Einführung in die Chemie / Lebenswissenschaften

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Sekretärin

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This course

- me × 6 + Dirk Wilrodt × 3

Sprache

- English / Deutsch

Diese Folien

- immer in "stine"

Administration

- Format each day
  - 9:15 - 10:45 lectures × 2
  - 11:00 -12:00 Übung
  - Zeit und Pause verhandelbar
  - Übung
    - not like real chemistry (no lab coats)

Textbook

- meine Folien
  - "Chemie – die Zentrale Wissenschaft"
    Brown, T.L., LeMay, H.E., Bursten, B.E.
  - expensive
  - in the library: www.sub.uni-hamburg.de
- ebenso gut..
  - "Chemie: Das Basiswissen der Chemie"
    Mortimer, C.E. & Müller, U.
    Thieme, 2003
    besuchen Sie unsere Bibliothek Webseite für Volltextzugang

Quick survey

- who has book or can get it soon ?
- who is here ?

What do I like ?

- proteins, RNA, evolution
- numerical simulations
- prediction
- analysis
  - methods for recognising properties
- design

Mission

- enough chemistry to do our MSc course

Content

- basic rules
  - atoms, bonds
  - geometry
  - reactions, kinetics, equilibria
- little
  - metals, phosphorus, heavier elements
  - not much on gases or solids
- no
  - nuclear chemistry, metals

Kapitel		
1	intro and units	
2	atoms, molecules	bonds
3	stoichiometrie	
4	reactions in water	
5	thermochemistry	
6	electronic structure	skip most of Bohr atom
7	periodic table	briefly, sizes of atoms, ionization
8	chemical bonding	octet rule
9	structure, bond types	
10	gases	no
11	intermolecular forces	
12	modern products	no
13	solution properties	no
14	kinetics	
15	chemical equilibria	
16	acid / base	
	wahrscheinlich Ende	
19	thermodynamics	
25	organic chemistry	introduction

Style

- Sometimes brief mention
  - make noise when concepts unclear

- Sometimes borders with school chemistry
  - make noise when too easy

- Definitions
  - more early on
  - easy definitions necessary to explain later ones

- Technical words
  - German or English ? Usually both
  - keine Sprachprüfung

Rules

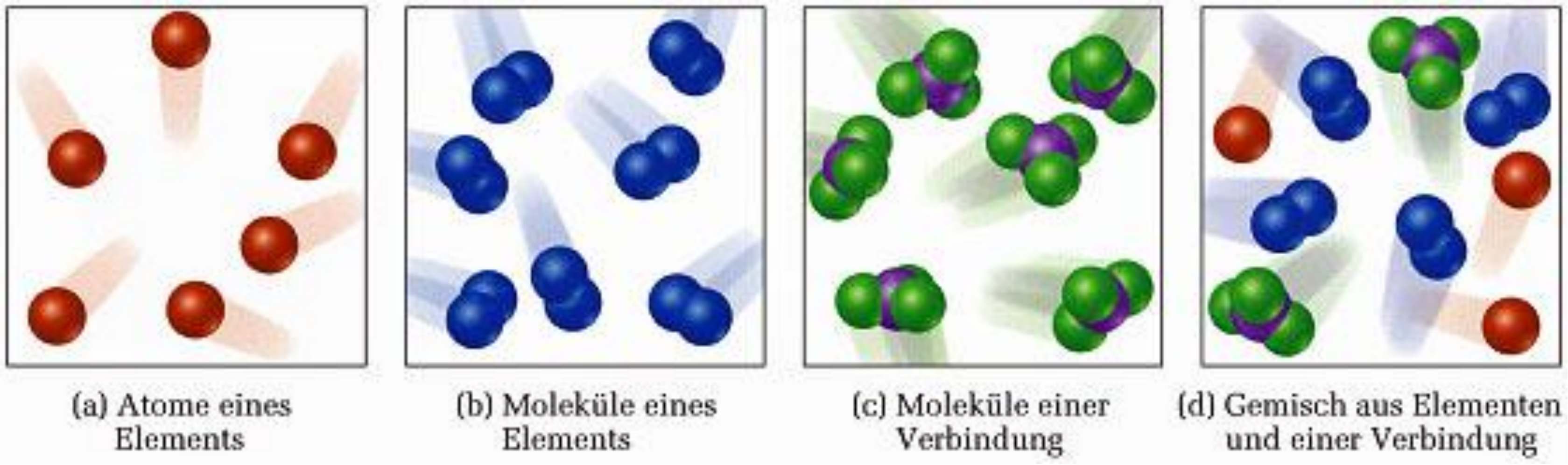
- SI units
- significant digits
  - if you have 2 significant digits in a problem do not quote 9.838375
- symbols for constants – use standard ones
  - *k*, *h*, *R*, … in context, do not need explanation
- symbols – some are very common
  - charge is always *q*, mass is always *m*

$$E = \frac{q_1 q_2}{4\pi\varepsilon_0 r}$$

- symbols are italics (*a*, *b*, *c*)
- units are roman (m, kg, s)
- follow conventions from good text books

Gemische, Elemente

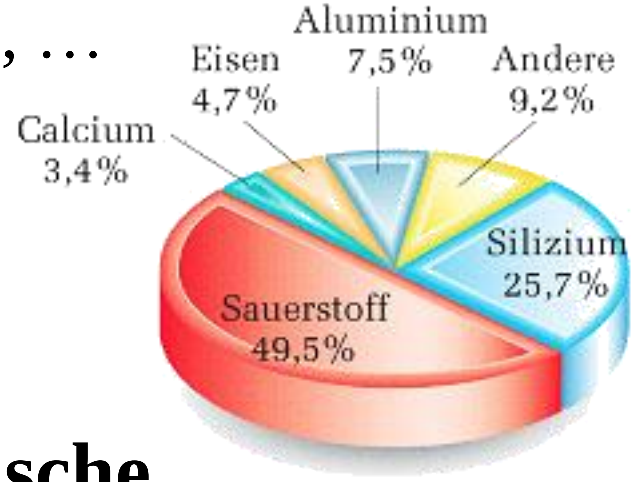
- Elements (Elemente) one kind of atom
- Compounds (Verbindungen) – some atoms bound together, H_2O, sugar, NaCl
- O_2 is not a compound, but who cares ?


(a) Atome eines Elements
(b) Moleküle eines Elements
(c) Moleküle einer Verbindung
(d) Gemisch aus Elementen und einer Verbindung

- Examples of these four

Elemente & Verbindungen

- 6 elements = more than 90 % of earth crust
- numerous compounds
  - think of oxygen compounds CO_2, H_2O, …



(a) Erdkruste

Verbindungen & Gemische

- Pure sugar or salt is a pure compound
  - ratio of elements is always the same
- Mixtures: concrete, coffee, washing powder
  - ratio of elements varies a bit
  - more than one type of molecule

Units

- nearly only SI units
- base units

masse	mass	kilogram	kg
länge	length	meter	m
zeit	time	second	s
temperatur	temperature	kelvin	K
stoffmenge	quantity of substance	mole	mol

- + prefixes k, M, G, m, µ, p
- not °Kelvin, not "sec"

Derived units

force	newton	N	m kg s^{-2}
energy, work, heat	joule	J	N m
pressure	pascal	Pa	N m^{-2}

…volts V, Ω, Hz, … all are derived units

illegal

- invent your own symbols

Exceptions

- few
  - Angstrom Å
  - atomic mass unit u (1.7×10^{-27} kg)

To remember

- units for
  - volume, density, energy, pressure

- dimension analysis
  - MLT (most things)
  - Θ temperature
  - Q charge

- is this high school ?
- Θ is big theta

Atomic structure

Atoms

- protons, neutrons, electrons

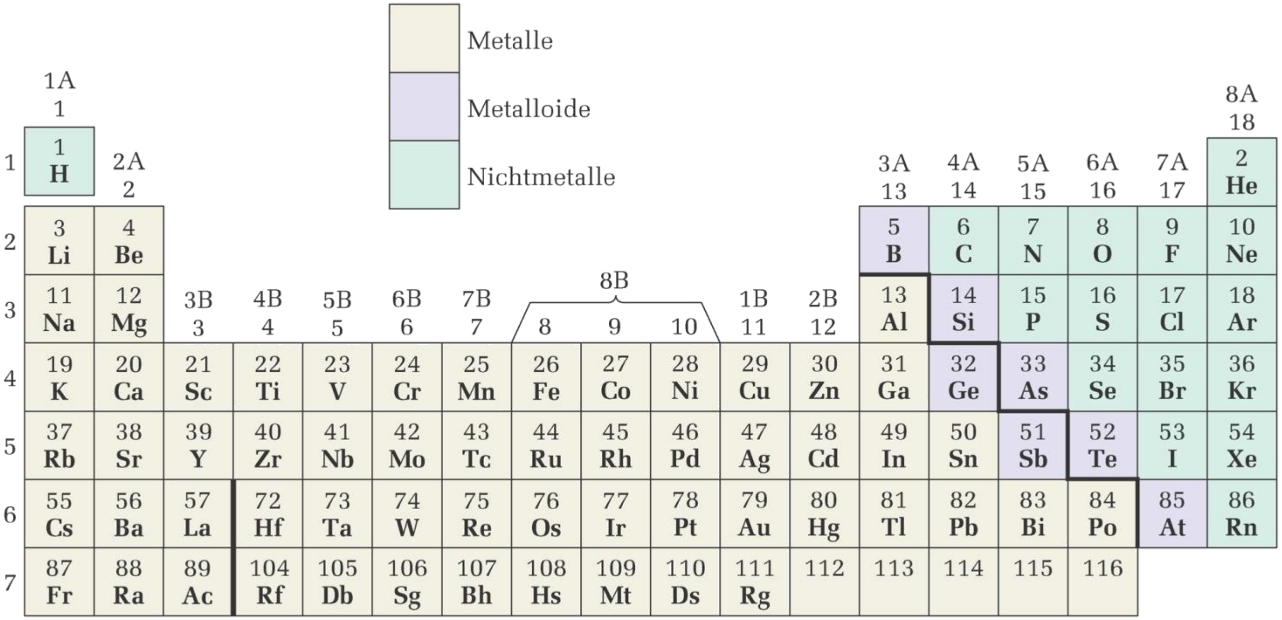
- mass - exception to my claim about SI units
  - protons and neutrons mass 1 u / amu/ame = 1.7×10^{-27} kg
  - electrons ? who cares
- charge – another exception
  - elementary charge $e = 1.6 \times 10^{-19}$ C or As (Ampere is the SI unit)

- more high school ?

Atomic number / mass

- atomic number
  - how many electrons does an atom have
  - how many protons
  - how to find the element in periodic table
  - C is 6, O is 8

- atomic mass
  - C is 12, O is 16



Metalle

Metalloide

Nichtmetalle

	1A 1	2A 2	3B 3	4B 4	5B 5	6B 6	7B 7	8B 8	9	10	1B 11	2B 12	3A 13	4A 14	5A 15	6A 16	7A 17	8A 18
1	1 **H**																	2 **He**
2	3 **Li**	4 **Be**											5 **B**	6 **C**	7 **N**	8 **O**	9 **F**	10 **Ne**
3	11 **Na**	12 **Mg**											13 **Al**	14 **Si**	15 **P**	16 **S**	17 **Cl**	18 **Ar**
4	19 **K**	20 **Ca**	21 **Sc**	22 **Ti**	23 **V**	24 **Cr**	25 **Mn**	26 **Fe**	27 **Co**	28 **Ni**	29 **Cu**	30 **Zn**	31 **Ga**	32 **Ge**	33 **As**	34 **Se**	35 **Br**	36 **Kr**
5	37 **Rb**	38 **Sr**	39 **Y**	40 **Zr**	41 **Nb**	42 **Mo**	43 **Tc**	44 **Ru**	45 **Rh**	46 **Pd**	47 **Ag**	48 **Cd**	49 **In**	50 **Sn**	51 **Sb**	52 **Te**	53 **I**	54 **Xe**
6	55 **Cs**	56 **Ba**	57 **La**	72 **Hf**	73 **Ta**	74 **W**	75 **Re**	76 **Os**	77 **Ir**	78 **Pt**	79 **Au**	80 **Hg**	81 **Tl**	82 **Pb**	83 **Bi**	84 **Po**	85 **At**	86 **Rn**
7	87 **Fr**	88 **Ra**	89 **Ac**	104 **Rf**	105 **Db**	106 **Sg**	107 **Bh**	108 **Hs**	109 **Mt**	110 **Ds**	111 **Rg**	112	113	114	115	116		

- what is most useful ?
  - usually mass

Atomic mass

Will re-appear next semester - isotopes

  - always written as ^{yy}X like
  - rules – not C^{13}

^{12}C	normal
^{13}C	NMR
^{14}C	radioactive label
^{1}H	normal
^{2}H	deuterium

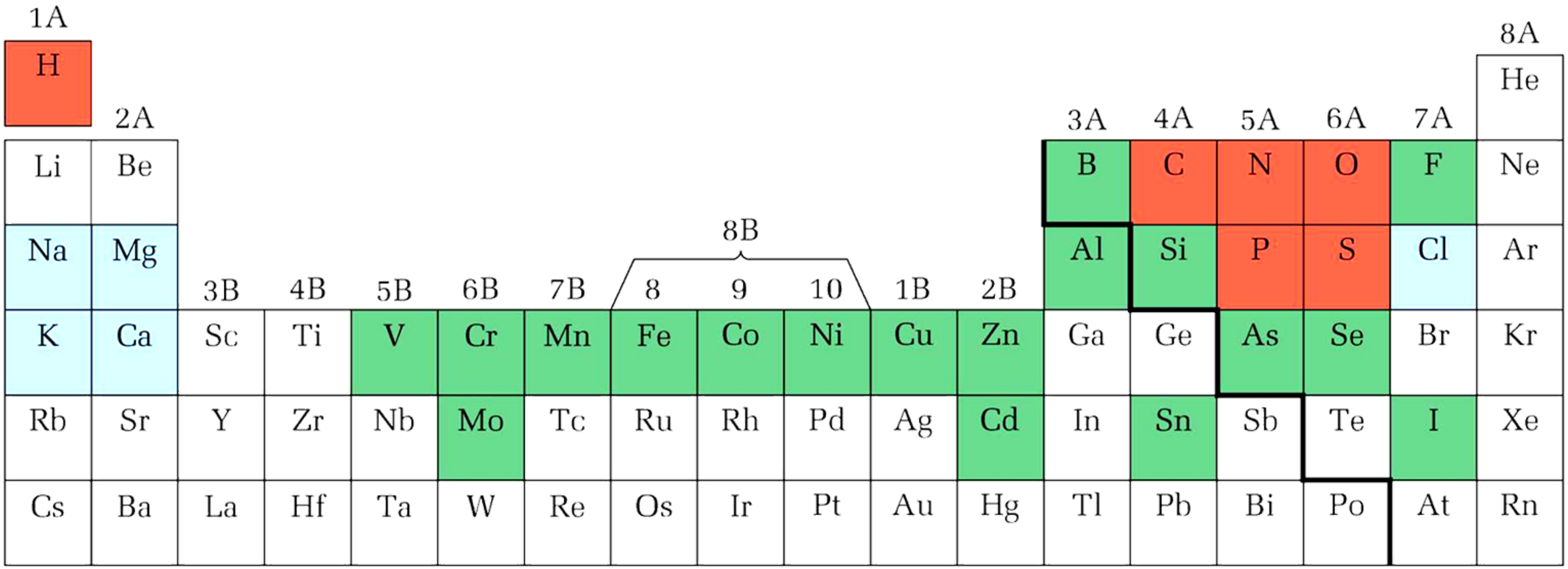
- unless stated, work with common isotope

- where does mass matter ?
  - calculation of quantities in reactions

- most elements have single stable isotope which is most common (^{1}H, ^{16}O, ^{12}C,)
  - exception Cl, mass 35.5

Periodic system

- limited to the relevant bits for our course
  - who will we meet most ?



