General Information

Instructions

- Write your name on each page and number these.
- You have three hours to solve the problems. Wait for the **START** signal before you begin.
- Use a new page for each problem. Clearly indicate what problem you are working on.
- Write all necessary calculations legibly.
- Put your pages into the provided envelope at the end of the exam. Do not seal the envelope.
- Finish your work immediately when the **STOP** signal is given.
- Leave your seat only when allowed to do so.
- Only **answers written on the answer sheets** can be considered.
- This exam has **11** problems.

Viel Erfolg!

Bonne chance!

Buona fortuna!

Good luck!

Physical Constants and Formulae

Constants

Planck constant	$h = 6.626 \times 10^{-34}\,\mathrm{J\,s}$
Boltzmann constant	$k_B = 1.381 \times 10^{-23}\,\mathrm{J\,K^{-1}}$
Speed of light	$c = 2.998 \times 10^{8}\,\mathrm{m\,s^{-1}}$
Elementary charge	$e = 1.602 \times 10^{-19}\,\mathrm{C}$
Avogadro constant	$N_A = 6.022 \times 10^{23}\,\mathrm{mol^{-1}}$
Universal gas constant	$R = 8.314\,\mathrm{J\,mol^{-1}\,K^{-1}}$
Faraday constant	$F = 9.648 \times 10^{4}\,\mathrm{C\,mol^{-1}}$
Standard pressure	$p_0 = 1 \times 10^{5}\,\mathrm{Pa}$
Electronvolt	$1\,\mathrm{eV} = 1.602 \times 10^{-19}\,\mathrm{J}$
Absolute zero	$0\,\mathrm{K} = -273.15\,^{\circ}\mathrm{C}$
Ångstrom	$1\,\text{Å} = 1 \times 10^{-10}\,\mathrm{m}$
Pi (π)	$\pi \approx 3.141592$
Euler's number	$e \approx 2.718281$

Formulae and Equations

Ideal gas law	$pV = nRT = Nk_BT$
Gibbs free energy	$\Delta G = \Delta H - T\Delta S$
Relation between ΔG and K	$\Delta G = -RT \ln(K)$
Relationship between ΔG and ΔE_{cell}	$\Delta_r G^0 = -nF\Delta E^0_{cell}$
Nonstandard ΔG	$\Delta_r G = \Delta_r G^0 + RT \ln(Q)$
Reaction quotient Q for reaction aA+bB $\rightleftharpoons$ cC+dD	$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}$
Nernst equation	$E = E^0 - \frac{RT}{nF} \ln(Q)$
Electric current	$I = \frac{Q}{t}$
Arrhenius law	$k = Ae^{-\frac{E_A}{RT}}$
Lambert-Beer law	$A = \epsilon Lc = \log\left(\frac{I_0}{I}\right)$
Buffer equation	$\mathrm{pH} = \mathrm{pK}_a + \log\left(\frac{[A^-]}{[HA]}\right)$
Energy of a photon	$E = h\nu = \frac{hc}{\lambda}$
Half life for a first-order reaction	$t_{\frac{1}{2}} = \frac{\ln(2)}{k}$
Activity of a radioactive sample	$A = kN$
Surface area of a sphere	$A = 4\pi R^2$
Volume of a sphere	$V = \frac{4\pi}{3}R^3$

For the calculation of equilibrium constants and all concentrations, refer to the standard concentration 1 mol dm^{-3} = 1 mol L^{-1}. If not stated otherwise in a task, consider all gases ideal throughout this exam.

Periodic Table of the Elements

Periodic Table of Elements

1 H 1.008																	2 He 4.003
3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.63	33 As 74.92	34 Se 78.97	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.95	43 Tc [98]	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	57–71	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po [209]	85 At [210]	86 Rn [212]
87 Fr [223]	88 Ra [226]	89–103	104 Rf [267]	105 Db [268]	106 Sg [269]	107 Bh [270]	108 Hs [270]	109 Mt [278]	110 Ds [281]	111 Rg [282]	112 Cn [285]	113 Nh [286]	114 Fl [289]	115 Mc [290]	116 Lv [293]	117 Ts [294]	118 Og [294]

57 La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 140.24	61 Pm [145]	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.05	71 Lu 174.97
89 Ac [227]	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np [237]	94 Pu [244]	95 Am [243]	96 Cm [247]	97 Bk [247]	98 Cf [251]	99 Es [252]	100 Fm [257]	101 Md [258]	102 No [259]	103 Lr [266]

