point.

all cubes 1x

Na°	Mg°	Al°	Sn°	Cu°	Fe°	Ca°	Zn°	Ag°
	°	°	N_2°	S°	O_2°	F_2°	Cl_2°	Br_2°
H_2CO_3	H_2SO_3	H_2SO_4	H_2S	NH_3	HNO_2	HNO_3	H_3PO_4	OH^-

hemCube - Acids and Bases

4	5	6	7	8	9	10	11	12	HS

2.1 Which species occur at different pH-value?

Preparation:
Place the different acid and base cubes (see below) on a table with 2-4 students. The students have to place and turn all cubes so, that the fully protonated form lies side up on the table (H_2CO_3, H_2SO_3, H_2SO_4, H_2S, NH_4^+, HNO_2, HNO_3, H_3O^+, ...). The acidity constant (pK_a-value) can be looked up - turning the cube forward - at the bottom of the protonated species.
Playing rules: If the pH-value in an aqueous solution containing an acid (e.g. H_2CO_3) is lower than the pK_a-value (pH < pK_{a1} = 6.4), then the species facing up remains the main species . If pH-value is higher than the pK_{a1}-value (pH > pK_{a1} = 6.4) of acid 1, you will have to turn this cube to the left and acid 1 (H_2CO_3) has been deprotonated to base 1 (HCO_3^-). A cube will be turned from acid 1 to its corresponding base 1 if pH-value is higher then pK_{a1} of acid 1.
If base 1 (HCO_3^-) can act as acid 2, the cubes can be turned on, if pH is higher than pK_{a2} (1):

$$H_2CO_3\,(aq) \xrightleftharpoons{pK_{a1} = 6.4} HCO_3^-\,(aq) \xrightleftharpoons{pK_{a2} = 10.4} CO_3^{2-}\,(aq) \qquad (1)$$

acid 1	base 1	
	acid 2	base 2
pH 0 bis 6	pH 7-10	pH 11-14

If you start at basic conditions, e.g. pH-value of 12, than the main species in example (1) is carbonate CO_3^{2-} (base 2). If you lower the pH of the solution below pK_{a2} of the corresponding acid 2, e.g. by adding a strong acid, you turn the cube the right (HCO_3^-).

Game 1: Start with an acidic solution with pH = 0.

pH = 0	Place all the cubes with the main species, that exists at pH = 0, facing up. In which form do the different acids occur at pH = 0 ?
pH = 1	What happens if the pH-value is increased to pH = 1 ?
...	Increase pH-value by increments of 1 and turn the appropriate cubes. Note the main species of the different cubes for each pH-value.
pH = 7	In which form (species) occur the different acids and bases at pH = 7 ?
...	Increase pH-value again by increments of 1 and turn the appropriate cubes. Note species.
pH = 14	In which form (species) occur the different acids and bases at pH = 14 ?

Game 2: Start with an basic solution with pH = 14.

pH = 14	Start at a pH-value of 14 and decrease the pH-value stepwise by increments of 1. Turn the appropriate cubes.
pH = 0	...

1 of each per student or team of 2

H_2CO_3	H_2SO_3	H_2SO_4	H_2S	NH_4^+	HNO_2	HNO_3	H_3PO_4	H_3O^+

2.2 pH-value and acidity constant pK_a

Theory

The acidity constant pK_a stands for the pH-value, at which an acid species (**HB**) and its corresponding base (**B**$^-$) occur at a ratio of 1:1 or 50 % : 50 %. That means that, at a pH-value of pH = pK_a , out of 10 cubes of the same acid 5 occur in the protonated form (acid), the other 5 cubes in the deprotonated form (base).

At a pH-value of pH = pK_a - 1, only 10 % of the acid (1 cube out of 10) occur in the deprotonated form (base) and 90 % in the acid form (9 out of 10 cubes). If you reach this pH-value, starting at an even lower pH, then you turn the first of 10 acid cubes to its corresponding base.

At a pH-value of pH = pK_a + 1, 90 % of the acid (9 cube out of 10) occur in the deprotonated form (base) and 10 % in the acid form (1 out of 10 cubes).