							8B										
1A	2A	3B	4B	5B	6B	7B	8	9	10	1B	2B	3A	4A	5A	6A	7A	8A
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn

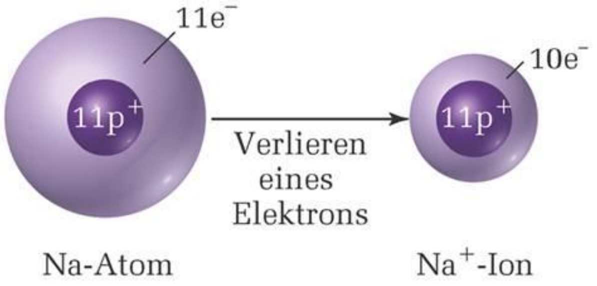
- example [Na^+] and [Cl^-] > 100mM

Bonds - covalent

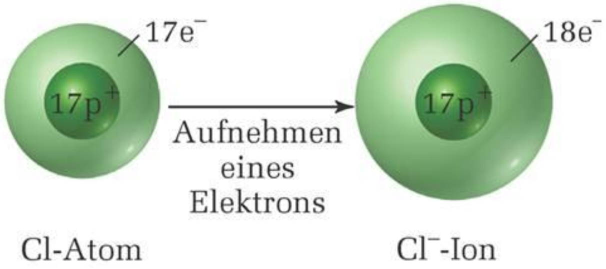
- look at O_2
- neither O is charged
  - as if the electrons are shared
- similar for CH_4, CO, CO_2

- dissolve O_2 in water, mostly
  - H_2O and O_2

Ionic bonds



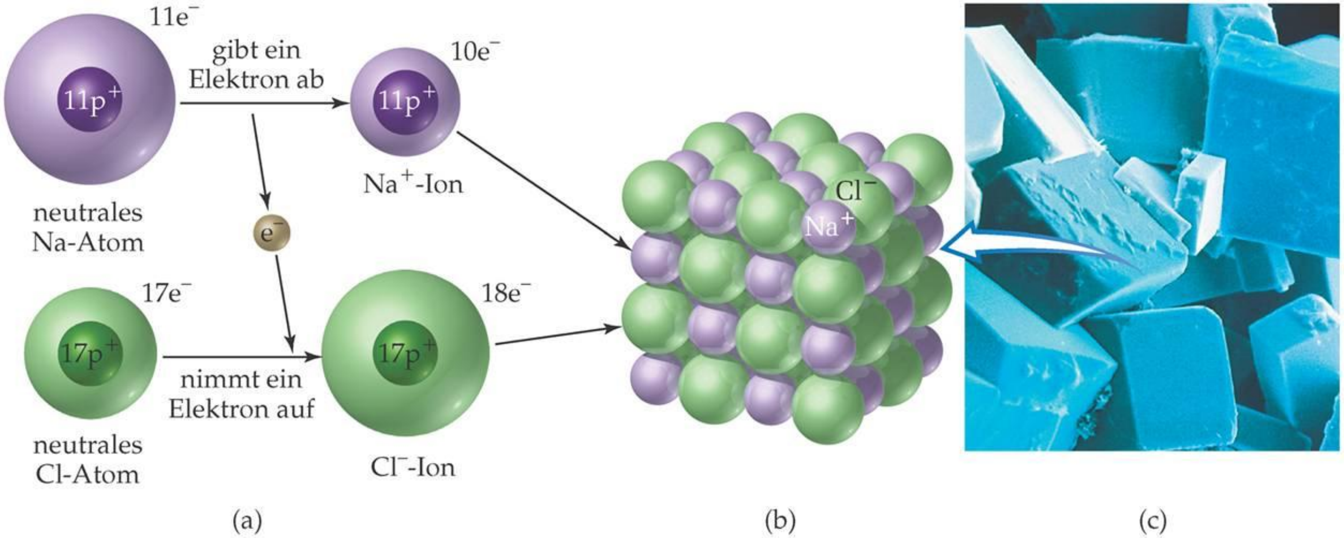
- best example NaCl
- pure Na atoms ? metal Na is fun
- Na is happy to lose an electron $Na \rightarrow Na^+ + e^-$



- pure Cl ? does not really exist (Cl_2)
- happy to gain an electron $Cl_2 + 2e^- \rightarrow 2\ Cl^-$

Ionic bonds

- table salt is formally NaCl
  - structure is more $Na^+ Cl^-$
- strong electrostatic attraction



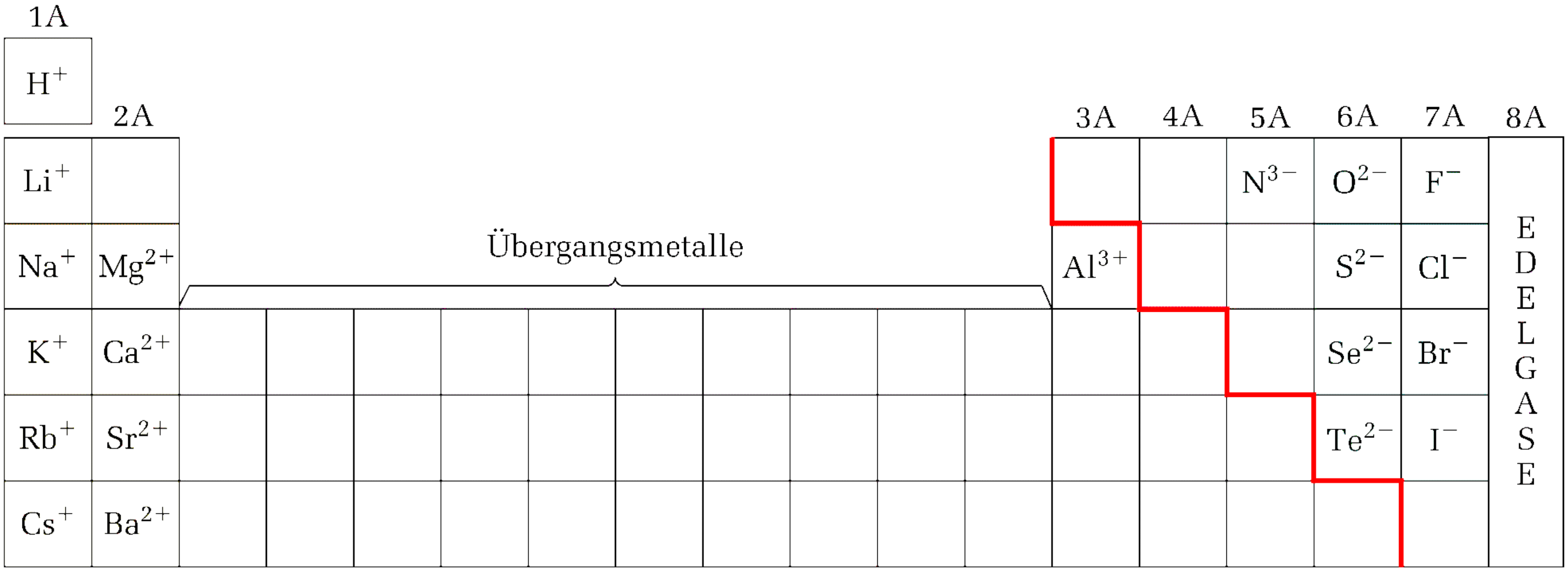
- dissolve in water gives
  - H_2O and Cl^- and Na^+ more correctly
  - $(H_2O)_nCl^-$ and $(H_2O)_nNa^+$

Covalent versus ionic

	covalent	ionic
	molekulare Verbindungen	Ionische Verbindungen
	non-metals	metal + non metal
if soluble – dissolves as	AB	A^+ and B^-
	electrons shared	electron(s) given from A to B

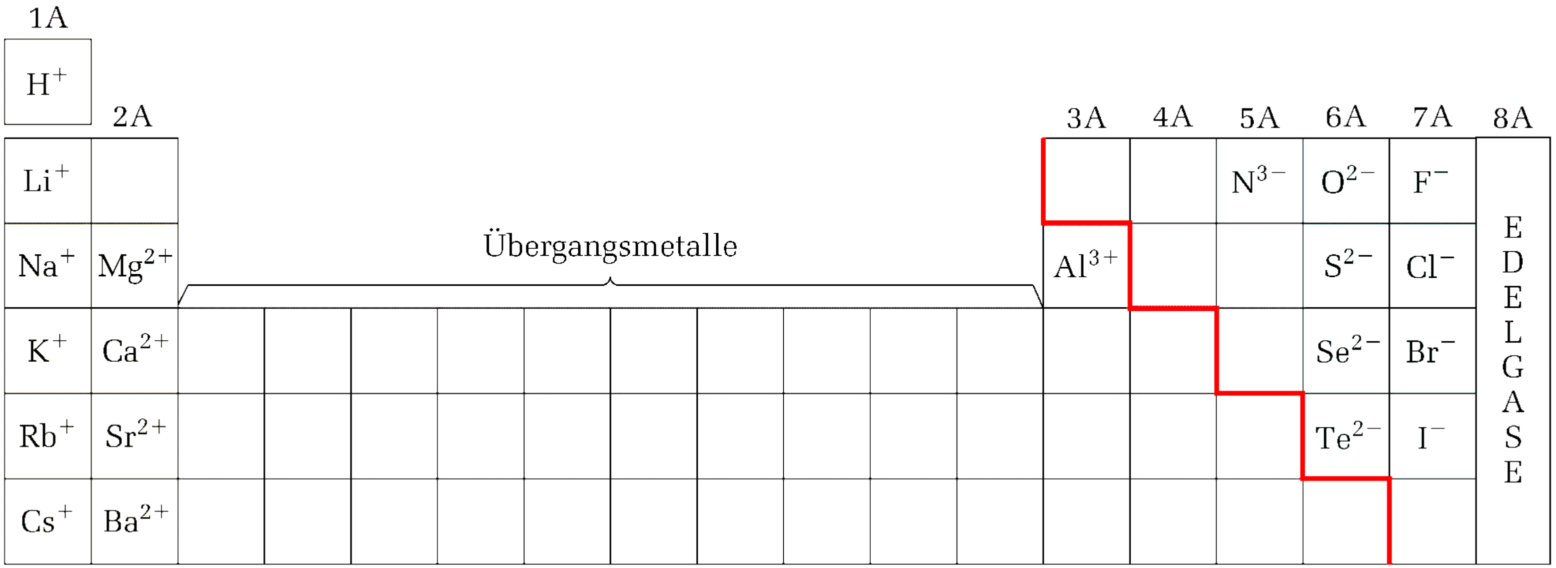
Ions

- Some elements are very friendly and predictable



- For an element, is it energetically OK to
  - gain / lose 1, 2 or 3 electrons ?
- Many elements rarely form ionic compounds, C, P, ..
- Many form more than one kind of ion, Fe^{2+}, Fe^{3+}

Ionic compounds



- What can one predict from the table ?
    - ionic compound must be neutral
        - NaCl, $CaCl_2$, what would Al and O be ?

Ionic compounds

- many anions are not ions from atoms
  - OH^{-}, SO_4^{2-}, CO_3^{2-}, PO_4^{3-}
  - compound ions – stable group of atoms with some extra electrons
    - more later

Chap 3

Stöchiometrie / Stoichiometry

Stöchiometrie / Stoichiometry

- formula, chemical equation
- burn H_2 and O_2, to make water H_2O
  - do not say $H_2 + O_2 \rightarrow H_2O$
  - H on left = 2 & on right = 2
  - O on left = 2 & on right = 1 ✗
  - $H_2 + ½ O_2 \rightarrow H_2O$ OK
  - $2 H_2 + O_2 \rightarrow 2 H_2O$ best (convention)

who cares ?

- essential for working out how much of something is used up (sugar, O_2,..)
- how much O_2 will I need to burn some sugar ?
- how much CO_2 will be made from kg of sugar / protein?
- how much product is made (sugar, CO_2, H_2O)

stoichiometry rules

- amount of each element is same on left & right hand sides
- not allowed to change composition of a compound
  - CO_2 never becomes CO_3
- prefer to have whole integers
  - $2\ H_2 + O_2 \rightarrow 2\ H_2O$ better than $H_2 + \frac{1}{2}\ O_2 \rightarrow H_2O$

examples

in	out
O_2 , NO	NO_2
CH_4 , O_2	CO_2 , H_2O
Al , HCl	
ethylene & O_2	

Rules for examples

- Breakdown reactions
  - products are the most stable forms
    - N_2, CO_2, … not exotic compounds
- burning
  - complete oxidation assumed, CO_2, H_2O
  - example – burnt in air..
    - C_3H_8
    - methanol
    - glucose ($C_6H_{12}O_6$)

Molecular weight

- M_r or m.w. or FG in textbook
- atomic mass unit “u”
- “ame” in book, “amu” in English books
- sometimes Dalton
- weight of a hydrogen atom (1/12 of ^{12}C atom)
  - we will forget this in a moment and work with kg
- summed mass of component atoms in correct ratio

- M_r of $H_2NO_3 = 2 \times 1\text{ u} + 14\text{ u} + 3 \times 16\text{ u} = 64\text{ u}$
- more examples $Al(OH_3)_3$ or fraction of mass of elements in C_{12}, H_{22}, O_{11}

	M_r
Al	27
Ca	40

Avagadro’s number

- important $N_A = 6.0 \times 10^{23}$
- N_A = how many atoms are in 12g of ^{12}C
- N_A of something is 1 mole (mol)

- 1 mol of $O_2 = 6.0 \times 10^{23}$ molecules of O_2 (1.2×10^{24} O atoms)
- 1 mol of O $= 6.0 \times 10^{23}$ atoms of O
- 1 mol of Cl^- ions is 6.0×10^{23} atoms
- 1 mol of € is much money

- why ? 1 mol of a chemical is convenient

molar masses

- 1 atom ^{12}C is M_r=12, 1 mol ^{12}C is 12g, molar mass is 12g
- M_r of Cl is 35.5, 1 mol Cl is 35.5 g, molar mass is 35.5g
- 1 mol of NO_3^-, NaCl, …

- Normal example questions
- How many moles in
  - 500g of Na_2CO_3 ?
  - 500g of $NaHCO_3$?

- formula of vitamin C
  - 40.92 %C, 4.58 %H, 54.5 % O
- my sample from oil has 3 C: 4 H and mol wt of 121
  - what is formula ?

More example calculations

- an organic compound made of C, H and O is oxidised
  - 204 g of the compound at start
  - 528 g CO_2 and 252 g H_2O
  - what is the formula of the compound ?

- How many g water do we get from burning 1g glucose ($C_6H_{12}O_6$) ? No calculator necessary

Limited Reactions

- what happens with
  - 26 g O_2 and 4 g of H_2 ?
  - 32 g O_2 and 2 g of H_2 ?

Limited Reactions

- how many g O_2 do I need to burn
  - 10g of sugar $C_{12}H_{24}O_{12}$?
  - 5g of ethanol ?

- 2 Na_3PO_4 (aq) an $Ba(NO_3)_2$ (aq) gives $Ba_3(PO_4)_2$ (s) & $NaNO_3$ (aq)
- balance the reaction
- how many g of barium phosphate do I get from
  - 330g of sodium posphate +
  - 800g of barium nitrate ?

(aq)	aqueous
(s)	solid
(l)	liquid
(g)	gas

	M_r
Ba	137
Na	23
O	16
N	14
P	32

Chap 4
Reactions in water

Reactions in Water (chap 4)

- Reactions in general
  - solid phase ? bit special
  - solid + liquid common
  - gas phase ? common, but not so in biochemistry
  - in water (aqueous) most important for biochemistry
- Topics
  - precipitation reactions
  - acid-base
  - redox (simple)
  - properties of ions in solution

nomenclature

- what is the state of something ?

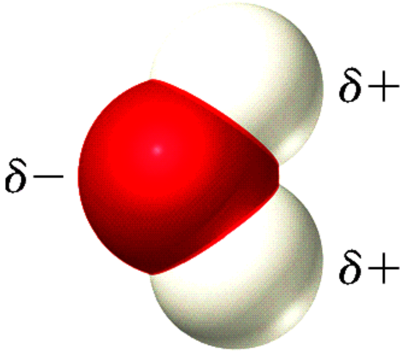
l	liquid
g	gas
s	solid
aq	aqueous

- language independent
- We usually say
  - X(aq) + Y(aq) → A(aq) + B(s)
- most of our chemistry is (aq)

Reactions in water

- Most important
  - typical of reactions in cell

Ionic solutions



- solutions are ionic / not ionic
- water is neutral but polar

- think of NaCl – really Na^+ and Cl^-
- throw in water
  - who would an Na^+ like to be with ?
    - competition of Cl^- and H_2O
      - there is a lot more water than Cl^-
        - how much more - next slide

Typical numbers for a solution

- 5.85 g table salt in 1l water – some spoons – tastes salty

- $5.85\text{g} = \left(\frac{5.85}{23+35.5}\right)\text{mol} = 0.1\ \text{mol}$

- 1l water = 1kg water is $\frac{1000}{18}\text{g} = 55.5\ \text{mol}$

- what is ratio of H_2O to Na^+ or Cl^- ?
  - 555 : 1

- why is this a simplification ?
  - 1l water will be a bit less – volume of salt

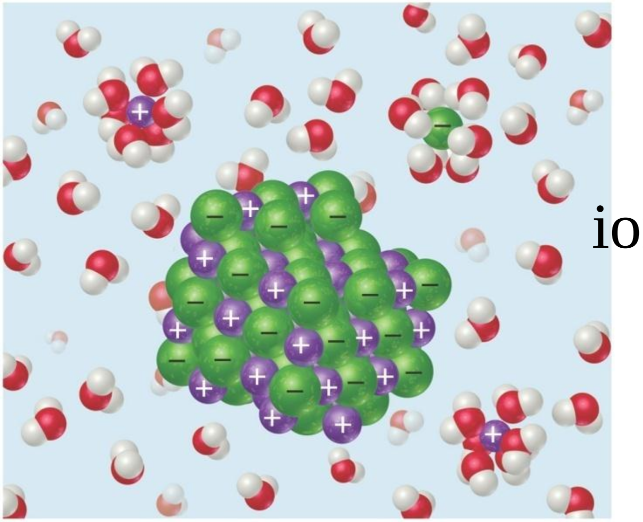
non-ionic solutions

when do we have an ionic solution ?