Score Sheet

NOT TO BE FILLED IN BY PARTICIPANT

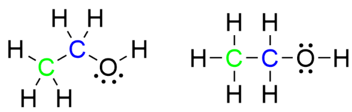
Name of participant:

Problem	Title	Maximum points	Achieved points	Pages
Q1	Mixed questions	17.5		1
Q2	Uranium, radium, and other fun elements	11.0		1
Q3	The Ecstasy of Gold and Stoichiometry	10.0		1
Q4	Solubility of Calcium Salts	15.5		1
Q5	Titration	9.0		1
Q6	Redox Chemistry	7.5		1
Q7	Electrons two ways: VSEPR and Resonance	10.5		1
Q8	Explosions and maybe Fire	14.0		2
Q9	Kinetics of Methylene Blue Discoloration	9.0		2
Q10	Organic Chemistry	6.0		1
Q11	Assorted Organic Reactions	9.0		2
Total		119.0		14

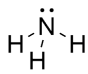
Mixed questions (17.5 points)

1.1 Draw the Lewis structures of the following compounds and determine the oxidation states of all atoms: C_2H_5OH, NH_3, HNO_3, H_2SO_4, OF_2. — 5.0 pt

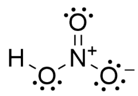
SOLUTION:



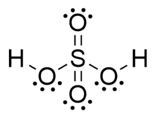
H: all +I
O: -II
C1: -I
C2: -III



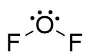
N: -III
H: +I



H: +I
O: -II
N: +V



H: +I
O: -II
S: +VI



O: +II
F: -I

0.5 pts per structure (0.25 for correct bonds, 0.25 for correct charges/lone pairs)
0.5 pts per correct assignment of oxidation states for each molecule (0.25 pts if half or less of the atoms are correctly assigned)

1.2 What is the pH value of a 0.05 mol l^{-1} nitric acid solution? — 1.0 pt

SOLUTION:

$\mathrm{pH} = -\log\left(0.05\,\mathrm{mol\,l^{-1}}\right) = 1.3$

0.5 pts for the formula, 0.5 pts for the numeric result

1.3 When an atom is struck by a light beam of sufficient energy, it may be ionised and lose an electron. More energy is needed to remove a 2nd electron, then more for a third, etc. The first eight successive ionisation energies for an element's atom from the 3rd period (sodium through argon) are as follows (all in $MJ\,mol^{-1}$): 1.0 pt

0.78	1.57	3.23	4.65	16.1	19.8	23.7	29.2

What is the name and chemical symbol of this element?

SOLUTION:

Si

DE: Silizium, FR: Silicium, IT: Silicio, EN: Silicon

0.5 pts each for name and symbol

1.4 Some students in the lab were tasked with labelling containers with the sum formulas of the substances inside. However, they didn't do a good job and some formulas make no sense at all. Here are all the formulas, write on your answer sheet which ones make sense and which ones don't: 1.5 pt

CH_4Cl, $CHCl_3$, CHS, CH_2Cl_2, H_2O_2, CO_5H

SOLUTION:

CH_4Cl, CHS, CO_5H don't make sense; $CHCl_3$, CH_2Cl_2, H_2O_2 make sense

0.25 pts for each correct assignment (true or false)

1.5 How much iron is contained in 25 mol magnetite Fe_3O_4? Express your result in kilograms, rounded to two decimal places. 1.0 pt

SOLUTION:

$n(Fe) = 3 \cdot n(Fe_3O_4) = 3 \cdot 25\,mol = 75\,mol$

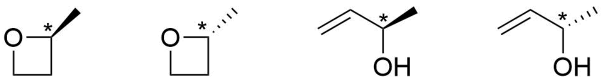
$m(Fe) = n(Fe) \cdot M(Fe) = 75\,mol \cdot 55.85\,g\,mol^{-1} = 4188.75\,g = 4.19\,kg$

0.5 pts for correct mathematical reasoning, 0.5 pts for correct numerical result.