	Acid (HB)	Base (B$^-$)
pH = pK_a - 2	99 %	1 %
pH = pK_a - 1	90 %	10 %
pH = pK_a	**50 %**	**50 %**
pH = pK_a + 1	10 %	90 %
pH = pK_a + 2	1 %	99 %

	H_2CO_3(aq)	HCO_3^-(aq)
pH = 4.4	99 %	1 %
pH = 5.4	90 %	10 %
pH = 6.4	**50 %**	**50 %**
pH = 7.4	10 %	90 %
pH = 8.4	1 %	99 %

Preparation:

Place 10 cubes of one acid e.g. carbonic acid (H_2CO_3(aq)) on a table.

Start of the game:

pH = 0	Place all the cubes with the main species, that exists at pH = 0, facing up.
pH = pK_{a1} - 1	Increase the pH-value slowly to **pH = pK_{a1} - 1**. Turn the first of cubes from the acid to its corresponding base (turn cube to the left).
pH = pK_{a1}	Increase the pH-value slowly to **pH = pK_{a1}** and turn 4 more cubes from the acid to its corresponding base (turn cubes to the left).
pH = pK_{a1} + 1	Turn 4 more cubes from the acid to the corresponding base untill in total 90 % of the cubes are deprotonated and occur in the base form.
pH = pK_{a1} + 2	Turn the last cube. At this pH-value 99 % of the species occur in the base form.

If in the meantime the second acidity constant is close (pH = pK_{a2} -1), turn the first cube from acid 2 to base 2, etc.

- Repeat this game with 10 cubes of another acid: H_2SO_3, H_2SO_4, H_2S, NH_4^+, HNO_2, HNO_3, ...)
- Repeat this game with 10 cubes each of 2 or 3 different acids.
- Repeat this game with different numbers of cubes (e.g. 4 A, 6 B, 8 C, 10 D) of 3 or 4 different acids.

H_2CO_3	H_2SO_3	H_2SO_4	H_2S	NH_4^+	HNO_2	HNO_3	H_3PO_4	H_3O^+

2.3 Titration of an acid with sodium hydroxide

Theory

In the first titration we let an ***acid*** react with a strong ***base*** (e.g. sodium hydroxide solution) as *titration medium*. In this reaction the acid HB(aq) is deprotonated by the hydroxide ion OH^-(aq) (1).

$$\underset{\textit{acid}}{\mathbf{HB(aq)}} + \underset{\substack{\textit{base}\\ \textit{titration medium}}}{\mathbf{OH^-(aq)}} \rightleftharpoons B^-(aq) + H_2O(l) \qquad (1)$$

$$\underset{\textit{carbonic acid}}{H_2CO_3(aq)} + \underset{\substack{\textit{base}\\ \textit{titration medium}}}{\mathbf{OH^-(aq)}} \rightleftharpoons HCO_3^-(aq) + H_2O(l) \qquad (2)$$

	pK_a acid (HB)	base (B^-)
pH = pK_a - 2	**99 %**	1 %
pH = pK_a - 1	90 %	10 %
pH = pK_a	**50 %**	**50 %**
pH = pK_a + 1	10 %	90 %
pH = pK_a + 2	1 %	99 %

	pK_{a1}=6.4 H_2CO_3(aq)	HCO_3^-(aq)
pH = 4.4	**99 %**	1 %
pH = 5.4	90 %	10 %
pH = 6.4	**50 %**	**50 %**
pH = 7.4	10 %	90 %
pH = 8.4	1 %	99 %

Preparation:

Place **10 cubes** of an acid, e.g. carbonic acid **H_2CO_3(aq)** on the table in front of you. Take a water cube with the hydroxide species **OH^-(aq)** facing up in your hand.

Start of the titration game:

pH = pK_{a1} - 2 — Start pH-value of titration: Place all the 10 cubes with the predominant species at pH = pK_{a1} - 2 side up. Take the **OH^-(aq)** cube in your hand.