- most times when a compound is easy to ionise / happy to form $^{+}/^{-}$
  - K, Na and other first and second column metals
  - Cl, F and other halogens

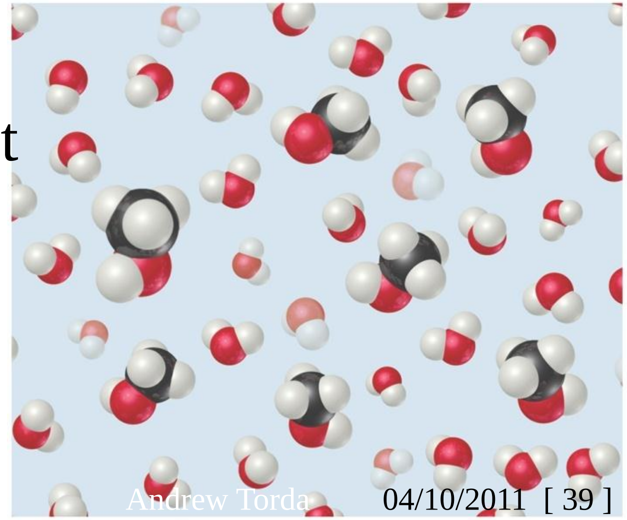
when do we have a non-ionic solution

- when the bonds are covalent
  - sugars, alcohols

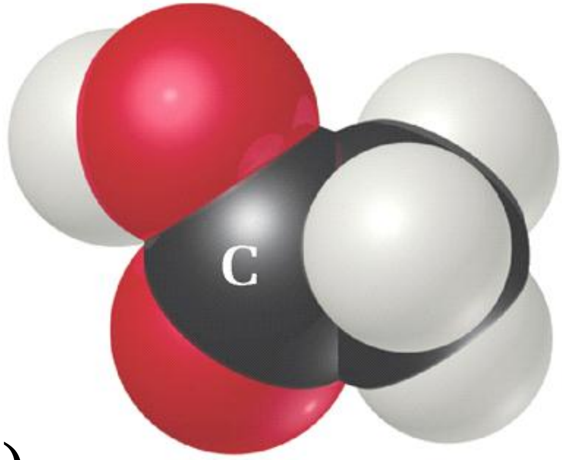


ionic

covalent



In between



partially ionic / partially non-ionic

- many examples – typical of weak acids

acetic acid (vinegar)

- CH_3COOH (aq) $\rightleftharpoons$ CH_3COO^- (aq) + H^+ (aq)
- but there is an equilibrium
- there are
  - whole CH_3COOH molecules
  - CH_3COO^- ions + H^+ ions

other possibility – something is not soluble – precipitate

  - $Mg(NO_3)_2$ is not very soluble
  - ~~$Mg(OH)_2$ (s)+ H_2O (l)→ Mg^{2+} (aq) + 2 OH^- (aq)~~

when would we see this ?

- $Mg(NO_3)_2$ (aq) + 2 NaOH(aq)→
  $Mg(OH)_2$(s) + 2$NaNO_3$(aq)

Solubility, dissociation

Where does this happen ?

- partially ionised forms are important
  - PO_4^{3-} , CH_3COO^- and lots of organic acids are only partially ionised
  - cells are full of these
- insoluble compounds ?
  - not floating around in cells
  - may be part of structures – cell walls, bones, membranes

Solubility rules

- guidelines
- nomenclature [A] is the concentration of A, mol l^{-1}
- for compounds AB there is a threshold [A] [B] ionic product. AB will form precipitate if [A][B] is above this threshold
- either A or B may be a complex ion (PO_4^{3-},NO_3^-, CH_3COO^-, ..)

Equations with ions

- Dissolve an ionic compound like NaCl or KI
- there is hardly any of the compound
  - most is Na^+, K^+, Cl^-, I^-
- You can write an equation
  - $Pb(NO_3)_2(aq) + 2\ KI\ (aq) \rightarrow PbI_2(s) + 2\ KNO_3\ (aq)$
- maybe more sensible to write
  - $Pb^{2+}(aq) + 2\ NO_3^-\ (aq) + 2\ K^+\ (aq) + 2\ I^-(aq) \rightarrow$ $PbI_2(s) + 2\ NO_3^-\ (aq) + 2\ K^+\ (aq)$
- this is true, but some ions on both sides – net reaction
  - $Pb^{2+}(aq) + 2\ I^-(aq) \rightarrow PbI_2(s)$
- the others were "spectator ions"
- if everyone is a spectator ion, there is no reaction
  - ~~$Na^+ + Cl^- + K^+ + NO_3^- \rightleftharpoons Na^+ + Cl^- + K^+ + NO_3^-$~~

Acid –base reactions

- What is H ? proton + electron
- H^+ is just a proton

- acid is proton donor, can be weak or strong

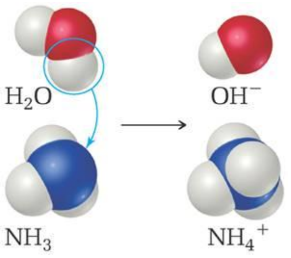
$HNO_3\ (aq) \rightarrow H^+\ (aq) + NO_3(aq)$ strong

$HCl\ (aq) \rightarrow H^+\ (aq) + Cl^-(aq)$

$CH_3COOH\ (aq) \rightleftharpoons H^+\ (aq) + CH_3COO^-\ (aq)$ weak

$NaHCO_3\ (aq) \rightleftharpoons H^+\ (aq) + NaCO_3^-\ (aq)$

Base



- Base = something that will accept a proton

- $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$
- $NaCH_3COO + H_2O \rightleftharpoons CH_3COOH + OH^- + Na^+$

- $NaOH \rightarrow Na^+ + OH^-$ then
- OH^- + H-anything → H_2O + anything$^-$
- hydroxide groups like to take protons from other things

- what happens when one mixes an acid and a base ?

Neutralization

- first – what is a salt ?
  - ionic compound, NaCl, $CaCO_3$

- mix acid + base (metal hydroxide)   - example
  - $HCl + NaOH \rightarrow NaCl + H_2O$
  - $2CH_3COOH + Ca(OH)_2 \rightarrow Ca(CH_3COO)_2 + 2\ H_2O$
  - $H_2SO_4 + 2\ KOH \rightarrow 2K\ SO_4 + 2\ H_2O$

- theme = salt + water
- where have ions gone ?
  - $NaOH + HCl \rightarrow NaCl + H_2O$ is really
    - $Na^+ + OH^- + H^+ + Cl^- \rightarrow Na^+ + Cl^- + H_2O$
    - = salt + water
    - $y\ BH + M\ (OH)_x \rightarrow\ ?\ H_2O + ?\ B\ M$

Last words on acids and bases

- acid – anything that can donate a proton
- base – anything that can accept a proton

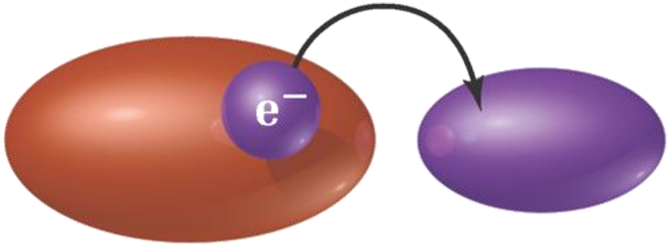
- bases can be things like
  - $NaCH_3COO$ since $CH_3COO^- + H^+ \rightleftharpoons CH_3COOH$
- ammonia is a base $NH_3 + H^+ \rightleftharpoons NH_4^+$
- something may be an acid or base HCO_3^-
    - as a base..
- $H^+ (aq) + HCO_3^- (aq) \rightleftharpoons H_2CO_3 (aq) \rightleftharpoons H_2O (l) + CO_2(g)$
    - as an acid
- $NaOH (aq) + HCO_3^- (aq)$ really
  - $Na^+ + OH^- (aq) + HCO_3^- (aq) \rightarrow H_2O + Na^+ + CO_3^{2-}$
  - $OH^- (aq) + HCO_3^- (aq) \rightarrow H_2O (l) + CO_3^{2-} (aq)$

Oxidation / Reduction

- So far: H^+ reactions (exchange of protons)
- oxidation does not necessarily involve O_2
- reduction = giving electrons
  - if X is reduced it gains an electron
- oxidation = having electron taken away

$Ca(s) + 2H^+ (aq) \rightarrow Ca^{2+} + H_2 (g)$

- solid calcium is "dissolved" in acid

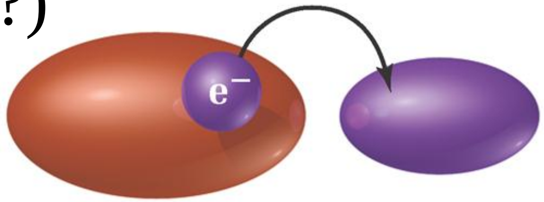


Substanz wird **oxidiert** (gibt Elektronen ab)

Substanz wird **reduziert** (nimmt Elektronen auf)

Oxidation / Reduction

- $Ca(s) + 2H^+ (aq) \rightarrow Ca^{2+} + H_2 (g)$
- H_2 gas released
- Ca has become charged
- reaction is not complete – we have neglected the anions
  - Cl^- or NO_3^- or SO_4^- or …(why not OH^- ?)



Substanz wird **oxidiert** (gibt Elektronen ab)

Substanz wird **reduziert** (nimmt Elektronen auf)

- Why is it called oxidation ? Historic
  - Example $2 Ca (s) + O_2(g) \rightarrow 2 CaO$
- Nomenclature
  - something is reduced by a reductant
  - A reduces B, B is reduced by A
  - A is oxidised by B, B is an oxidant
- more nomenclature – oxidation numbers

Oxidation numbers / states

- mixture of book-keeping and real world
- simple example
  - how do you meet Na ? As Na or Na^+
  - in one case there is no charge (oxidation state 0)
  - in other case, there is a charge of +1
  - oxidation states 0 or 1

  - Solid sodium oxidation state 0
  - table salt Na is +1, Cl is −1

- Labelling to tell us how likely reduction/oxidation is
- Oxidation states are associated with atoms/ions not complex ions (CO_3^{2-}, NO_3^-, ..)

Oxidation numbers / states - Rules

- single atom ion – oxidation number is the charge
  - Ca^{2+}, H^+, Cl^-,
- In elemental form, oxidation state is 0
  - Na, P_4, O_2, H_2, Ar
- in a neutral compound oxidation numbers sum to 0
- in a complex ion, sum of oxidation numbers is charge of ion

Some rules have exceptions..

- Oxygen is usually −2 in compounds (H_2O, CO_3^{2-}, ..)
- Metals usually go +1, +2, .. (they happily lose electrons)
- H is usually +1 (important exceptions)
- Halogens are usually −1, F is almost always −1

Example oxidation states

- To discuss – each element in
  - KOH
  - CH_4
  - CCl_4
  - HCO_3^-
  - CH_3COONa − not really a good question CC bond is so covalent

- Problem – oxidation states are best for purely ionic systems
- Strategy for answers – start with known reliable cases
  - O^{2-}, halide$^-$,

Why do some things oxidise / reduce ?

- Detour – acids and bases
  - strong acid = something that will happily give up an H^+
  - weak acid – not so enthusiastic
  - strong base = energy becomes much better (more negative) when it meets a proton

- Oxidation / reduction
  - you can rip an electron off almost anything
  - with some atoms you only have to ask gently
  - some reach a good energy state when they lose/gain 1 or 2 electrons
  - examples

easy / hard to oxidize

- how hard is it to take an electron off some atom ?

lithium	→	$Li+$	+	e^-	easy to
natrium (sodium)	→	$Na+$	+	e^-	lose e^-
..					
zinc	→	Zn^{2+}	+	$2e^-$	
…					
wasserstoff (hydrogen)	→	$H+$	+	e^-	hard to
..					lose e^-
gold	→	Au^{3+}	+	$3e^-$	

- many more in text book
- how to remember ?
  - think of gold – does not oxidize
  - think of sodium – rarely seen as metal, fizzes in water

Concentrations

- you have to mix some chemicals for a reaction
- you are working with solutions
- you want to know how many atoms / molecules you are dealing with – how many atoms are there in my solution?

- only one answer / one common unit
- molarity = molarität = moles l^{-1}
- usage: *x* M solution = *x* moles per liter (often mM)
- lots of examples
  - 6.7g of a sugar $C_6H_{12}O_6$ in 100 ml water
  - 117 g table salt in 1/5 l water

more molarity examples

- how many g of $NaHSO_4$ do we need for 400 ml of 0.5M?
- How many g of O_2 do I need to burn
  - 100g ethanol (CH_3CH_2OH) ?
  - 100g methanol (CH_3OH) ?

- K_3PO_4 & $AgNO_3$ are soluble
- Ag_3PO_4 is not
- I have 100mM K_3PO_4 What volume do I need to get 85g of silver phosphate from a bucket of $AgNO_3$?

H	1	O	12
C	12	K	39
N	14	Ag	108

Summary of solutions

- strong and weak electrolytes
- reactions that give solid (Fällungsreaktionen) or gas
- strong and weak acids and bases – transfer of protons
- oxidation / reduction – transfer of electrons
- molar calculations

chap 5 - Thermochemistry

chap 5 - Thermochemistry

- Later (summer semester) – everything is based on energies

- kinetic versus potential
- kinetic E_{kin} = ½ mv^2 applies from atoms to trucks
- dimensions ?
- units ? kg m^2 s^{-2} / joules

- potential energy
  - E_{pot} in many forms
    - elastic, lennard-jones, bonds, …

$$E_{el} = \frac{q_1 q_2}{4\pi\varepsilon_0 r_{12}}$$

$$E_{grav} = \frac{G m_1 m_2}{r_{12}}$$

- everything tries to go to lower (more negative) energy

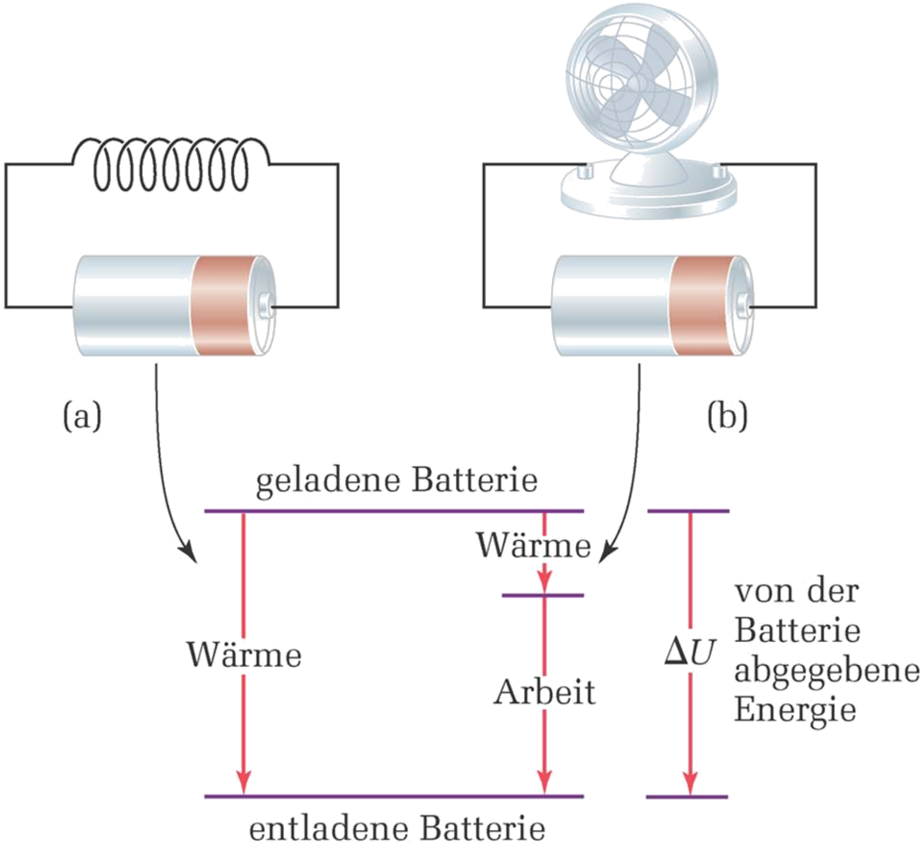
Energy

- Energy put into a system is work W
- If you like forces W = force · distance
    - check the dimensions

- who cares about work ?
    - usually we do not worry about absolute energy
    - ΔE is more important
    - usually we talk about the internal energy U
    - ΔU is most important
- Heat is like work (gives energy or heat is given out)
    - how can the energy of a system change ?
    - $\Delta U = Q + W$ Q is heat
    - Q can be +ve or −ve

Work and Heat

- Are they the same ? Almost



Conventions

- ΔU negative system has lost energy
- W negative: work is done by the system
- Q negative: the system gives out heat

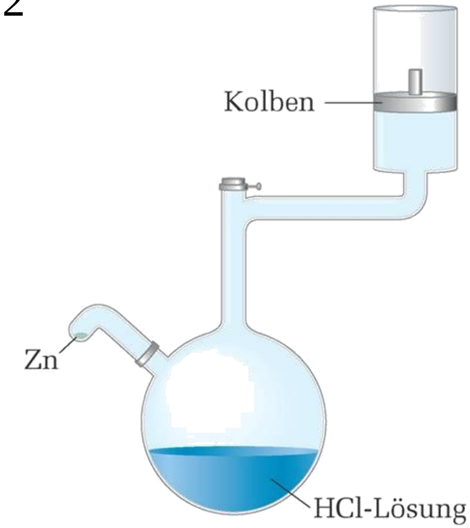
Energy and reactions

- A reaction will go forwards
  - if it gives out heat or
  - if you can do work on the system

- how can we see work ?
  - fan example
  - gas ?
- work done on a gas $W = -p\Delta V$ (pressure p, volume V)
- what is the total energy of a system ?
  - enthalpy = internal + pressure and volume
  - $H = U + pV$
    there is some kind of energy associated with pressure
  - (think about zero pressure – no energy there)

pressure / volume / work

How can a reaction like $Zn(s) + 2H^+ \rightarrow Zn^{2+} + H_2$ do work?