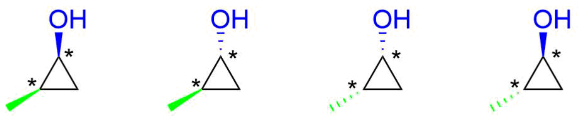
1.7 The sum formula C_4H_8O describes 32 different compounds. Draw 8 of them which have at least one chiral centre. Mark chiral centres with an asterisk (*) and add the correct descriptor (*R*/*S*) to the appropriate positions. 8.0 pt

SOLUTION:

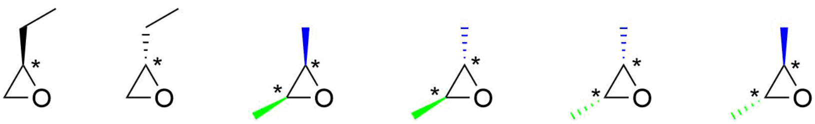
All 14 possible isomers:



(*S*) (*R*) (*R*) (*S*)



(1*S*,2*R*) (1*R*,2*R*) (1*R*,2*S*) (1*S*,2*S*)

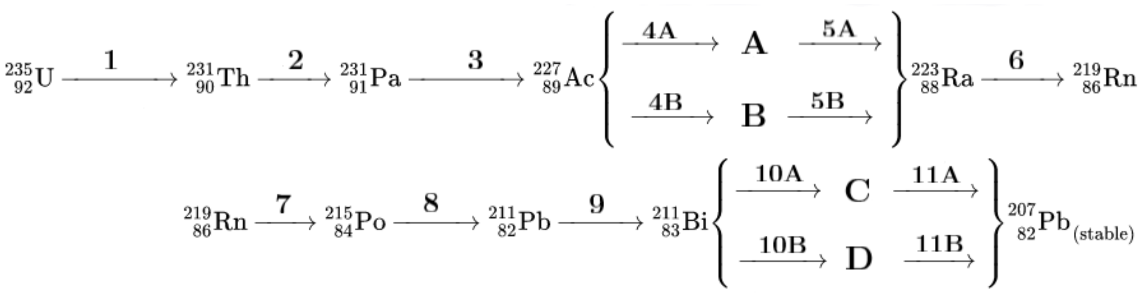


(*R*) (*S*) (2*R*,3*S*) (2*S*,3*S*) (2*S*,3*R*) (2*R*,3*R*)

0.5 pts per correct unique structure, 0.5 pts for correct stereo assignment and asterisk placement

Uranium, radium, and other fun elements (11.0 points)

Uranium-235 is a naturally occurring radionuclide with a half-life of 703.8 million years. Its decay chain is as follows:



Decay chain of $^{235}_{92}U$ to $^{207}_{82}Pb$.

2.1 Name the kind of radioactive decay occurring in reactions **1** – **11**, as well as the intermediates **A** – **D**. 5.75 pt

SOLUTION:

Reaction	Decay type
1	α
2	$\beta-$
3	α
4A, 4B	$\beta-$, α
5A, 5B	α, $\beta-$
6	α
7	α
8	α
9	$\beta-$
10A, 10B	α, $\beta-$
11A, 11B	$\beta-$, α

Intermediates:

A	$^{227}_{90}Th$
B	$^{223}_{87}Fr$
C	$^{207}_{81}Tl$
D	$^{211}_{84}Po$

0.25 pts for each correctly named decay type, 0.5 pts for each correctly named intermediate (no points if wrong isotope or wrong element). ATTENTION: In total, for 4A-5B and 10A-11B four combinations of decay series with intermediates are possible! Be very vigilant as to how the student answered the question. Also, no points are to be deducted if the student switched 4A with 5A and 4B with 5B, or 10A with 11A and 10B with 11B, so long as the correct intermediate is given. If possible, the correcting of this task should be signed off by one of the authors or reviewers (Chantal, Richard, Fabian, Yves).

2.2 Radium-223, which is part of the decay chain shown above, has a medical application as $^{223}RaCl_2$ in treating metastatic bone cancers. What could be a reason for using radium in specifically targetting bone cancers? Keep your answer short. 1.0 pt

SOLUTION:

EN: Chemical similarity to calcium, since calcium is essential for bone formation.
DE: Chemische Ähnlichkeit zu Kalzium, da Kalzium essentiell für Knochenbildung ist.
FR: Similitude chimique avec le calcium, car le calcium est essentiel à la formation des os.
IT: Somiglianza chimica con il calcio, perché il calcio è essenziale per la formazione delle ossa.
0.5 pts for chemical similarity, 0.5 pts for connecting calcium to bones.