Start — Start the titration placing the **OH^-(aq)** cube (titration medium) at the side of an **H_2CO_3(aq)** cube and let them react together turning both cubes in the correct directions (see (1)). As now 10 % of the acid cubes are deprotonated, pH-value increases to: pH = pK_{a1} - 1.

pH = pK_{a1} - 1 — Take the **OH^-(aq)** cube in your hand again and repeat this reaction step 4-times with 4 other acid cubes. 50 % of the acid cubes are deprotonated: pH = pK_{a1}.

pH = pK_{a1} — Take the **OH^-(aq)** cube in your hand again and repeat this reaction step 4-times with 4 more acid cubes. 90 % of the acid cubes are deprotonated: pH = pK_{a1} + 1.

pH = pK_{a1} + 1 — Take another **OH^-(aq)** cube in your hand and let it react with the last acid cube. As now 100 % (99 %) of the acid cubes are deprotonated: pH = pK_{a1} + 2.

- What happens in this titration of **H_2CO_3(aq)** if you add another **OH^-(aq)** cube (or more)?
- Chose 10 (or another number) of cubes of another acid and repeat the titration.
- Try to find out which acids can be titrated well according to this procedure.

10x								1x
H_2CO_3	H_2SO_3	H_2SO_4	H_2S	NH_4^+	HNO_2	HNO_3	H_3PO_4	OH^-

2.4 Titration of a base with a strong acid

Theory

In this titration we let react a ***base*** with a strong ***acid***, e.g. chloric acid (c(HCl) = 1 mol/L: pH = 0). As chloric acid (pK_a = -6) is fully deptrotonated at pH = 0, the active species is **H_3O^+**(aq) (1):

$$HCl(aq) \quad + \quad H_2O\ (aq) \rightleftharpoons Cl^-\ (aq) \quad + \quad \mathbf{H_3O^+(aq)} \qquad (1)$$

H_3O^+(aq) reacts in the titration as follows with the base, e.g. NH_3(aq) (2):

$$\mathbf{NH_3(aq)} \quad + \quad \mathbf{H_3O^+(aq)} \rightleftharpoons NH_4^+\ (aq) \quad + \quad H_2O(l) \qquad (2)$$

base — *ammonia*
acid — *titration medium*

	pK_a acid (HB)	**base (B^-)**
pH = pK_a + 2	1 %	**99 %**
pH = pK_a + 1	10 %	90 %
pH = pK_a	**50 %**	**50 %**
pH = pK_a - 1	90 %	10 %
pH = pK_a - 2	99 %	1 %

	pK_a=9.2 NH_4^+(aq)	**NH_3(aq)**
pH = 11.2	1 %	**99 %**
pH = 10.2	10 %	90 %
pH = 9.2	**50 %**	**50 %**
pH = 8.2	90 %	10 %
pH = 7.2	99 %	1 %

Preparation:

Place **10 cubes** of a **base**, e.g. ammonia **NH_3(aq),** on the table in front of you. Take a water cube with the oxonium ion **H_3O^+(aq)** as titration medium facing up in your hand.

pH = pK_{a1} + 2	Start pH-value of the titration: Place the 10 base cubes on the table with the active species side up at the pH given (pH = pK_{a1} + 2), that means NH_3(aq) faces up.
Start	Start the titration placing the **H_3O^+** -cube in your hand at the side of the first ammonia cube and let the react. Both cubes are turned accordingly. The pH-value increases to: pH = pK_{a1} + 1.
pH = pK_{a1} + 1	Take the **H_3O^+**(aq)-cube once more in your hand and repeat this reaction step 4 times. Now half of the base cubes (50%) are protonated and pH = pK_{a1} .
pH = pK_{a1}	Take the **H_3O^+**(aq)-cube again in your hand and repeat this reaction step another 4 times. Now 90 % of the base cubes are protonated and pH = pK_{a1} - 1.
pH = pK_{a1} - 1	Let the last base cube react with **H_3O^+**(aq) and then all the bases (>99 %) are protonated. The pH < pK_{a1} - 2.
endpoint	If you add another **H_3O^+**(aq)-cube, it does not find another reaction partner and remains in the solution. The pH drops significantly. The end of the titration is reached.

- Chose 10 (or another number) of cubes of another base and repeat the titration.
- Try to find out which bases can be titrated well according to this procedure.