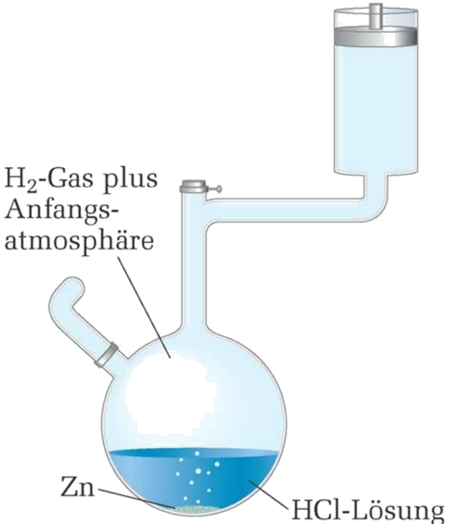


(a)

- in picture, we could see volume change

$$H = U + pV$$

- if we have a reaction at constant pressure
  - $\Delta H = \Delta(U + pV)$



H enthalpy
U internal energy
p pressure
V volume
Q heat

Work / heat

- reaction at constant pressure
  - $\Delta H = \Delta\,(U + pV)$

    $= \Delta U + p\,\Delta V$

    $= \Delta U - W$ since $W = -p\Delta V$

    or

    $= Q + W - W$ since $\Delta U = Q + W$

    $= Q$

- in this kind of reaction the change in energy will be seen as heat

- little detour and summary of terms so far

Summarise energies

E is just energy – kinetic or potential of some kind

- units / dimensions will always be the same
- in any equation $E = a + b + c$ then a, b, c are energies with same units

U is internal energy

- you can change it by heating or doing work
  - work =acceleration, moving in a field, compressing, …
  - the one form we have mentioned it $W = p\,\Delta V$
- heat has the same units as energy (not temperature)
  - what must be dimensions of p ?
- enthalpy H includes internal energy and work to organise the system $p\Delta V$

More energy summary

- Often we only care about changes ΔU or ΔV
- why so important ?
  - will reactions go forwards ?
  - how much work can I do from burning a kg of sugar ?
  - how much sunlight do I need to fix a kg of CO_2 ?

Reaction enthalpy

- $\Delta H = \Delta H_{\text{product}} - \Delta H_{reactant}$
- $2H_2\ (g) + O_2(g) \rightarrow 2H_2O\ (g)$ $\Delta H = -\ 484$ kJ
- $4H_2\ (g) + 2O_2(g) \rightarrow 4H_2O\ (g)$ $\Delta H = -\ 968$ kJ
  - moles as given in reaction
- why do I say *H* and not *E* or *U* ?
- must specify (s), (l), (aq), (g)
- $2\ H_2O\ (l) \rightarrow 2\ H_2O\ (g)$ $\Delta H = +88$ kJ

- exothermic $\Delta H < 0$ likely to go forwards
- endothermic $\Delta H > 0$ not likely to go forwards

- calculate energy release to make *n* g of H_2O
  - $2\ H_2O_2\ (l) \rightarrow 2\ H_2O\ (l) + O_2(g)$ $\Delta H = -196$ kJ

energies / additivity

- energy is always conserved (sometimes not obvious)
- a total energy will be the sum of steps
- A+B → C → D + E has $\Delta H_{A+B\rightarrow D+E}$
- $\Delta H_{\mathrm{A+B\rightarrow D+E}} = \Delta H_{\mathrm{A+B\rightarrow C}} + \Delta H_{C\rightarrow D+E}$
- we can go further and include change of states
- A(l) + B (l)→ C(l) → D(l) + E(g) will be the same as
- A(l) + B (l)→ C(l) → D(l) + E(l) → D(l) + E(g)

  - can work out total ΔH if we know parts

- consequences…

Enthalpy changes

- ΔH for A→B→C→D is same as A→R→Q→S→T→D
- $\Delta H = 0$ A→B→A
- $\Delta H = 0$ A→B→C→D→E→A (cycle)
- water → steam → water $\Delta H = 0$ kJ

- my battery (akku) NiMH or NiCd
- $\Delta H_{charge} = -\,\Delta H_{discharge}$
- Can we make a very general set of rules ?
  - standard enthalpies

standard enthalpy of formation

Definition

- standard enthalpy of formation $\Delta H^0 = 0$ for an element in most stable form
- $\Delta H^o (O_2) = 0$, ΔH^o (C, graphite) = 0

- this is not true for other forms
  - C(graphite) → C(diamond) $\Delta H = ?$
  - what will the sign be ? …

standard enthalpy of formation

Definition

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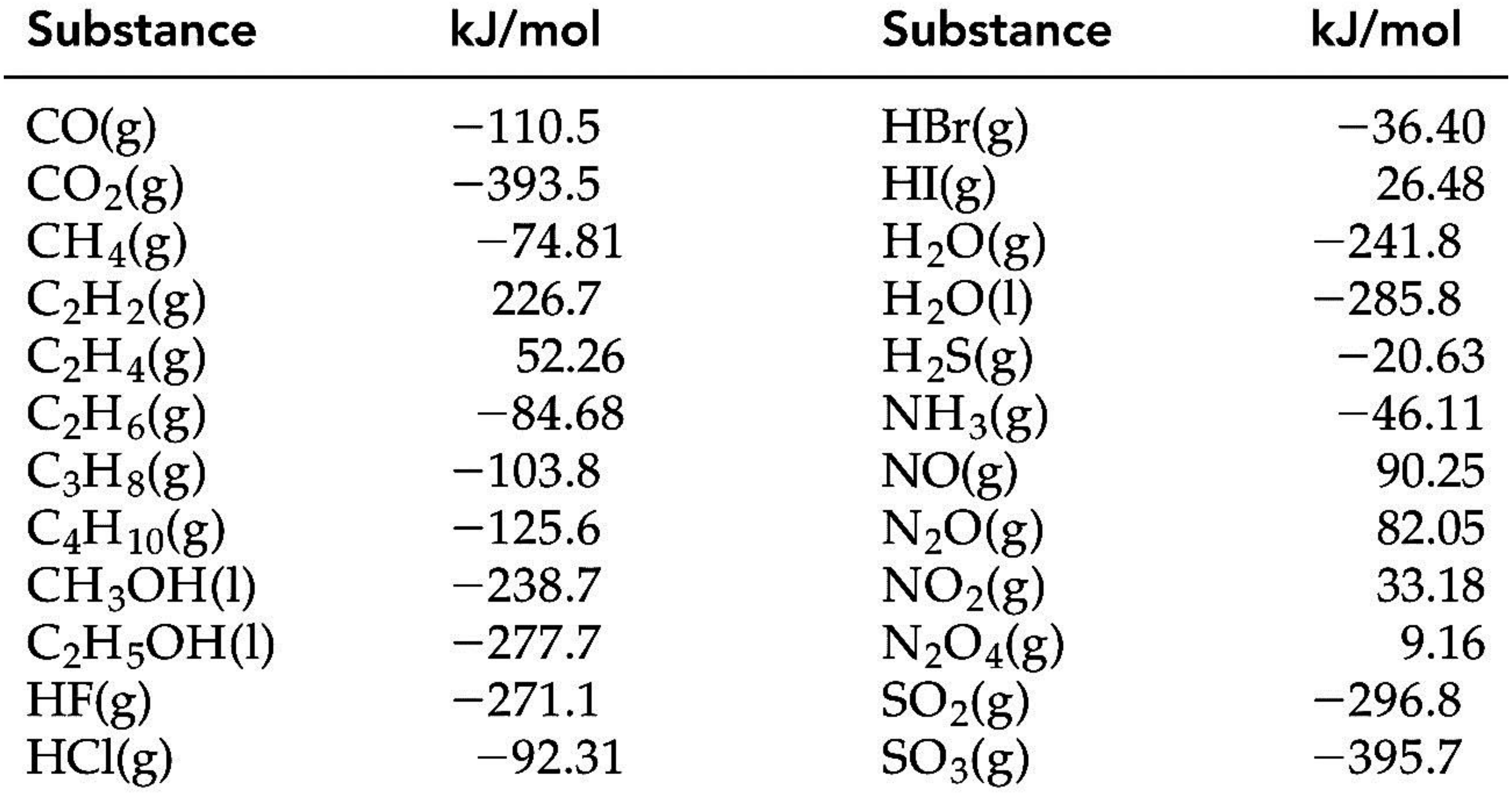
  - $\Delta H^o (O_2) = 0$, ΔH^o (C, graphite) = 0

- this is not true for other forms
  - C(graphite) → C(diamond)
  - graphite is more stable, so we need to put in energy
  - $\Delta H^o > 0$ (about 1.8 kJ mol^{-1})
- why is this helpful ?
  - make tables of common compound ΔH_f^o then we can work out new ΔH_f^o

example enthalpies of formation

- For some compound $A_mB_n(x)$ we have tables of
  ΔH_f^o for $m\,A$ (standard) + $n B$(standard) $\rightarrow A_mB_n$ (l)
- standard tables for forming 1 mol of substance at 298 K



Substance	kJ/mol	Substance	kJ/mol
$CO(g)$	−110.5	$HBr(g)$	−36.40
$CO_2(g)$	−393.5	$HI(g)$	26.48
$CH_4(g)$	−74.81	$H_2O(g)$	−241.8
$C_2H_2(g)$	226.7	$H_2O(l)$	−285.8
$C_2H_4(g)$	52.26	$H_2S(g)$	−20.63
$C_2H_6(g)$	−84.68	$NH_3(g)$	−46.11
$C_3H_8(g)$	−103.8	$NO(g)$	90.25
$C_4H_{10}(g)$	−125.6	$N_2O(g)$	82.05
$CH_3OH(l)$	−238.7	$NO_2(g)$	33.18
$C_2H_5OH(l)$	−277.7	$N_2O_4(g)$	9.16
$HF(g)$	−271.1	$SO_2(g)$	−296.8
$HCl(g)$	−92.31	$SO_3(g)$	−395.7

Examples

- ΔH_f^o for forming gas formaldehyde HCHO = −108.6 kJmol^{-1}
  - what is the reaction with correct numbers ?
- $H_2(g) + \frac{1}{2} O_2(g) + C\ (graphite) \rightarrow HCHO\ (g)$
- what is the standard enthalpy of burning ethane (C_2H_6) ?
- $C_2H_6(g) + 7/2\ O_2(g) \rightarrow 2CO_2\ (g) + 3\ H_2O\ (l)$

energy of combustion

$C_2H_6(g) + 7/2\ O_2(g) \rightarrow 2CO_2\ (g) + 3\ H_2O\ (l)$

- imagine

  $2C(\text{graphite}) + 7/2\ O_2 + 3/2\ H_2$

  $\rightarrow 2\ CO_2\ (g) + 3H_2O\ (g)$ ΔH_f^o of CO_2 & H_2O

  $\rightarrow C_2H_6(g)$ ΔH^o of combustion

  $\rightarrow 2C\ (\text{graphite}) + 7/2\ O_2 + 3/2\ H_2$ ΔH_f^o of $C_2H_6(g)$

total $\Delta H^o = 0$ (cycle)

LHS = − 86 + 0

RHS = 2 ×−394 + 3 × −286 = −1646

difference = −1 560 kJ mol−1

- do the same for burning ethanol CH_3CH_2OH

Stop here summary

- different kinds of energy, potential, kinetic
- energy, work, heat, $p\Delta V$
- enthalpy
- enthalpy calculation from tables

- problems start on p 238 of book

Chap 11
Intermolecular Forces

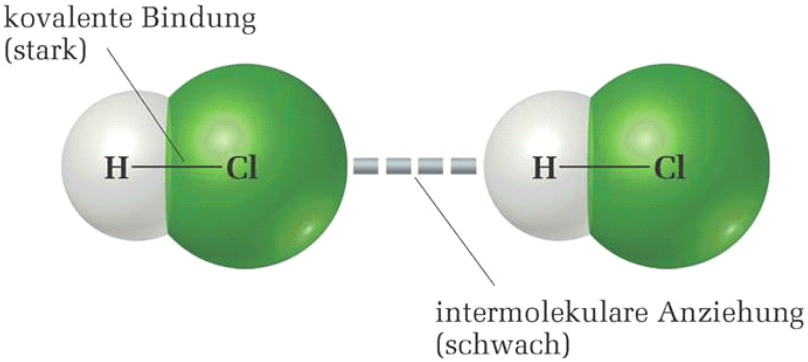
Chap 11 intermolecular forces

- when does a protein bind a therapeutic ?
- when does a molecule dissolve in cell or membrane ?

- when does something form a gas ? liquid ? solid?

- all parts of intermolecular forces

- what holds substances together ?



charges and rules

- charge – charge energy / coulombs law $U(r_{ij}) = \frac{q_i q_j}{4\pi\varepsilon r_{ij}}$
  - say $U(r_{ij}) \approx r_{ij}^{-1}$

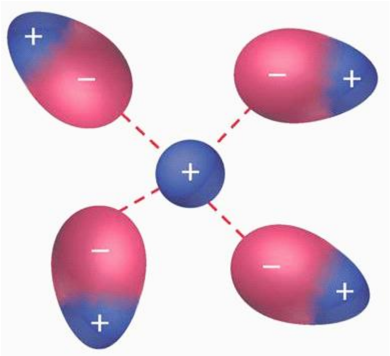
- charge – dipole
  - $U(r_{ij}) \approx r_{ij}^{-2}$ + an angular term

- dipole – dipole
- $U(r_{ij}) \approx r_{ij}^{-3}$ + an angular term

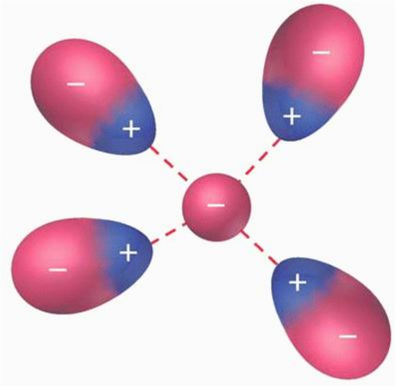
even weaker

- induced dipoles

Ion – dipole attraction



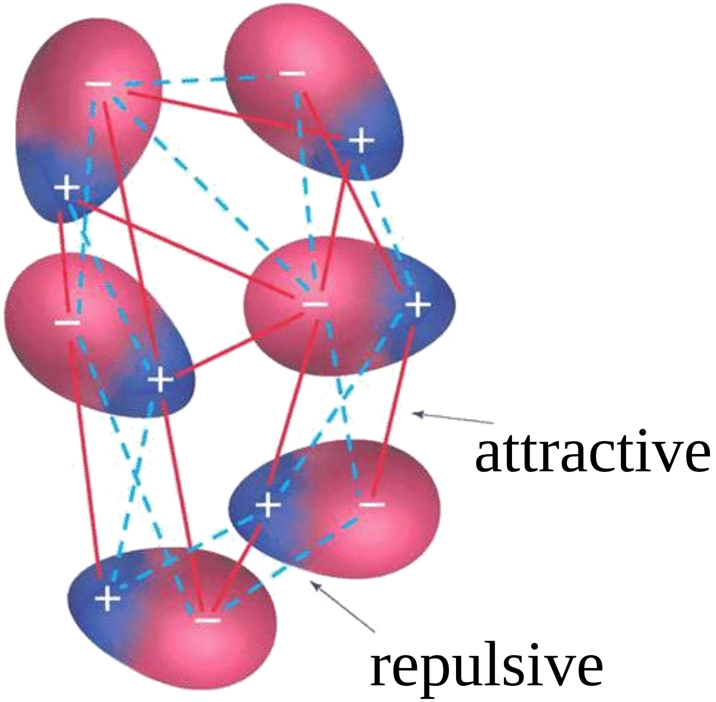
cation - dipole



anion - dipole

- most important ionic solutions, polar solvents
  - NaCl in water

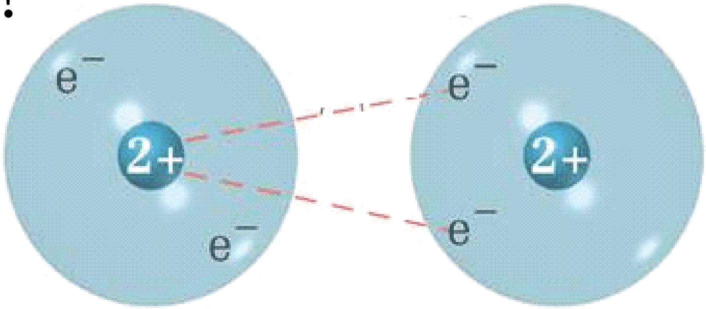
dipole-dipole forces



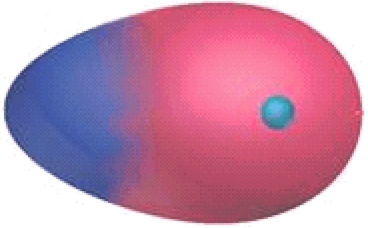
- important for polar liquids (H_2O)
- the more polar a liquid
  - higher boiling point
- remember distance dependence
  - weaker forces which fall off with r^{-2}

London dispersion forces

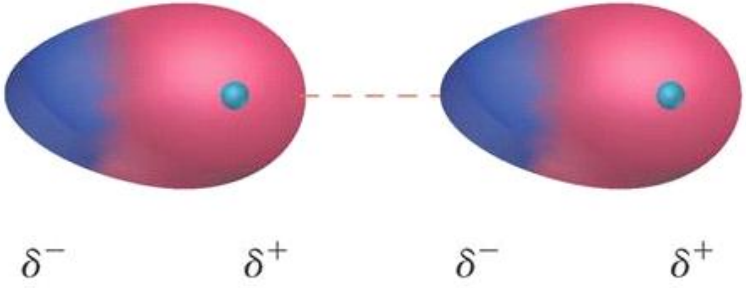
- much more in summer semester
- why does argon form a liquid ?
- why would these two He atoms attract ?
- on average electron clouds are spherical