2.3 Radium-223 has a half-life of 11.434 days. Based on this information, calculate the rate constant of the decay. 1.25 pt

SOLUTION:

$1\,\mathrm{d} = 86\,400\,\mathrm{s}$

$11.434\,\mathrm{d} = 987\,897.6\,\mathrm{s}$

$\tau = \frac{\ln 2}{k} \implies k = \frac{\ln 2}{\tau} = \frac{\ln 2}{987\,897.6\,\mathrm{s}} = 7.016 \times 10^{-7}\,\mathrm{s^{-1}}$

0.75 pts for correct equation ($\tau = \frac{\ln 2}{k}$), 0.5 pts for correct numerical result, 0.25 pts for correct eqn without inserting numbers, 0 pts for result if unit is missing.

2.4 An activity of one decay per second ($1\,\mathrm{s^{-1}}$) is often described as one Becquerel (1 Bq), named after Henri Becquerel. The activity of Xofigo, a medication based on $^{223}RaCl_2$, is formulated to be $1100\,\mathrm{kBq\,mL^{-1}}$. 2.5 pt

Now, you are tasked with creating 1000 L of Xofigo. How much isotopically pure $^{223}RaCl_2$ (in mg) do you need to weigh in for this? If you couldn't solve problem 2.3, assume the rate constant for the decay of the isotope to be $k_{^{223}\mathrm{Ra}} = 5 \times 10^{-6}\,\mathrm{s^{-1}}$.

SOLUTION:

Desired activity: $A_{\mathrm{des}} = 1 \times 10^6\,\mathrm{mL} \cdot 1.1 \times 10^6\,\mathrm{s^{-1}\,mL^{-1}} = 1.1 \times 10^{12}\,\mathrm{s^{-1}}$

Activity of 1 mol $^{223}RaCl_2$: $A_m(^{223}\mathrm{RaCl_2}) = N_A \cdot A(^{223}\mathrm{RaCl_2}) = 6.022 \times 10^{23}\,\mathrm{mol^{-1}} \cdot 7.016 \times 10^{-7}\,\mathrm{s^{-1}} = 4.225 \times 10^{17}\,\mathrm{s^{-1}\,mol^{-1}}$

Number of moles of $^{223}RaCl_2$ needed: $n_{^{223}\mathrm{RaCl_2}} = \frac{1.1 \times 10^{12}\,\mathrm{s^{-1}}}{4.225 \times 10^{17}\,\mathrm{s^{-1}\,mol^{-1}}} = 2.603 \times 10^{-4}\,\mathrm{mol}$

$M(^{223}\mathrm{RaCl_2}) = 223\,\mathrm{g\,mol^{-1}} + 2 \cdot 35.453\,\mathrm{g\,mol^{-1}} = 293.906\,\mathrm{g\,mol^{-1}}$

$m(^{223}\mathrm{RaCl_2}) = 2.603 \times 10^{-4}\,\mathrm{mol} \cdot 293.906\,\mathrm{g\,mol^{-1}} = 7.650 \times 10^{-2}\,\mathrm{g} = 76.504\,\mathrm{mg}$

If student used provided value for activity:

Desired activity: $A_{\mathrm{des}} = 1 \times 10^6\,\mathrm{mL} \cdot 1.1 \times 10^6\,\mathrm{s^{-1}\,mL^{-1}} = 1.1 \times 10^{12}\,\mathrm{s^{-1}}$

Activity of 1 mol $^{223}RaCl_2$: $A_m(^{223}\mathrm{RaCl_2}) = N_A \cdot A(^{223}\mathrm{RaCl_2}) = 6.022 \times 10^{23}\,\mathrm{mol^{-1}} \cdot 5 \times 10^{-6}\,\mathrm{s^{-1}} = 3.011 \times 10^{16}\,\mathrm{s^{-1}\,mol^{-1}}$

Number of moles of $^{223}RaCl_2$ needed: $n_{^{223}\mathrm{RaCl_2}} = \frac{1.1 \times 10^{12}\,\mathrm{s^{-1}}}{3.011 \times 10^{16}\,\mathrm{s^{-1}\,mol^{-1}}} = 3.653 \times 10^{-5}\,\mathrm{mol}$

$M(^{223}\mathrm{RaCl_2}) = 223\,\mathrm{g\,mol^{-1}} + 2 \cdot 35.453\,\mathrm{g\,mol^{-1}} = 293.906\,\mathrm{g\,mol^{-1}}$

$m(^{223}\mathrm{RaCl_2}) = 3.653 \times 10^{-5}\,\mathrm{mol} \cdot 293.906\,\mathrm{g\,mol^{-1}} = 1.073\,63 \times 10^{-1}\,\mathrm{g} = 107.363\,\mathrm{mg}$

1.5 pts for correct mathematical reasoning, 1.0 pt for correct numerical result.