				10x				1x
H_2CO_3	H_2SO_3	H_2SO_4	H_2S	NH_3	HNO_2	HNO_3	H_3PO_4	H_3O^+

3.1 Metals react with non-metals and form salts

Theory

When metals react with non-metals they form salts, that means ionic compounds:

metal		non-metal		salt formula		ion-notation	
2 $Na°(s)$	+	1 $Cl_2°(g)$	$\longrightarrow$	2 $NaCl$ (s)	=	Na^+ + Cl^-	(1)
sodium		chlorine		Sodiumchloride			

Two uncharged elementary substances react to a ionic compound. If the salt formula is written in the ion-notation you can see, that electrons have been transferred in this reaction. We call it a redox reaction, where the metal is oxidized - gives away electrons - and the non-metal is reduced - takes up electrons:

				e^- balance	
Oxidation: (e⁻ donation)	$Na°$	$\longrightarrow$	Na^+ + 1 e^-	x 2	(2)
Reduction: (e⁻ uptake)	Cl_2 + 2 e^-	$\longrightarrow$	2 Cl^-	x 1	(3)

Preparation:

Chose a **metal** and a **non-metal** cube and take 5 of each. Place the **metal** cubes (5x) on the left side and the **non-metal** cubes (5x) in the middle of the table. Combine a ionic compound on the right of the table so, that the charges of the ions forming the salt cancel each other. Write down the complete reaction with the salt formula and its ion-notation (1).

Note also the part reactions of the oxidation (2) and the reduction (3), including the electron balance.

metal + non-metal $\longrightarrow$ salt formula = ion notation

e^- balance

Oxidation:

Reduction:

$Na°$	$Mg°$	$Al°$	$Sn°$	$Cu°$	$Fe°$	$Ca°$	$Zn°$	$Ag°$
	°	°	$N_2°$	$S°$	$O_2°$	$F_2°$	$Cl_2°$	$Br_2°$

3.2 Recognizing redox reaction - oxidation numbers

Changes of font color, while turning a cube, indicate a chemical reaction in this step. Select all cubes, where font color change occurs (A).
There are also species, that exist on different cubes. Group these cubes, that have species in common (B).
Chose one cube (A) or a group of cubes (B) and try to explain the chemistry taking place in those turning steps, where the font color changes.

Task:

- Note a correct chemical reaction that might take place in this turning step.
- Is this reaction a **redox reaction**? Use the concept of oxidation numbers to find out.
- **If yes**, note the part reactions of the oxidation and the reduction. **If not**, reason (begründen) your answer.

Results:

Reaction:

Lewis:

e^- balance

Oxidation: $\longrightarrow$
(e^- donation)
Reduction: $\longrightarrow$
(e^- uptake)

all cubes 1x

Na°	Mg°	Al°	Sn°	Cu°	Fe°	Ca°	Zn°	Ag°
	°	°	N_2°	S°	O_2°	F_2°	Cl_2°	Br_2°
H_2CO_3	H_2SO_3	H_2SO_4	H_2S	NH_3	HNO_2	HNO_3	H_3PO_4	H_3O^+