- electron clouds wobble
  - temporary dipole



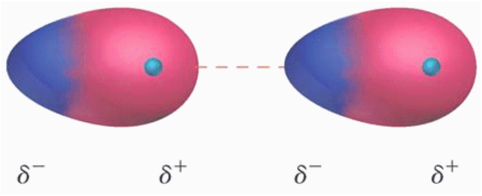
- what happens to a neighbouring atom ?



note partial charges – induced dipoles

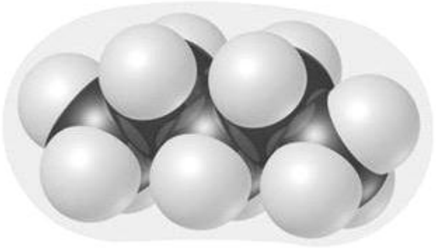
dispersion forces

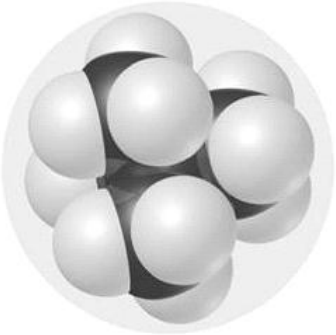
- the polarisation is not always there – comes and goes
- how important is it ?
  - if you have large electron clouds
    - polarisable



- He – not very polarisable (very hard to liquify)
- Ar – much easier

- compounds like alkanes are not polar, but have lots of electrons



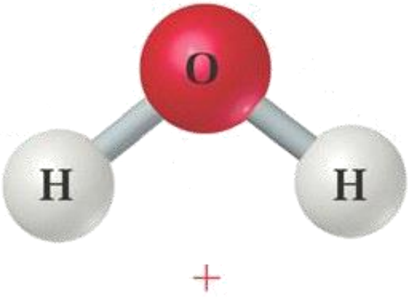


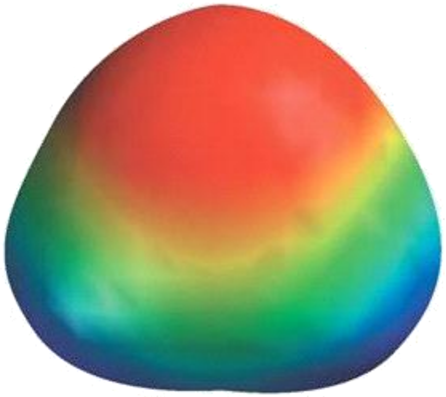
dispersion forces

- not important
  - weak
- important – apply everywhere
  - apply to polar molecules (weaker than ion or dipole)
  - apply to apolar atoms/molecules
    - the only important force
- very short distance $U(r_{ij}) \approx r_{ij}^{-6}$

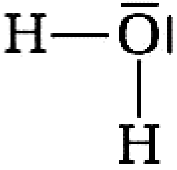
Hydrogen bonds

- very important in biological systems
  - basis of protein, RNA and DNA folding and water structure
- water story
  - unusually high melting (273 K), boiling point (373 K), heat capacity, energy of vapourisation (l→g)
  - strong forces hold water molecules together
- water is very polar
  - electron density around O is high
  - at the hydrogen very +ve

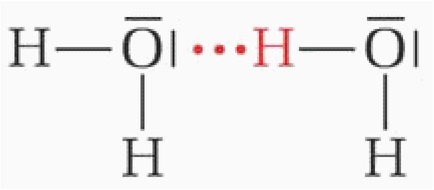




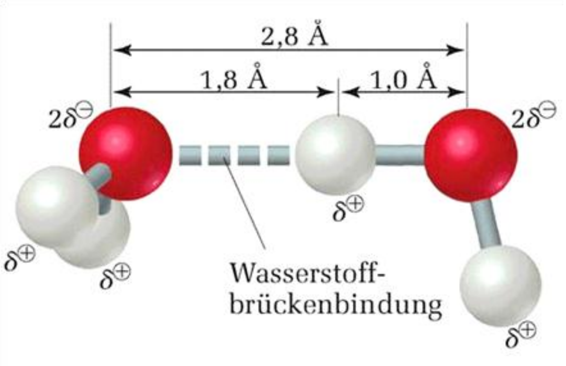
water and H-bonds



- electronic structure of water
  - free electron pairs (lone electrons)
  - other end is very positive

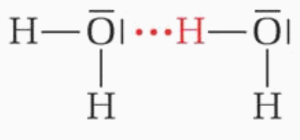


- what does ice look like ?
- 1.8 Å is small - almost a bond
  - H-bond

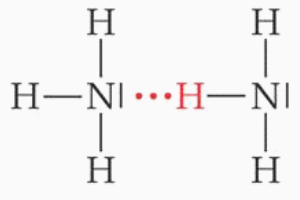


H-bonds

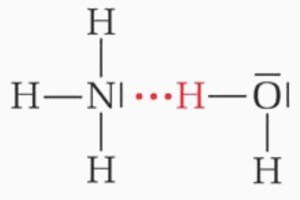
- water is not the only example – one needs
  - H bound to very electronegative atom (O, N, F)
  - atom with free electron pair (usually O, N, F)



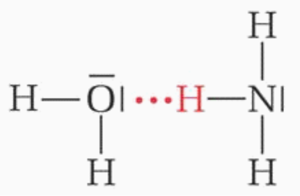
water (acceptor) water (donor)



ammonia (acceptor) ammonia (donor)

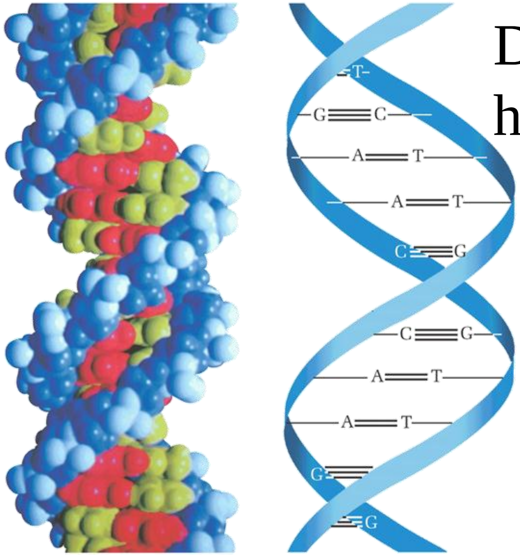


ammonia (acceptor) water (donor)

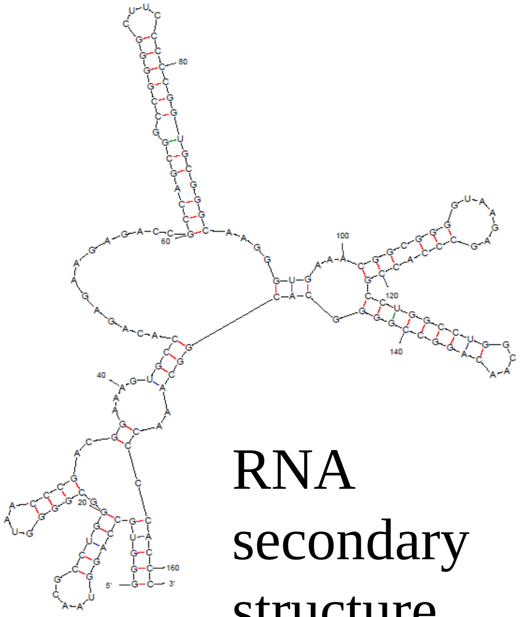


water (acceptor) ammonia (donor)

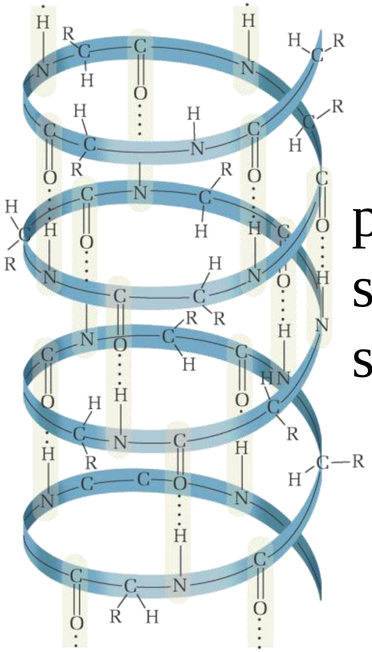
H bonds



DNA double helix



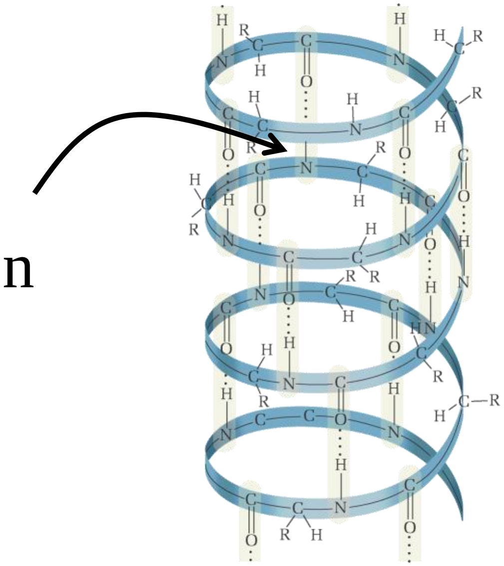
RNA secondary structure



protein secondary structure

H bonds

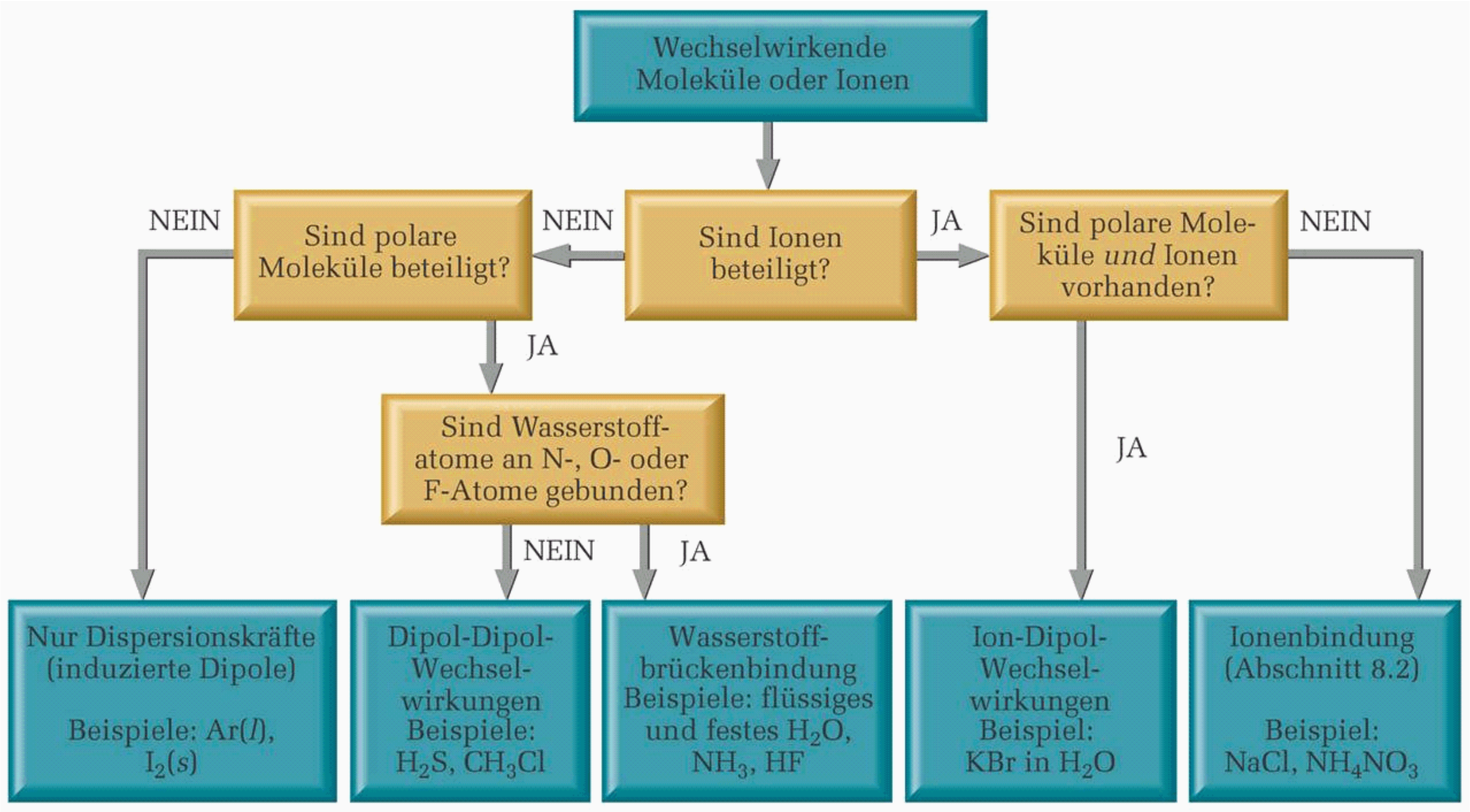
- In general
  - DH … A
    - donor – H … acceptor
- energy −4 to −25 $\mathrm{kJmol^{-1}}$
- in some systems
  - they are fixed (ice)
  - they come and go (water, macromolecules in water)
- competition for donors/acceptors



water / O
competition

intermolecular forces summary

dispersion	induced dipoles	weak
dipole-dipole	polar molecules	
H-bonds	donor and acceptor	
ion - dipole	salts in water	
ionic bonds	solid salts	strong



how to decide what is important

intermolecular forces - end

- these forces are most important in liquids and solids
- there are solids based on
    - dispersion – not so important
    - dipole-dipole – not so important
    - H-bonds – ice
    - ionic – salts
- if you put in enough energy (heat) things melt
- these forces responsible for
    - melting, boiling temperatures
    - heat of vaporisation
    - viscosity of liquids
    - solubility
    - brittleness / flexibility of solids
    - ..

Chap 14
Kinetics

Chap 14 kinetics

- how fast do reactions go ?
  - reactions are not only the obvious ones
- will reach simple equations (can be very complicated)

- factors
  - state (s, l, g; surface reactions, mostly liquids for us)
  - concentration
  - temperature; T↑ rate ↑
  - catalysts – something that accelerates a rate

reaction velocity

- concentration is formally mol m^{-3}
- chemists use mol l^{-1}, M, molar solution [X]
- 1 mM solution of A
  - [A] = 1mM
  - 1mM of A in1 liter of water

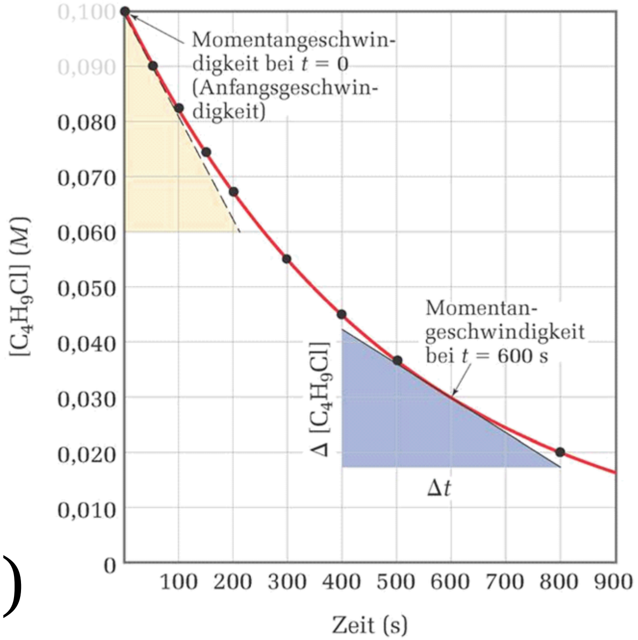
- how to describe a reaction velocity ?
  - change in concentration with time
  - M s^{-1}
  - could be for forward, backward, creation, breakdown
    - $A + B + C + D \leftrightarrow Q + R$ you just have to explain

$$\frac{\Delta[A]}{\Delta t}$$

- not always so useful – reaction rates change

reaction rates

- in a closed system $A + B \leftrightarrow Q + R$
  - at first lots of reactants [A], [B] high
  - later very little
    - Δ[A] and Δ[B] must also be smaller
- let us avoid talking about velocity like this



- $NH_4^+(aq) + NO_2^- (aq) \rightarrow N_2(g) + 2H_2O (l)$
  - reaction velocity depends on concentrations
  - velocity is $k[NH_4^+][NO_2^-]$
- more general

reaction velocity rule

$a\ \mathrm{A} + b\ \mathrm{B} \rightarrow c\ \mathrm{C} + d\ \mathrm{D}$

- velocity is $k[\mathrm{A}]^m[\mathrm{B}]^n$ for some constants m and n
- k is the reaction constant
- a and b let us make guesses, but there are lots of exceptions

exponents m and n

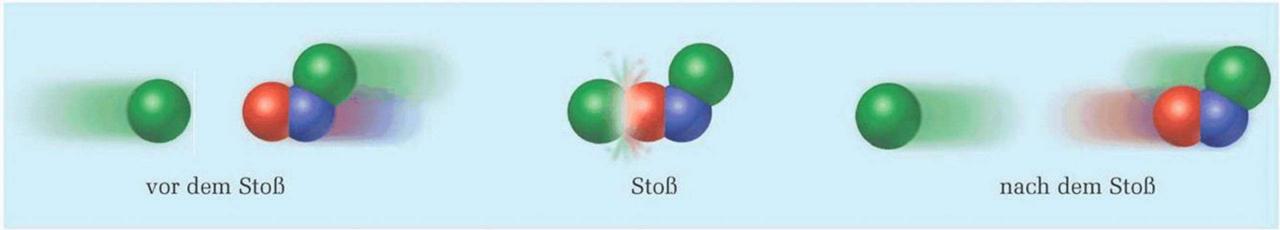
- for simple reactions, often 1
- $NH_4^+(aq) + NO_2^- (aq) \rightarrow N_2(g) + 2H_2O\ (l)$
- velocity = $k[NH_4^+][NO_2^-]$
  - first order in ammonium and first order in nitrite
  - second order reaction
- intuitively reasonable
  - reaction requires two ions to collide

reaction rate exponents

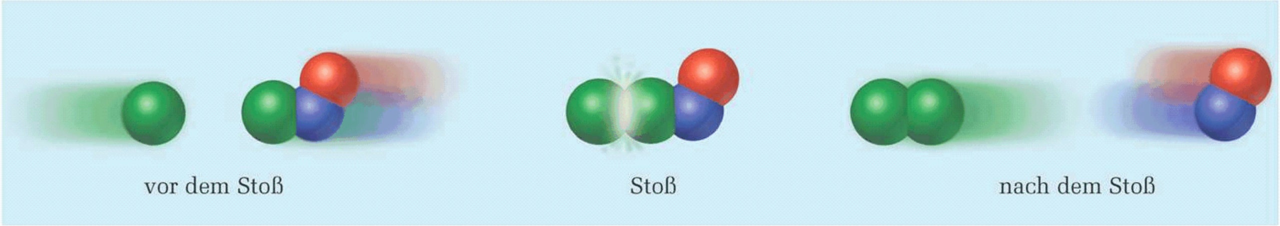
- for A + B → C+ D
- usually reaction rate depends on collision frequency
  - [A] and [B]
- the constant *k* hides all the details (how often does a collision lead to a reaction ?)
- surprises
  - $CHCl_3(g) + Cl_2(g) \rightarrow CCl_4(g) + HCl(g)$
    - velocity is $k\,[CHCl_3]\,[Cl_2]^{½}$
    - what does it mean ?
      - reaction is not a simple matter of collision
      - what could explain it ?