2.5 ^{89}Sr can be used to treat bone cancers for the same reason as outlined in problem 2.2, however its decay to ^{89}Y is sometimes problematic. Name the type of decay occurring here, and give a reason for that being an issue. 0.5 pt

SOLUTION:

$^{89}_{38}\mathrm{Sr} \xrightarrow{\beta^-} {}^{89}_{39}\mathrm{Y} + e^- + \bar{\nu}_e$

Beta-minus radiation (electrons) is more capable of penetrating soft tissues than the heavy alpha particles emitted by ^{223}Ra, and thus can cause more collateral damage.

0.25 pts for correct decay type, 0.25 pts for reasoning (more damage caused).

The Ecstasy of Gold and Stoichiometry (10.0 points)

3.1 Balance the following reaction equations properly. All stoichiometric coefficients must be integers. 4.75 pt

1. $C_{13}H_{26}O_2 + O_2 \longrightarrow CO_2 + H_2O$
2. $P + KClO_3 \longrightarrow P_4O_{10} + KCl$
3. $FeS_2 + O_2 + H_2O \longrightarrow FeSO_4 + H_2SO_4$
4. $HNO_3 + HCl + Au \longrightarrow HAuCl_4 + NOCl + H_2O$

SOLUTION:

1. $2\,C_{13}H_{26}O_2 + 37\,O_2 \longrightarrow 26\,CO_2 + 26\,H_2O$
2. $12\,P + 10\,KClO_3 \longrightarrow 3\,P_4O_{10} + 10\,KCl$
3. $2\,FeS_2 + 7\,O_2 + 2\,H_2O \longrightarrow 2\,FeSO_4 + 2\,H_2SO_4$
4. $3\,HNO_3 + 11\,HCl + 2\,Au \longrightarrow 2\,HAuCl_4 + 3\,NOCl + 6\,H_2O$

0.25 pts for each correct coefficient.

Reaction **4** occurs when gold is dissolved in Aqua Regia (Latin for "royal water"), so named since it is one of the few mixtures capable of dissolving "noble metals", e.g. gold.

One day, a fellow chemist hands you a sample of chloroauric acid ($HAuCl_4$), made from a gold medal. You are tasked with retrieving the gold from the sample. You know that adding an aqueous solution of sodium metabisulfite ($Na_2S_2O_5$) to the chloroauric acid reduces the gold to its elemental form. Since freshly precipitated gold looks rather dull, you melt it down in a forge and let it form a medal to restore its former shiny appearance.

3.2 Formulate a balanced reaction equation for the process outlined above, knowing that sodium hydrogen sulfate and hydrochloric acid are formed over the course of the reaction. 2.5 pt

SOLUTION:

$3\,Na_2S_2O_5 + 4\,HAuCl_4 + 9\,H_2O \longrightarrow 6\,NaHSO_4 + 16\,HCl + 4\,Au\downarrow$

1.0 pt for reaction equation, 0.25 pts for each correct coefficient.

The sample you were given contained 150 g of chloroauric acid, however your colleague told you that the original medal weighed 120 grams. Because you're an excellent chemist but not a great metalworker, you expect that your approach returns $97.5\,\%$ of the gold from the initial sample.

3.3 Determine the original gold content (in $\%$ w/w) of the medal. Additionally, determine how many carats the medal originally was. 3.0 pt

SOLUTION:

$m(HAuCl_4) = 150.00\,g$, $n(HAuCl_4) = \frac{m(HAuCl_4)}{M(HAuCl_4)} = \frac{150.00\,g}{339.785\,g\,mol^{-1}} = 4.414 \times 10^{-1}\,mol = n(Au)$

$m_{exp}(Au) = n(Au) \cdot M(Au) = 4.414 \times 10^{-1}\,mol \cdot 196.967\,g\,mol^{-1} = 86.95\,g$

$m_{original}(Au) = \frac{86.95\,g}{0.975} = 89.18\,g$

% w/w of Au in medal = $\frac{89.18\,g}{120.0\,g} \cdot 100\,\% = 74.3\,\%$

Carats: 100 % Au = 24 ct, therefore the medal was $24 \cdot 0.743 = 17.83\,ct$

1.5 pts for correct mathematical reasoning, 1.0 pt for correct numerical result, 0.5 pts for correct number of carats, max. 2 pts total if yield was not calculated.