ChemCube - Standard Reduction Potential E°

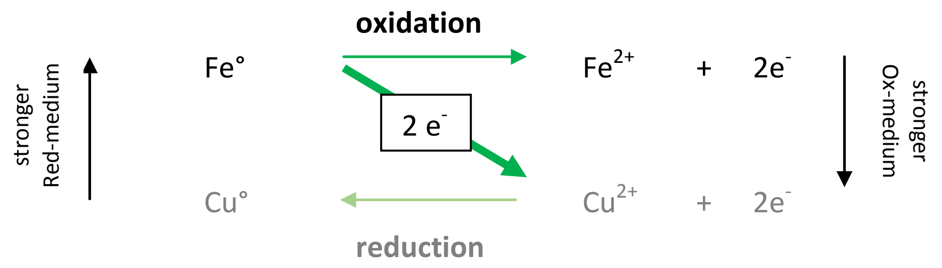
4	5	6	7	8	9	10	11	12	HS

3.3 Predicting redox reactions using E°

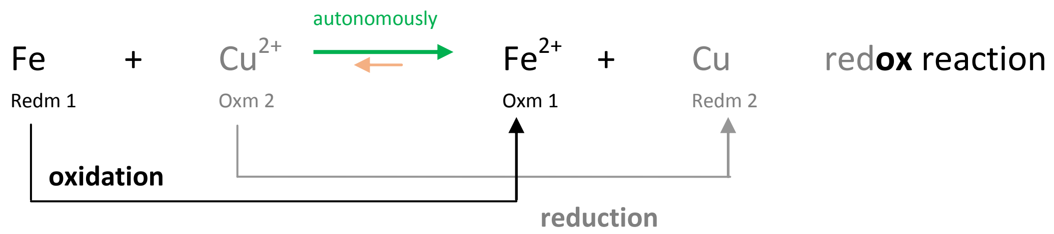
Theory

In the table below the redox-pairs (corresponding reduction- and oxidation medium) are sorted by the strength of its standard reduction potentials E° in a way, that the stronger reduction medium with the more negative E° comes first. The stronger reduction medium (top left) reacts with the stronger oxidation medium (bottom right) and this reaction will take place autonomously (freiwillig, selbstständig).

reduction medium | oxidation medium + $x \cdot e^-$ | E°[V]



redox reaction:



task:

- Write down 5 reaction equations using the cubes from the first and/or the second line below (optionally from the 3rd line) and a table with standard reduction potentials E° for redox reactions that might take place autonomously (freiwillig) in an experiment (hypothesis).
- Note also the partial reactions of the oxidation and the reduction step.
- Try out one or another hypothesis of your choice in the laboratory. Talk first to the teacher and verify your choice.

all cubes 1x

Na°	Mg°	Al°	Sn°	Cu°	Fe°	Ca°	Zn°	Ag°
	°	°	N_2°	S°	O_2°	F_2°	Cl_2°	Br_2°
H_2CO_3	H_2SO_3	H_2SO_4	H_2S	NH_3	HNO_2	HNO_3	H_3PO_4	H_3O^+

ChemCube - Carbon Cycle

4	5	6	7	8	9	10	11	12	HS

4.1 Carbon - Carbon dioxide - Carbonic acid - Carbonate

Theory

In the photosynthesis reaction taking place in plants and algae carbon dioxide CO_2 is transformed into biomass $<\mathbf{C}H_2O>$ or short in organically bound carbon **C(org)** (1):

$$CO_2\,(g, aq) \quad + \quad H_2O\,(l) \quad \xrightarrow{\text{photosynthesis}} \quad \underset{\text{biomass}}{<\mathbf{C}H_2O>\,(org)} \quad + \quad O_2\,(aq) \qquad (1)$$

Burning solid carbon C(s) or the respiration of organic carbon compounds C(org) with oxygen results in carbon dioxide gas. Its partial pressure in the atmosphere is: $p_i(CO_2(g))$= 400 ppm.

$$\underset{\text{carbon}}{C} \quad + \quad \underset{\text{oxygen}}{O_2\,(g)} \quad \longrightarrow \quad \underset{\text{carbon dioxide}}{CO_2\,(g)} \qquad \underset{\text{exothermic reaction}}{\Delta H_R < 0} \qquad (2)$$

Carbon dioxide gas CO_2(g) dissolves in water (rain, rivers, lakes, the ocean) and forms an equilibrium with the carbon dioxide dissolved in water CO_2(aq):

$$CO_2\,(g) \quad \rightleftharpoons \quad CO_2\,(aq) \qquad (3)$$

If dissolved carbon dioxide CO_2(aq) reacts with water carbonic acid H_2CO_3(aq) is formed.

$$CO_2\,(aq) \quad + \quad H_2O(l) \quad \rightleftharpoons \quad H_2CO_3\,(aq) \qquad (4)$$

Depending on pH-value of the water carbonic acid deprotonates to hydrogen carbonate or carbonate:

$$H_2CO_3\,(aq) \quad \overset{pK_{a1} = 6.4}{\rightleftharpoons} \quad HCO_3^-\,(aq) \quad \overset{pK_{a2} = 10.4}{\rightleftharpoons} \quad CO_3^{2-}\,(aq) \qquad (5)$$