Reaction velocity - collisions

- mechanical view.. $Cl + NOCl \rightarrow NO + Cl_2$



boring collision same before and after



hotter collision

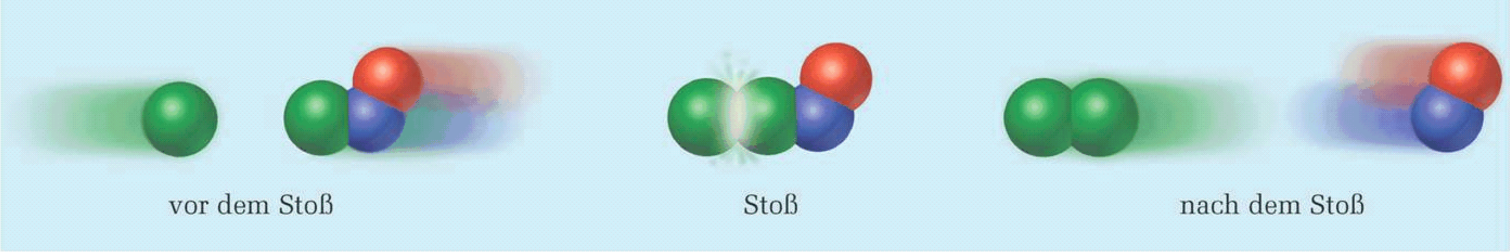
- collisions effective or ineffective
  - orientation (not much you can do)
  - temperature…
- good rule: everything goes faster with higher temperature

Reaction rate – activation energy

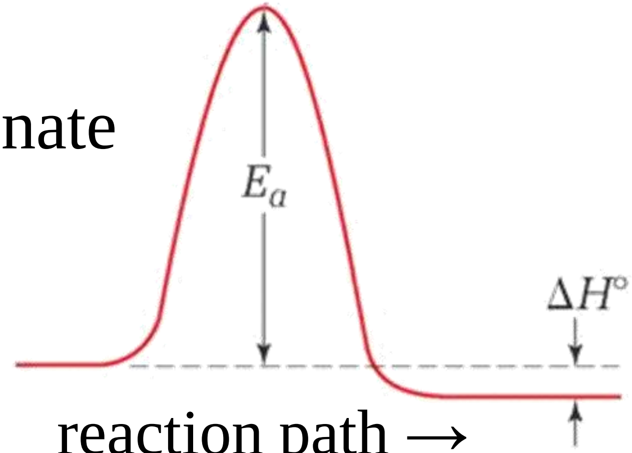
- one needs a minimum energy to break bonds, bring atoms together

potential energy

low high low



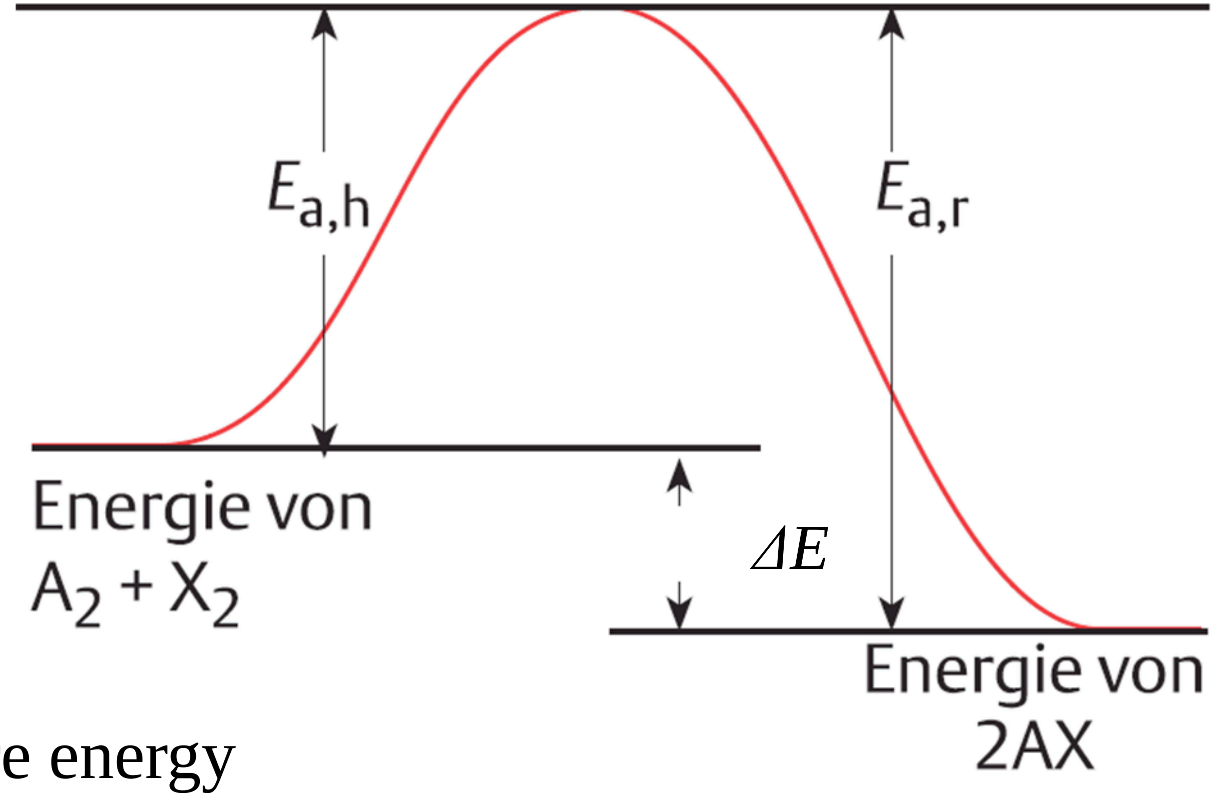
- treat this as a path or coordinate
- E_a is the minimum energy
  - activation energy



reaction path →

Reaction and activation energy

- almost every reaction is characterised by activation energy – example $A_2 + X_2 \rightarrow 2AX$



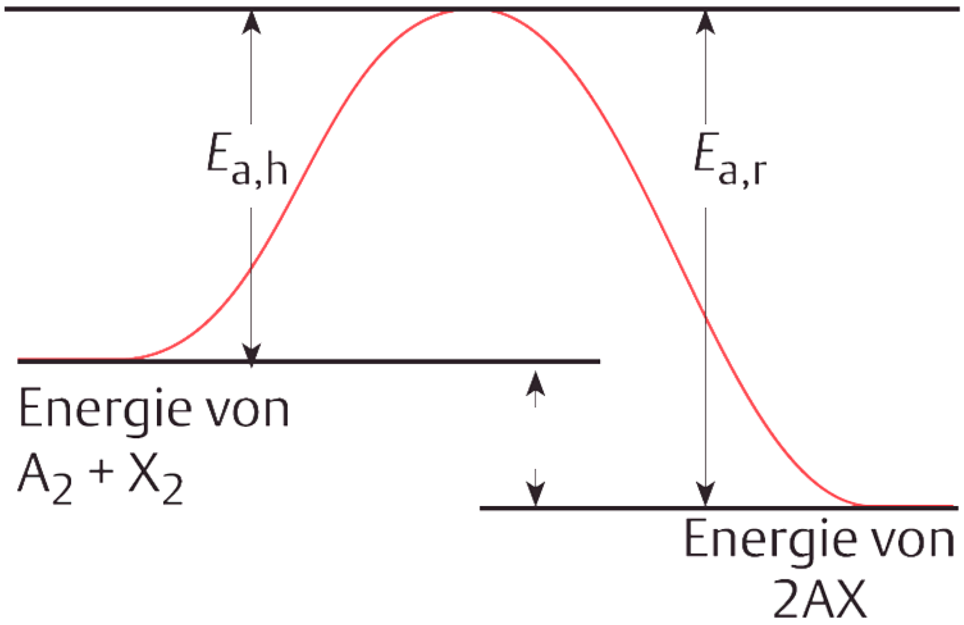
- If you measure energy change
  - see ΔH (here I use ΔE)

Activation energy

- E_a is activation energy of forwards reaction
  - imagine – how much energy must one add to have a successful collision

- what would $E_{a,r}$ be ?

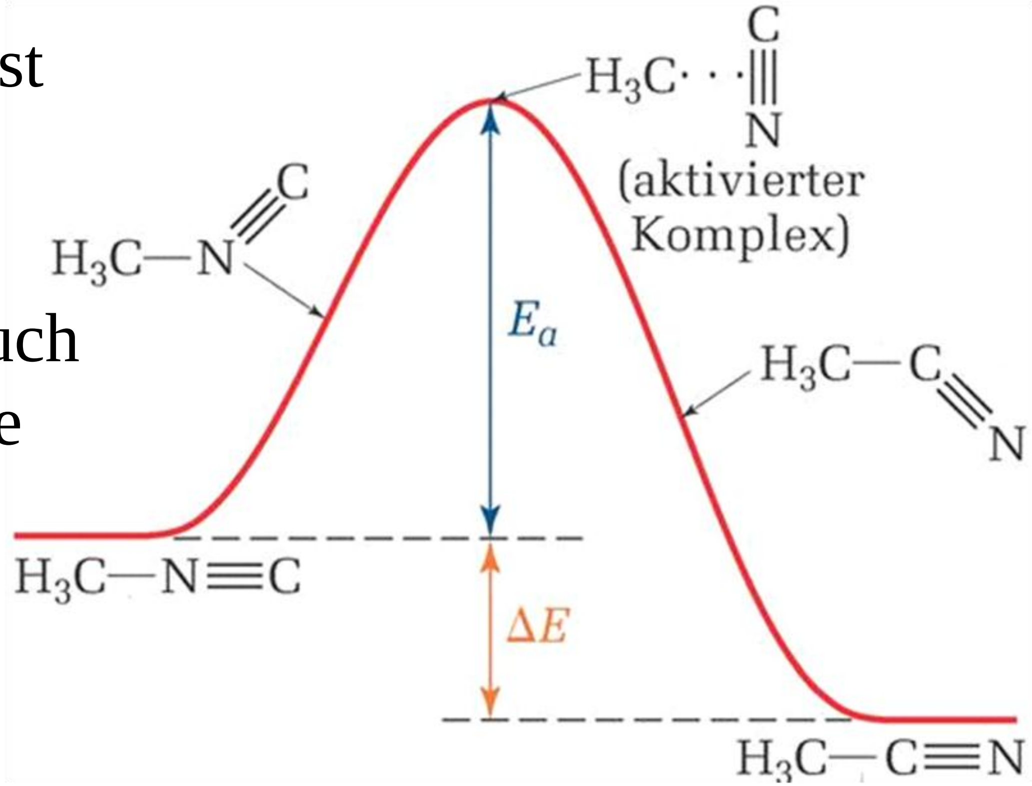
- what if E_a is
  - small or large ?



Energy of reaction and activation energy

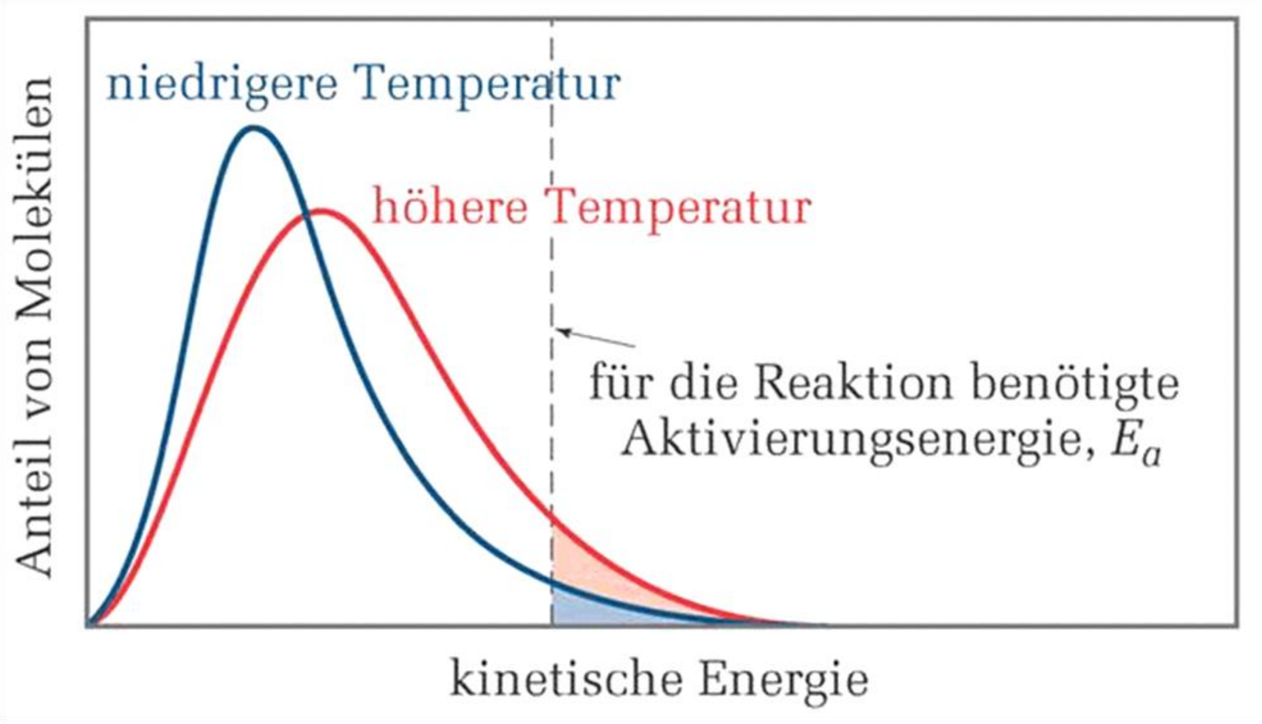
- the activation energy may not be for a collision
  - it always means going over some barrier

- if E_a is small – reaction is fast
- if ΔE is big
  - heat released
- a reaction which releases much energy need not be a fast one



Temperature and reaction velocity

- how many particles have enough energy to react ?



- fraction with enough energy $f = e^{-E_a/RT}$
    - R is gas constant

effect of temperature

- reaction rate is proportional to the fraction of particles with enough energy

$$f = e^{-E_a/RT}$$

- then $k = Ae^{-E_a/RT}$

- practice / Übung
  - how would you determine activation energy from rate measurements at two temperatures ?

more complicated pictures

- not discussed here
  - reactions might have several steps
    - often a few steps dominate

equilibria

- what if E_a is very small ?
  - reaction might seem instantaneous
- what is ΔE is very –ve, very +ve, near zero
- draw pictures

- more on equilibria later

Catalysis

- what if you have a reaction
  - $A + B \rightarrow C + D$
  - velocity seems to be independent of [A], [B] ?
  - explanation : reaction is really
  - $A + B + X \rightarrow X + C + D$

  - X goes into reaction and comes out unchanged
  - reaction very dependent on X
  - if you have small amount of X, it is the limiting component – does not matter how much A or B

- very general – catalysts might be
  - exotic metals in your exhaust pipes
  - very big proteins - enzymes

Catalysis – simple example

- $2H_2O_2$ (aq) → $2H_2O$ (l) + O_2(g)
  - reaction is exothermic, but not really spontaneous (you can buy H_2O_2
- What if I add some HBr ?