Solubility of Calcium Salts (15.5 points)

Calcium carbonate is a salt often encountered in everyday life, most commonly as limescale in the kitchen or bathroom, especially if you have hard water. It can also be found as limestone or chalk in nature, creating for example the white cliffs of Dover. Generally speaking, calcium carbonate is poorly water soluble, having a solubility product $K_S = 3.36 \times 10^{-9}$ mol^2 L^{-2}.

4.1 Calculate the amount of calcium carbonate (in mol) that can be dissolved in 0.5 L of water. 1.0 pt

SOLUTION:

$K_S = c(\text{Ca}^{2+}) \cdot c(\text{CO}_3{}^{2-})$

$c_{sol}(\text{CaCO}_3) = c(\text{Ca}^{2+}) = c(\text{CO}_3{}^{2-}) = \sqrt{K_S} = 5.80 \times 10^{-5}\ \text{mol L}^{-1}$

$n = c \cdot V = 5.80 \times 10^{-5}\ \text{mol L}^{-1} \cdot 0.5\ \text{L} = 2.90 \times 10^{-5}\ \text{mol}$

0.5 pts for correct mathematical reasoning, 0.5 pts for the numerical result.

4.2 Calculate the solubility of calcium carbonate in g L^{-1}. 1.0 pt

SOLUTION:

$M(\text{CaCO}_3) = 40.078\ \text{g mol}^{-1} + 12.011\ \text{g mol}^{-1} + 3 \cdot 15.999\ \text{g mol}^{-1} = 100.086\ \text{g mol}^{-1}$

$C = \frac{m}{V} = \frac{n \cdot M}{V} = c_{sol}(\text{CaCO}_3) \cdot M = 5.80 \times 10^{-5}\ \text{mol L}^{-1} \cdot 100.086\ \text{g mol}^{-1} = 5.80 \times 10^{-3}\ \text{g L}^{-1}$

0.5 pts for correct mathematical reasoning, 0.5 pts for the numerical result, max. 0.75 pts total if wrong M was obtained.

4.3 Limescale in the kitchen is often removed using acidic cleaning agents. When a cleaning agent containing hydrochloric acid is applied to limescale-covered counter top, the chalky residue dissolves readily. Write down the essential reaction equation(s) taking place here, and give a reason as to why said reaction(s) take(s) place at all. 1.0 pt

SOLUTION:

$\text{CaCO}_3 + 2\,\text{HCl} \longrightarrow \text{CaCl}_2 + \text{H}_2\text{CO}_3$ (1)

$\text{H}_2\text{CO}_3 \rightleftharpoons \text{H}_2\text{O} + \text{CO}_2\uparrow$ (2)

Reaction 1 occurs due to the difference in pK_a between HCl and H_2CO_3. Additionally, the CO_2 escaping in reaction 2 drives the equilibrium towards the product side according to Le Châtelier's principle.

0.25 pts for each correct reaction equation, 0.5 pts for arguing with Le Châtelier's principle correctly.

4.4 You have a solution of $0.5\,\text{mol}\,\text{L}^{-1}$ Na_2CO_3 and add $CaBr_2$ to it. Calculate the maximum concentration of dissolved calcium bromide that can be reached before calcium carbonate precipitates (assume the protonation of carbonate to be negligible). 3.0 pt

SOLUTION:

Sodium carbonate and calcium bromide are well soluble in water:

$$Na_2CO_3 \xrightarrow{H_2O} 2\,Na^+\,(aq) + {CO_3}^{2-}\,(aq)$$

$$CaBr_2 \xrightarrow{H_2O} Ca^{2+}\,(aq) + 2\,Br^-\,(aq)$$

Calcium carbonate will start to precipitate as soon as the solubility product is reached: $Ca^{2+}\,(aq) + {CO_3}^{2-}\,(aq) \longrightarrow CaCO_3\downarrow$

$$K_S = c(Ca^{2+}) \cdot c({CO_3}^{2-}) = x \cdot 0.5\,\text{mol}\,\text{L}^{-1}$$

$$x = \frac{K_S}{0.5\,\text{mol}\,\text{L}^{-1}} = 6.72 \times 10^{-9}$$

$$\Longrightarrow c_{sol}(CaBr_2) = c(Ca^{2+}) = 6.72 \times 10^{-9}\,\text{mol}\,\text{L}^{-1}$$

2.0 pts for correct mathematical reasoning, 1.0 pt for numerical result.