Many aquatic organisms such as corals, snails, mussels but also microorganisms can build up shells out of calcium carbonate. After death these shells form a sediment of chalk:

$$Ca^{2+}\,(aq) \quad + \quad CO_3^{2-}\,(aq) \quad \overset{pK_L = 8.3}{\rightleftharpoons} \quad \underset{\text{Calciumcarbonat}}{CaCO_3\,(s)} \qquad (6)$$

Connect and lay these reactions on the table using the cubes given below. All reactions, that are formulated as equilibrium with a double arrow, are reversible.

Task: Try to connect the reactions (2) to (6) with one another in a scheme (A4 paper).

Questions:

- The water solubility of carbon dioxide is smaller at higher water temperatures. What does this mean for its partial pressure in the atmosphere $p_i(CO_2(g))$?
- What does this mean for global warming and the greenhouse effect?

12x							2x	1x
H_2CO_3	H_2SO_3	H_2SO_4	H_2S	NH_4^+	HNO_2	HNO_3	Ca^{2+}	H_2O

4.2 Sulfur - sulfur dioxide - sulfuric acid - gypsum

Theory

If sulfur **S** or organic compounds containg sulfur **S(org)** are burnt or react with oxygen sulfur dioxide gas SO_2(g) is formed (1). This gas can dissolve in water (2):

$$\underset{\text{sulfur}}{S} + \underset{\text{oxygene}}{O_2\,(g)} \longrightarrow \underset{\text{sulfur dioxide}}{SO_2\,(g)} \qquad \underset{\text{exothermic reaction}}{\Delta H_R < 0} \qquad (1)$$

$$SO_2\,(g) \rightleftharpoons SO_2\,(aq) \qquad (2)$$

Dissolved sulfur dioxide can react with water to sulfurous acid (H_2SO_3 (aq)), which can be oxidized with dissolved oxygen to sulfuric acid (H_2SO_4 (aq)). Both compounds are - besides others - responsible for acidic rain:

$$SO_2\,(aq) + \underset{\text{Wasser}}{H_2O\,(fl)} \rightleftharpoons \underset{\text{sulfurous acid}}{H_2SO_3\,(aq)} \xrightarrow{\frac{1}{2}O_2} \underset{\text{sulfuric acid}}{H_2SO_4\,(aq)} \qquad (3)$$

Depending on pH-value of the solution (water, natural fount, rain, ...) these two acids can exist in the form of the following species:

$$H_2SO_3\,(aq) \overset{pK_{a1} = 1.9}{\rightleftharpoons} HSO_3^-\,(aq) \overset{pK_{a2} = 7.2}{\rightleftharpoons} SO_3^{2-}\,(aq) \qquad (4)$$

$$H_2SO_4\,(aq) \overset{pK_{a1} = -3}{\rightleftharpoons} HSO_4^-\,(aq) \overset{pK_{a2} = 1.9}{\rightleftharpoons} SO_4^{2-}\,(aq) \qquad (5)$$

With the evaporation of sea water (or in hot springs) containing calcium and sulfate, gypsum and andydrite (6) can fall out and sediment in the early phase of carbonate precipitation (7):

$$Ca^{2+}\,(aq) + SO_4^{2-}\,(aq) \overset{pK_L = 4.6}{\rightleftharpoons} \underset{\text{Gips}}{CaSO_4 * 2\,H_2O(s)} \underset{T < 66\,°C}{\overset{T > 66\,°C}{\rightleftharpoons}} \underset{\text{Anhydrit}}{CaSO_4\,(s)} \qquad (6)$$

$$Ca^{2+}\,(aq) + CO_3^{2-}\,(aq) \overset{pK_L = 8.3}{\rightleftharpoons} \underset{\text{Calciumcarbonat}}{CaCO_3\,(s)} \qquad (7)$$

Connect and lay these reactions on the table using the cubes given below. All reactions, that are formulated as equilibrium with a double arrow, are reversible.