  2 Br^- + H_2O_2 (aq) + $2H^+$(aq) → Br_2 (aq) + $2H_2O$ (l)

  then

  Br_2 (aq) + H_2O_2 (aq) → 2 Br^- (aq) + $2H^+$(aq) + O_2(g)

  - add these together gives

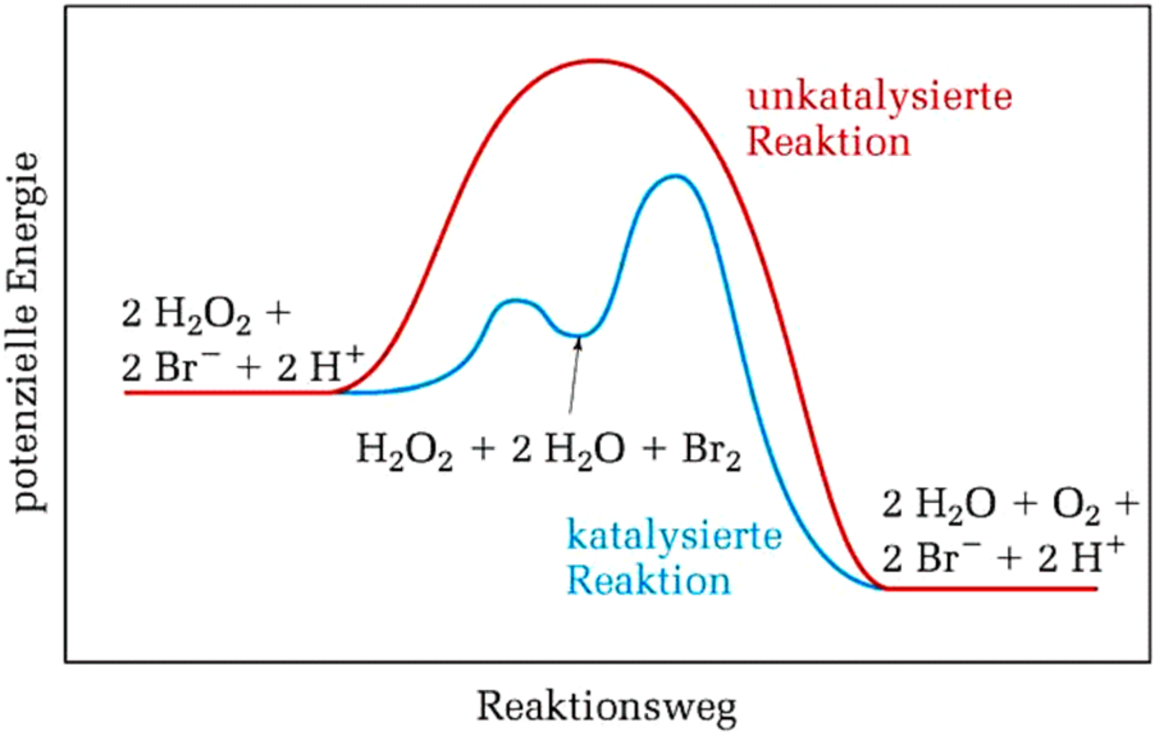
  H_2O_2 (aq) → $2H_2O$ (l) + O_2(g)

  - example of general principle

- catalyst changes the path of a reaction, but not start and end points

catalysts

- Many types of catalysis
- something provides an alternative reaction path (HBr)
- something binds to intermediate and lowers energy
- something orients the reactants – increases probability of successful collision
- biological catalysts



Enzymes

- an enzyme is just a catalyst
- large molecules
- most enzymes are proteins
- many proteins are enzymes

catalysts – last words

- some are well understood – many not
- reaction velocity may be too slow to measure without a catalyst
- may speed reaction by factor of 2 or 2^{20}
- may be big like a protein, solid as in exhausts or small as a proton

Summarise reaction velocities

- instantaneous velocity
- reaction constant k
- (zero), first, second order reactions
- idea of collisions / some high energy state
- if we do not have an energy barrier, difficult to speak of a reaction
- energy of a reaction is not the same as activation energy
- catalysts

Chap 15
Equilibria / Gleichgewicht

Chap 15 Equilibria

- here in chemistry context
- next summer semester in statistical mechanics context

- most reactions spoken about look like

$$A + B \rightarrow C + D$$

- can a reaction go

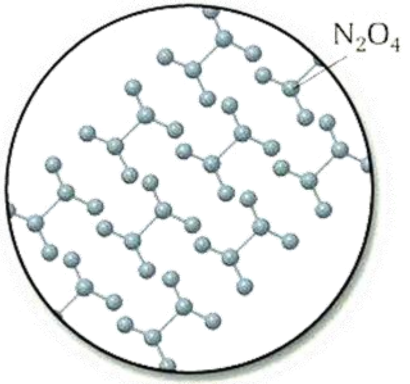
$$C + D \rightarrow A + B$$

- usually a bit
  - sometimes very much
- write it differently..

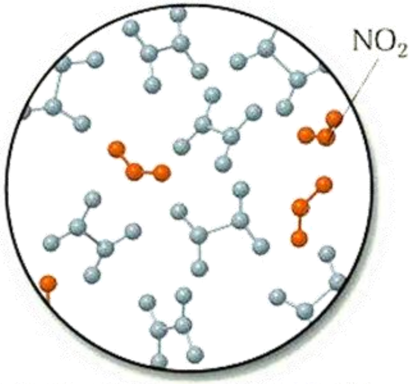
$$A + B \leftrightarrow C + D$$

equilibria

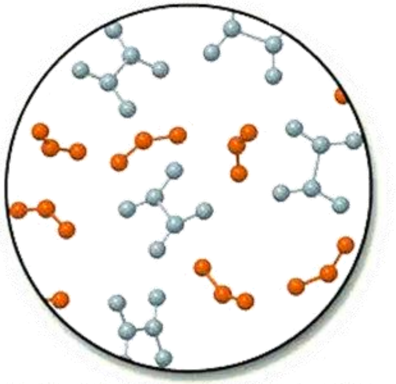
- N_2O_4 (g) ↔ 2 NO_2 (g) treat this as two reactions
  - N_2O_4 (g) → 2 NO_2 (g) velocity $k_f\,[N_2O_4]$
  - 2 NO_2(g) → N_2O_4 (g) velocity $k_b\,[NO_2]^2$



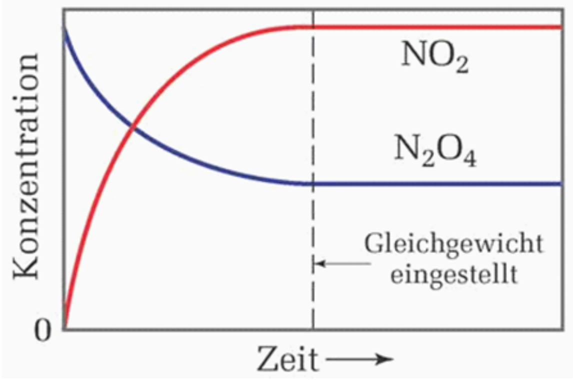
$N_2O_4(s)$

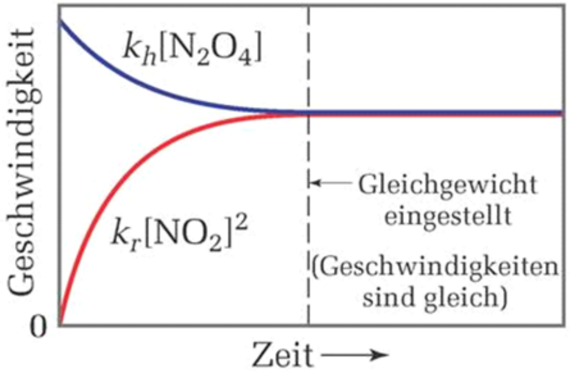


$N_2O_4(g) \longrightarrow 2\,NO_2(g)$



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

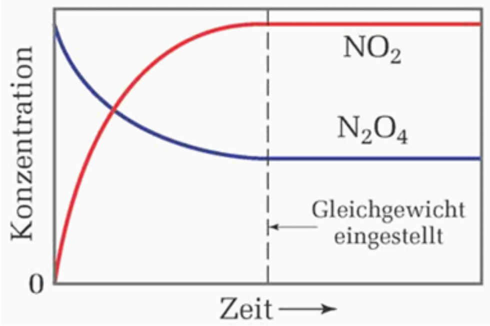




equilibria

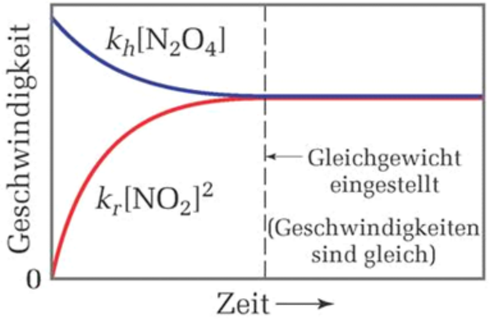
at equilibrium

- velocity of → and ← is equal
- concentrations are not equal



$N_2O_4\,(g) \rightarrow 2\,NO_2\,(g)$ velocity $k_f\,[N_2O_4]$

$2\,NO_2(g) \rightarrow N_2O_4\,(g)$ velocity $k_b\,[NO_2]^2$



$$k_f[N_2O_4] = k_b[NO_2]^2$$

$$\frac{[NO_2]^2}{[N_2O_4]} = \frac{k_f}{k_b} = k_c$$

- given $[NO_2]$ we know $[N_2O_4]$
  - more generally

equilibrium constant

- a A + b B ↔ c C + d D $$k_c = \frac{\text{products}}{\text{reactants}} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$
- $N_2(g) + 3\ H_2\ (g) \leftrightarrow 2\ NH_3\ (g)$ $$k_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$
- how big are the numbers ?
- $2\ C_6O_6H_6 + 9\ O_2 \rightarrow 12\ CO_2 + 6\ H_2O$ $k_c >> 1$
  - write with a →
- $CH_3COOH\ (aq) \leftrightarrow CH_3COO^-\ (aq) + H^+\ (aq)$ $k_c \approx 10^{-4.8}$
  - not so strong, but enough so you can detect ions
- lots of biochemical reactions are equilibria

Example calculation

$2ONCl\ (g) \leftrightarrow 2NO\ (g) + Cl_2(g)$

- at equilibrium, 10 % of ONCl is dissociated what is k_c ?

- $H_2(g) + I_2(g) \leftrightarrow 2HI(g)$ $k_c=64$
- at equilibrium with ½ mol HI, how much H_2 have we ?

  (no calculator necessary)

Example calculation

$2ONCl\,(g) \leftrightarrow 2NO\,(g) + Cl_2(g)$

- at equilibrium, 10 % of ONCl is dissociated what is k_c ?

- $H_2(g) + I_2(g) \leftrightarrow 2HI(g)$ $k_c=64$
- at equilibrium with ½ mol HI, how much H_2 have we ?

$$k_c = \frac{[\mathrm{HI}]^2}{[\mathrm{H}_2][\mathrm{I}_2]}$$

$$= \frac{[\mathrm{HI}]^2}{[\mathrm{H}_2]^2}$$

$$[\mathrm{H}_2]^2 = \frac{[\mathrm{HI}]^2}{k_c}$$

$$[\mathrm{H}_2] = \frac{[\mathrm{HI}]}{k_c^{1/2}}$$

Equilibrium constants

- big

  CO (g) + Cl_2 (g) ↔ $COCl_2$ (g)

$$k_c = \frac{[COCl_2]}{[CO][Cl_2]} = 5\times10^9$$

- near 1

  N_2O_4 (g) ↔ 2 NO_2 (g)

$$k_c = \frac{[NO_2]^2}{[N_2O_4]} = 0.2$$

- reverse reaction

  2 NO_2 (g) ↔ N_2O_4 (g) k_c = 1/0.2 = 5
- big k_c reaction goes forwards
- k_c near 1, reaction goes both directions

Combining reactions

- start

$2\ \mathrm{NOBr}\ (g) \leftrightarrow 2\ \mathrm{NO}\ (g) + \mathrm{Br_2}\ (g)$ $\qquad k_c = 0.01$

- add something to remove $\mathrm{Br_2}$

$\mathrm{Br_2}\ (g) + \mathrm{Cl_2}\ (g) \leftrightarrow 2\ \mathrm{BrCl}\ (g)$ $\qquad k_c = 7.2$

- total reaction

$2\ \mathrm{NOBr}\ (g) + \mathrm{Br_2}\ (g) + \mathrm{Cl_2}(g) \leftrightarrow 2\ \mathrm{NO}\ (g) + \mathrm{Br_2}(g) + 2\ \mathrm{BrCl}(g)$

- really

$2\ \mathrm{NOBr}\ (g) + \mathrm{Cl_2}(g) \leftrightarrow 2\ \mathrm{NO}\ (g) + 2\ \mathrm{BrCl}\ (g)$

$$k_c = \frac{[\mathrm{NO_2}]^2[\mathrm{Br_2}]}{[\mathrm{NOBr}]^2} \frac{[\mathrm{BrCl}]^2}{[\mathrm{Br_2}][\mathrm{Cl_2}]}$$

$$= \frac{[\mathrm{NO_2}]^2[\mathrm{BrCl}]^2}{[\mathrm{NOBr}]^2[\mathrm{Cl_2}]} \qquad = 7.2 \times 0.01 = 7 \times 10^{-2}$$

Equilibria – summary of obvious

- k_c known
  - which way does a reaction go
  - calculate equilibrium concentrations
- what you cannot do
  - calculate speed
  - spontaneity (will a reaction take place)

le Châtelier

- A + B ↔ C + D $$k_c = \frac{[\mathrm{C}][\mathrm{D}]}{[\mathrm{A}][\mathrm{B}]}$$
- system at equilibrium, add C
  - k_c= constant
  - only way is to move C+D → A + B
    - removes C
- le Châtelier
  - system responds so as to oppose changes

- let us quantify this

responding to changes in environment

$$k_c = \frac{[\mathrm{C}][\mathrm{D}]}{[\mathrm{A}][\mathrm{B}]}$$

- say k_c=1
- initial [A], [B], [C], [D] = 1
- add 1 unit of C
- what is the new [C] ?
- Say x amount of C will disappear then
  - x of A will appear, new [A] = $1 + x$
  - x of B will appear, new [B] = $1 + x$
  - x of C will disappear, new [C] = $2 - x$
  - x of D will disappear, new [D] = $1 - x$
- (may I write a, b, c, d ? to save typing)

$$k_c = \frac{cd}{ab} = \frac{(2-x)(1-x)}{(1+x)(1+x)}$$

Using equilibria

$$k_c = \frac{cd}{ab} = \frac{(2-x)(1-x)}{(1+x)(1+x)}$$

- this kind of calculation may not be in book

$$1 = \frac{x^2 - 3x + 2}{(x+1)^2}$$

$$\ldots$$

$$x = 1/5$$

- so [A] = [B] = 1 + x = 6/5
- [C] = 2−x = 9/5
- [D] = 1−x = 4/5
- check..

$$\frac{cd}{ab} = \frac{\frac{9}{5}\frac{4}{5}}{\frac{6}{5}\frac{6}{5}}$$

le Châtelier more generally

- PCl_5 (g) ↔ PCl_3 (g) + Cl_2 (g)
- 1 mol gas ↔ 2 mol gas

- start at equilibrium, increase pressure
  - more PCl_5 is formed (to compensate for pressure)

- making ammonia

N_2 (g) + $3H_2$ (g) ↔ $3NH_3$ (g) but $k_c < 1$

- if you keep removing NH_3 system keeps making more

- acid – base buffering
  - more from chapter

equilibria and energy

- Achtung ! Not in big red book
- detour
- Nernst $V = V_0 - \frac{RT}{zF} \ln \frac{a_{red}}{a_{ox}}$

- Boltzmann $\frac{p_1}{p_2} = e^{E_2 - E_1 / kT}$ $\Delta E = -kT \ln \frac{p_1}{p_2}$

- Today Gibbs free energy $\Delta G^\circ = -RT \ln K_c$
  - *R* gas constant
  - *T* temperature
- important implications

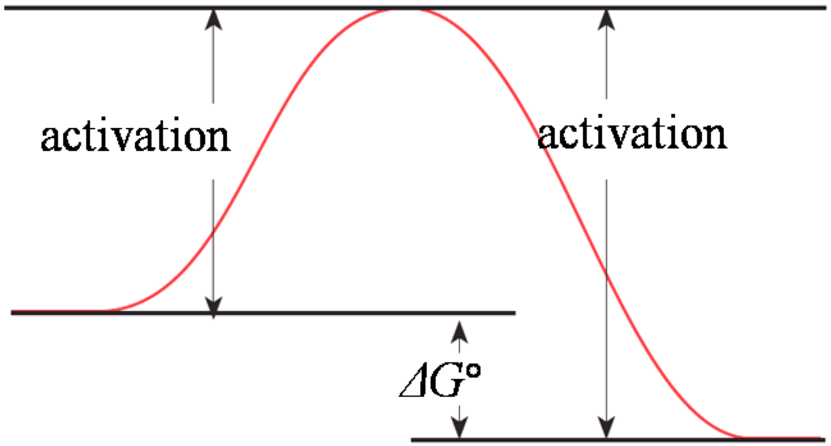
equilibrium constants and temperature

- textbooks use k_c for some temperature and 100 kPa
  - why must k_c be temperature specific ?