4.5 You have one litre of saturated calcium carbonate solution and one liter of saturated calcium hydroxide solution (K_S(Ca(OH)$_2$) $= 8 \times 10^{-6}$ mol^3 L^{-3}). You add both of these solutions to 3 L of water. Do you observe precipitation? If yes, which salt(s) precipitate(s)? Show your work. 6.5 pt

SOLUTION:

Numbering:

1. Calcium carbonate solution, initial
2. Calcium hydroxide solution, initial
3. Combination of solutions, prior to precipitation

Calcium carbonate solution (calculated earlier): $c_{sol,1}(\text{CaCO}_3) = c_1(\text{Ca}^{2+}) = c_1(\text{CO}_3{}^{2-}) = 5.80 \times 10^{-5}\,\text{mol L}^{-1}$

Calcium hydroxide solution: $K_S(\text{Ca(OH)}_2 = c(\text{Ca}^{2+}) \times c^2(\text{OH}^-) = y \times (2y)^2 = 4y^3$

$c_{sol,2}(\text{Ca(OH)}_2) = c_2(\text{Ca}^{2+}) = y = \sqrt[3]{\frac{K_S(\text{Ca(OH)}_2}{4}} = \sqrt[3]{\frac{8 \times 10^{-6}\,\text{mol}^3\,\text{L}^{-3}}{4}} = 1.26 \times 10^{-2}\,\text{mol L}^{-1}$

$c_2(\text{OH}^-) = 2y = 2.52 \times 10^{-2}\,\text{mol L}^{-1}$

1.0 pt for correct formulation of solubility product using concentration terms (-0.5 pts if division by 4 is missing), 0.5 pts for realising $c(\text{OH}^-)$ needs to be double of $\sqrt[3]{\frac{K_S}{4}}$

In 5 L solution prior to any precipitation (calculating dilutions):

$c_3(\text{CO}_3{}^{2-}) = \frac{c_1(\text{CO}_3{}^{2-})}{5} = 1.16 \times 10^{-5}\,\text{mol L}^{-1}$

$c_3(\text{OH}^-) = \frac{c_2(\text{OH}^-)}{5} = 5.04 \times 10^{-3}\,\text{mol L}^{-1}$

$c_3(\text{Ca}^{2+}) = \frac{c_1(\text{Ca}^{2+}) + c_2(\text{Ca}^{2+})}{5} = 2.53 \times 10^{-3}\,\text{mol L}^{-1}$

$Q_3(\text{CaCO}_3) = c_3(\text{Ca}^{2+}) \cdot c_3(\text{CO}_3{}^{2-}) = 2.93 \times 10^{-8}\,\text{mol}^2\,\text{L}^{-2} > K_S(\text{CaCO}_3) \implies$ precipitates

$Q_3(\text{Ca(OH)}_2) = c_3(\text{Ca}^{2+}) \cdot c_3^2(\text{OH}^-) = 6.42 \times 10^{-8}\,\text{mol}^3\,\text{L}^{-3} \implies$ does not precipitate

1.0 pt for all concentrations correctly adjusted (-0.25 pts if one incorrect, -0.75 pts if two incorrect), 1.0 pt for mathematical derivation of and correct $Q(\text{CaCO}_3)$, 1.0 pt for mathematical derivation of and correct $Q(\text{Ca(OH)}_2)$.

4.5 pts for correct mathematical reasoning as outlined above, 2.0 pts for results and interpretation.