Task: Try to connect the reactions (1) to (7) with one another in a scheme (A4 paper).

Questions: Which role play these reaction in stone formation?
Which influence has the pH-value of the water on these processes?

1x	5x	5x					5x	
H_2CO_3	H_2SO_3	H_2SO_4	H_2S	NH_4^+	HNO_2	HNO_3	Ca^{2+}	H_3O^+

4.3 Nitrogen - nitrogen oxides - nitrous acid - nitric acid

Theorie

Many combustion reaction produce lots of heat. At temperatures above 600 °C nitrogen $\mathbf{N_2}$ from the air can react with oxygen $\mathbf{O_2}$ in a side reaction and form nitrogen monoxide **NO** (1). At lower temperatures the react on to nitrogen dioxide $\mathbf{NO_2}$ (2).

$$N_2\,(g) + O_2\,(g) \xrightarrow{T > 600\ °C} 2\,NO\,(g) \qquad (1)$$

$$2\,NO\,(g) + O_2\,(g) \xrightarrow{T < 600\ °C} 2\,NO_2\,(g) \qquad (2)$$

Depending on pressure and temperature two $\mathbf{NO_2}$ molecules (brown gas) can form dinitrogen tetroxide $\mathbf{N_2O_4}$, a colorless gas (3). A great version of this experiment to demonstrate le Chatelier's principles can be found at the www.vsn-shop.ch.

$$2\,NO_2\,(g) \rightleftharpoons N_2O_4\,(g) \qquad (3)$$

Nitrogen dioxide can dissolve in water (4) and react on to nitrous and nitric acid, HNO_2 and HNO_3 respectively (5).

$$NO_2\,(g) \rightleftharpoons NO_2\,(aq) \qquad (4)$$

$$2\,NO_2\,(aq) + H_2O\,(l) \longrightarrow HNO_2\,(aq) + HNO_3\,(aq) \qquad (5)$$

Depending on pH-value these two acids are deprotonated to nitrite NO_2^- (6) and nitrate NO_3^- (7), respectively:

$$HNO_2\,(aq) \xrightleftharpoons{pK_{a1} = 3.3} NO_2^-\,(aq) \qquad (6)$$

$$HNO_3\,(aq) \xrightleftharpoons{pK_{a1} = -1.3} NO_3^-\,(aq) \qquad (7)$$

Connect and lay these reactions on the table using the cubes given below. All reactions, that are formulated as equilibrium with a double arrow, are reversible.

Task: Try to connect the reactions (1) to (7) with one another in a scheme (A4 paper).

H_2CO_3 | H_2SO_3 | H_2SO_4 | H_2S | NH_4^+ | HNO_2 | HNO_3 | Ca^{2+} | H_3O^+

4.4 Ammonia synthesis, nitrification und denitrification

Theory

Nitrogen fixation

a) Haber-Bosch process

Using the Haber-Bosch process nitrogen **N_2** from the air can react with hydrogen **H_2** to ammonia **NH_3** on a catalyst at high temperature and pressure (1).

$$N_2\,(g) \quad + \quad 3\,H_2\,(g) \xrightarrow{\textbf{T = 450 °C, p = 300 bar}} 2\,NH_3\,(g) \qquad (1)$$

b) Biological nitrogen fixation

Some cyano bacteria and rhizobium, living in symbiosis with some plant roots (leguminosae), are capable of binding nitrogen gas from air or dissolved in water (2):

$$\underset{\text{nitrogen}}{\mathbf{N_2}} + 12\,ATP + 6e^- + 6\,H_3O^+ \xrightarrow{\textit{z.B. Cyanobacterien}} \underset{\text{ammonia}}{\mathbf{2\,NH_3}} + 12\,ADP + \underset{\text{phosphate}}{12\;P_i} + 6\,H_2O \qquad (2)$$

Nitrification

Nitrification of ammonium to nitrate uses two steps, carried out by two different autotrophic bacteria: 1^{st} the ammonium oxidizer (*Nitrosomonas*) and 2^{nd} the nitrite oxidizer (*Nitrobacter*).