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

$$= -RT \ln \frac{\text{products}}{\text{reactants}}$$

$$k_c = e^{\frac{-\Delta G^\circ}{RT}}$$



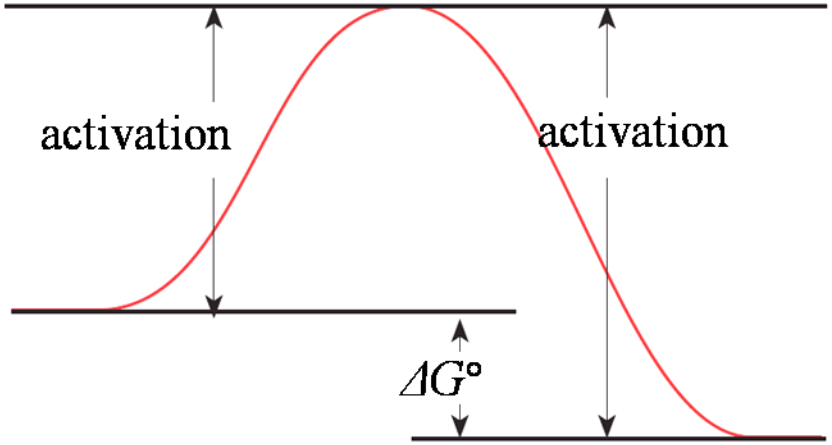
- what happens as T↓↑
  - extremes

constants and energy

- equilibrium constants are not constant
- books quote k_c, k_{eq}, … all are temperature dependent

k_c	quotient
k_{eq}	equilbrium
k_1,k_2	rates of reactions 1 and 2
k_f, k_b ..	forwards /backwards rates

$\}$ all will depend on temperature



Chap 16
Acid / Base
Säuren / Basen

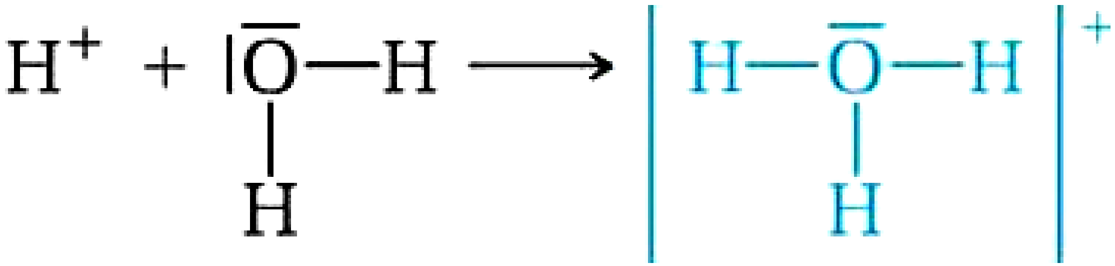
Chap 16 … acid / base (Säuren / Basen)

Important for this topic

- general definition (Brønsted-Lowry)
  - an acid can give up a proton
  - a base can accept a proton
- some compounds can do both (water)

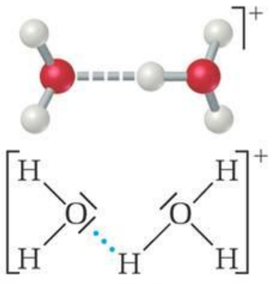
what do protons do in solution ?

- so far we have seen H^+
  - does not really exist – very small, very dense +ve charge



water as a base

- $H^+(aq) + H_2O\ (l) \rightarrow H_3O^+\ (aq)$
  - structures really temporary so $H_5O_2^+$ exists (and more)



$H_5O_2^+$

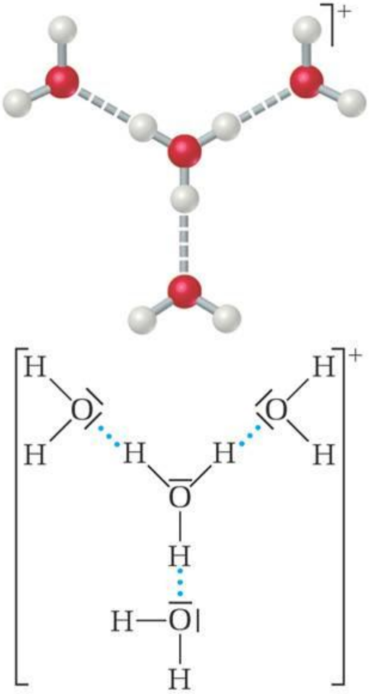
(a)

water as an acid / base

- water is a base (accepts a proton)
  - $HNO_3 + H_2O\ (l) \rightarrow NO_3^- + H_3O^+\ (aq)$ ammonia and water
- water is an acid (donates a proton)

$NH_3(aq) + H_2O\ (l) \leftrightarrow NH_4^+\ (aq) + OH^-\ (aq)$

- more generally



$H_9O_4^+$

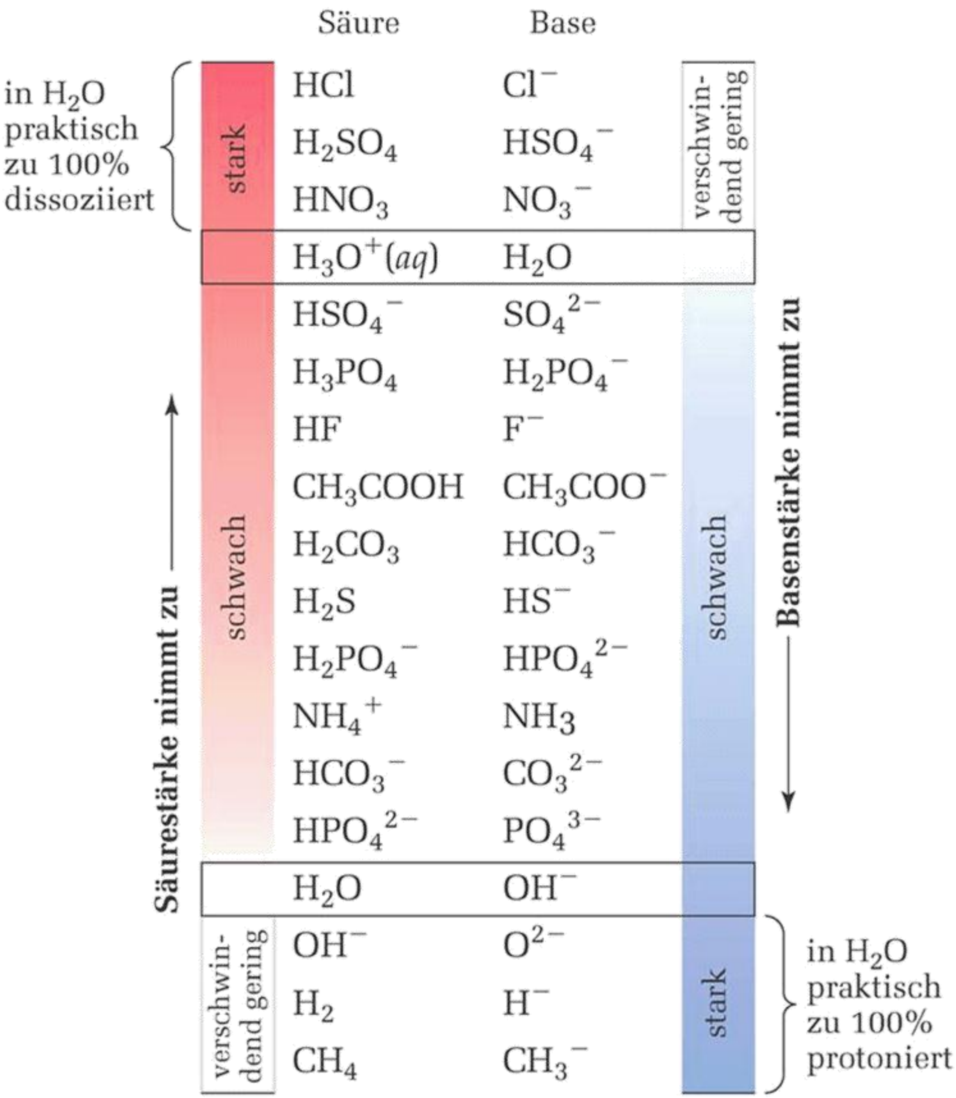
(b)

Acid-base pairs

- $HX + H_2O \leftrightarrow X^- + H_3O^+$
- HX is an acid, X^- a base

- just about anything with proton can be an acid – just a weak one

- strong acids
  - left column top
- strong bases
  - right column bottom



	Säure	Base	
stark	HCl	Cl^-	verschwin-dend gering
	H_2SO_4	HSO_4^-	
	HNO_3	NO_3^-	
	$H_3O^+(aq)$	H_2O	
schwach	HSO_4^-	SO_4^{2-}	schwach
	H_3PO_4	$H_2PO_4^-$	
	HF	F^-	
	CH_3COOH	CH_3COO^-	
	H_2CO_3	HCO_3^-	
	H_2S	HS^-	
	$H_2PO_4^-$	HPO_4^{2-}	
	NH_4^+	NH_3	
	HCO_3^-	CO_3^{2-}	
	HPO_4^{2-}	PO_4^{3-}	
	H_2O	OH^-	
verschwin-dend gering	OH^-	O^{2-}	stark
	H_2	H^-	
	CH_4	CH_3^-	

in H_2O praktisch zu 100% dissoziiert

Säurestärke nimmt zu

Basenstärke nimmt zu

in H_2O praktisch zu 100% protoniert

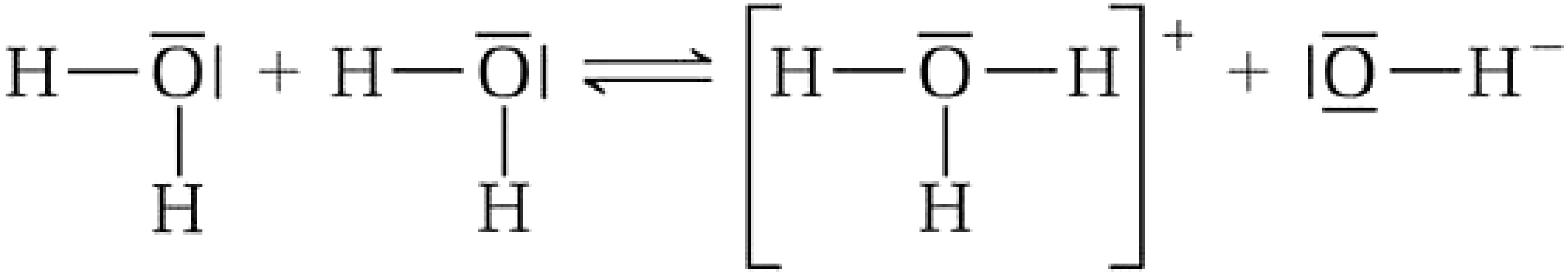
water ionic product

- water is an acid and a base

$2\ H_2O \leftrightarrow H_3O^+ + OH^-$

- or

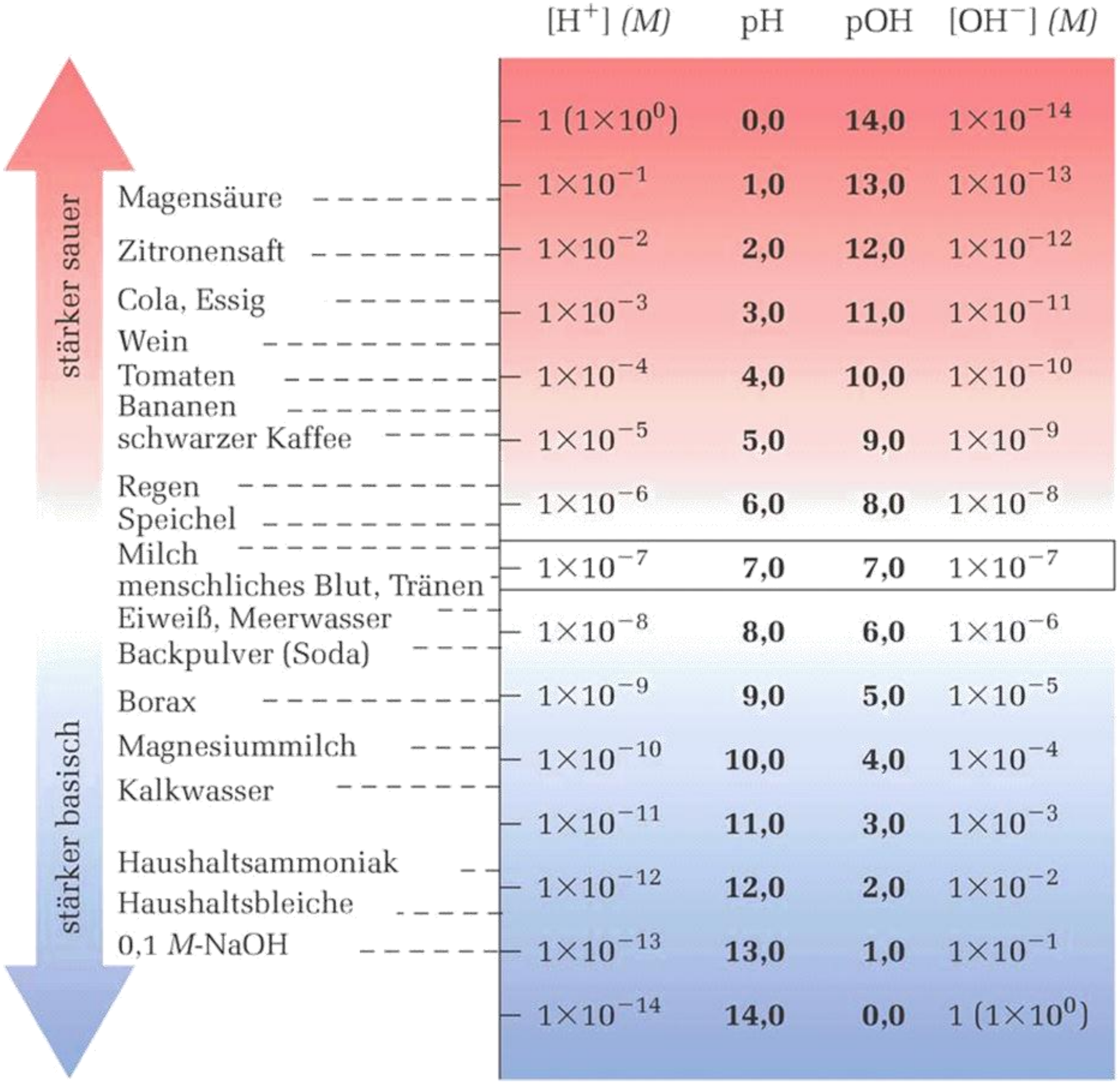
$H_2O \leftrightarrow H^+ + OH^-$



- quantify this ? like for any reaction there is k_c
- $H_2O \leftrightarrow H^+ + OH^-$ do **not** use $k_c = \xcancel{\frac{[H^+][OH^-]}{[H_2O]}}$
- use $k_w = [H+]\ [OH^-] = 10^{-14}$ dissociation constant for water
- only works at 298 K

pH

- neutral $[H^+] = [OH^-] = 10^{-7}$
- $pH = -\log_{10}[H+]$
  - example at pH = 3 $[H^+] = 10^{-3}$, $[OH^-]=10^{-11}$



$[H^+]$ (M)	pH	pOH	$[OH^-]$ (M)
1 (1×10^{0})	**0,0**	**14,0**	1×10^{-14}
1×10^{-1}	**1,0**	**13,0**	1×10^{-13}
1×10^{-2}	**2,0**	**12,0**	1×10^{-12}
1×10^{-3}	**3,0**	**11,0**	1×10^{-11}
1×10^{-4}	**4,0**	**10,0**	1×10^{-10}
1×10^{-5}	**5,0**	**9,0**	1×10^{-9}
1×10^{-6}	**6,0**	**8,0**	1×10^{-8}
1×10^{-7}	**7,0**	**7,0**	1×10^{-7}
1×10^{-8}	**8,0**	**6,0**	1×10^{-6}
1×10^{-9}	**9,0**	**5,0**	1×10^{-5}
1×10^{-10}	**10,0**	**4,0**	1×10^{-4}
1×10^{-11}	**11,0**	**3,0**	1×10^{-3}
1×10^{-12}	**12,0**	**2,0**	1×10^{-2}
1×10^{-13}	**13,0**	**1,0**	1×10^{-1}
1×10^{-14}	**14,0**	**0,0**	1 (1×10^{0})

pH / dissociation constant

- strong acids / bases – assume complete dissociation
  - HCl, HNO_3,..   & NaOH, KOH, ..
- weak acids / bases – we have an equilibrium constant k_s or k_a

$$k_a = \frac{[H^+][OH^-]}{[HA]}$$

- ways to use this
  - from concentration of acid/base – work out pH
  - given pH, work out how much of acid is ionised
- quick examples

Dissociation constant

- cheat with weak acids
- formic acid (ameisensäurelösung)
  - 0.1 M in water gives pH 2.38
  - $HCOOH \rightleftharpoons H^+ + HCOO^-$
    - get fraction ionised, get k_s
  - cheat and say it does not ionise too much so
    - $[H^+] \approx [HCOO^-]$ & $[H^+] = 10^{-2.38}$ M
    - $[HCOOH] \approx 0.1$ M

$$k_s = \frac{[H^+][HCOO^-]}{[HCOOH]}$$

$$= \frac{10^{-2.38} \cdot 10^{-2.38}}{0.1} = \frac{10^{-4.76}}{10^{-1}} = 10^{-3.76}$$

$$\approx 1.7 \times 10^{-4} \quad \text{mol l}^{-1}$$

this is a different
result to page 791
of the book – who
is right ?