1^{st} Ammonium oxidizer (e.g. *Nitrosomonas* bacteria)

Nitrosomonas-bacteria oxidize ammonium to nitrite (3):

$$2\;NH_4^+\,(aq) + 3\;O_2\,(aq) + 2\,H_2O \xrightarrow{\textit{Nitrosomonas}} 2\;NO_2^-\,(aq) + 4\,H_3O^+\,(aq) \qquad (3)$$

Note the partial reactions of the oxidation and reduction:

Oxidation:

Reduction:

2^{nd} Nitrite oxidizer (e.g. *Nitrobacter*)

Nitrobacter oxidize nitrite to nitrate (4):

$$2\ NO_2^-\,(aq) + O_2\,(aq) \xrightarrow{\textit{Nitrobacter}} 2\ NO_3^-\,(aq) \qquad (4)$$

Oxidation:

Reduction:

These two reactions for nitrification can be combined and simplified as follows (5):

$$2\ NH_4^+\,(aq) + 4\ O_2\,(aq) + 2\ H_2O \longrightarrow 2\ NO_3^-\,(aq) + 4\ H_3O^+\,(aq) \quad |\ :2$$

$$\mathbf{NH_4^+\,(aq) + 2\ O_2\,(aq) + H_2O \longrightarrow NO_3^-\,(aq) + 2\ H_3O^+\,(aq)} \qquad (5)$$

During nitrification ammonia is transformed to nitrate under oxygen consumption (aerobic conditions). The pH-value of the solution decreases. But nitrification only works at pH-values between 7.2 and 8. Does pH sink below 7.2, nitrification is ceased. In a lake dissolved hydrogen carbonate HCO_3^-(aq) helps to buffer the H_3O^+-ions produced.

Task: Play these buffer reactions using the cubes below and write them down.

Denitrification

Denitrification is - in contrast to nitrification - an anaerobic (or anoxic) process that runs in absence of oxygen. Nitrate is reduced stepwise to elementary nitrogen as shown below in detail. The {H} stand for hydrogen donors, which may provide H-atoms (or H^+ and e^-) such as e.g. NADH:

$$NO_3^- + 2\,\{H\} \longrightarrow NO_2^- + H_2O \qquad (6)$$

$$NO_2^- + \{H\} + H_3O^+ \longrightarrow NO(g) + 2\ H_2O \qquad (7)$$

$$\underset{\text{nitrogen monoxide}}{2\ NO} + 2\,\{H\} \longrightarrow \underset{\text{laughing gas nitrous oxide}}{N_2O(g)} + H_2O \qquad (8)$$

$$N_2O + 2\,\{H\} \longrightarrow N_2(g) + H_2O \qquad (9)$$

Task: Play these reactions using the cubes below and draw an A4 scheme. Think about the influence of the pH-value in these reaction steps.

H_2CO_3	H_2SO_3	H_2SO_4	H_2S	NH_4^+	HNO_2	HNO_3	Ca^{2+}	H_3O^+

$\longrightarrow$ $\longrightarrow$

pH-Scale

$\longrightarrow$ $\longrightarrow$

$\longrightarrow$ $\longrightarrow$

$\rightleftarrows$ $\rightleftarrows$

solution is...	…very acid …acid						… neutral			basic …very basic					
pH-value	**0**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**
pOH-value	**14**	**13**	**12**	**11**	**10**	**9**	**8**	**7**	**6**	**5**	**4**	**3**	**2**	**1**	**0**
$c(H_3O^+)$ $^{mol}/_{L}$	$1=10^{0}$	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}	10^{-6}	10^{-7}	10^{-8}	10^{-9}	10^{-10}	10^{-11}	10^{-12}	10^{-13}	10^{-14}
$c(OH^-)$ $^{mol}/_{L}$	10^{-14}	10^{-13}	10^{-12}	10^{-11}	10^{-10}	10^{-9}	10^{-8}	10^{-7}	10^{-6}	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	$1=10^{0}$

1 1 1 2 2 2 3 3 3

4 4 4 5 5 5 6 7 8

9 10 11 12 13 14

$\rightleftarrows$ $\rightleftarrows$

pH-scale	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14
pH...															