4.6 For the mixed solutions in task 4.5, calculate the final concentration of calcium ions in solution (after possible precipitation). 3.0 pt

SOLUTION:

Numbering: 4 = mixed solution after precipitation (V = 5 L)

Since calcium hydroxide does not precipitate: $c_4(\text{Ca(OH)}_2) = \frac{c_{sol,2}(\text{Ca(OH)}_2)}{5} = 2.52 \times 10^{-3}\,\text{mol L}^{-1}$

$K_S(\text{CaCO}_3) = c_4(\text{Ca}^{2+}) \cdot c_4(\text{CO}_3{}^{2-}) = (c_{sol,4}(\text{Ca(OH)}_2) + z) \cdot z$

$0 = z^2 + c_{sol,4}(\text{Ca(OH)}_2) \cdot z - K_S(\text{CaCO}_3)$

$z = 1.33 \times 10^{-6}\,\text{mol L}^{-1}, -3.36 \times 10^{-9}\,\text{mol L}^{-1}$

Omitting the negative concentration for obvious reasons, we obtain $c_4(\text{Ca}^{2+}) = c_{sol,4}(\text{Ca(OH)}_2) + z = 2.52 \times 10^{-3}\,\text{mol L}^{-1} + 1.33 \times 10^{-6}\,\text{mol L}^{-1} = 2.52 \times 10^{-3}\,\text{mol L}^{-1}$

2.5 pts for correct mathematical reasoning, 0.5 pts for correct numerical result. 1 pt if "no precipitation" is obtained in task 4.5 and the concentration obtained in 4.5 is taken as result for 4.6.

Titration (9.0 points)

You receive a sample of an unknown organic diprotic acid and decide that you want to find out its identity by titration with sodium hydroxide. You dissolve 8.689 g of the acid in 100 mL water. You titrate 10 mL of the obtained solution using phenolphthalein as an indicator.

5.1 You observe a colour change after adding 33.4 mL of a 0.5 mol L^{-1} NaOH solution. Calculate the concentration of acid in the original solution. 1.0 pt

SOLUTION:

$c_0 = c(\text{NaOH}) \times 0.5 \times \frac{V_{\text{NaOH}}}{V_0} = 0.5\ \text{mol L}^{-1} \times 0.5 \times \frac{0.0334\ \text{L}}{0.1\ \text{L}} = 0.835\ \text{mol L}^{-1}$

0.5 pts for correct mathematical reasoning, 0.5 pts for the numerical result.

5.2 Calculate the molecular weight of the acid. 0.5 pt

SOLUTION:

$M = \frac{m}{n} = \frac{m}{c \cdot V} = \frac{8.689\ \text{g}}{0.835\ \text{mol L}^{-1} \cdot 0.1\ \text{L}} = 104.06\ \text{g mol}^{-1}$

5.3 Knowing that the acid contains only carbon, hydrogen, and oxygen atoms, determine the correct sum formula for the titrated acid. Additionally, draw the chemical structure of the acid. 3.0 pt

SOLUTION:

Sum formula: $C_3H_4O_4$

$3 \times 12.011\ \text{g mol}^{-1} + 4 \times 1.008\ \text{g mol}^{-1} + 4 \times 15.999\ \text{g mol}^{-1} = 104.061\ \text{g mol}^{-1}$

This is malonic acid, $HOOC{-}CH_2{-}COOH$.

5.4 Write down the reaction equations for the two deprotonation steps of this acid in water (you may abbreviate the acid by its sum formula). 1.0 pt

SOLUTION:

Acid has semi-structural formula $HOOC{-}CH_2{-}COOH$ (malonic acid).

First deprotonation: $C_3H_4O_4 \xrightarrow{H_2O} C_3H_3O_4{}^{-} + H_3O^{+}$

Second deprotonation: $C_3H_3O_4{}^{-} \xrightarrow{H_2O} C_3H_2O_4{}^{2-} + H_3O^{+}$

Alternative reaction equations possible!

First deprotonation: $HOOC{-}CH_2{-}COOH \xrightarrow{H_2O} {}^{-}OOC{-}CH_2{-}COOH + H_3O^{+}$

Second deprotonation: ${}^{-}OOC{-}CH_2{-}COOH \xrightarrow{H_2O} {}^{-}OOC{-}CH_2{-}COO^{-} + H_3O^{+}$

0.5 pts per correct reaction equation, no points awarded if deprotonation is occuring on CH_2 group.

5.5 Independently of your prior experiments, you now want to prepare a phosphate buffer with pH 7.5 with a total concentration of 0.1 mol L^{-1} of the buffering agent. What is the concentration of bisphosphate ions $HPO_4{}^{2-}$ in the buffer? ($\mathrm{pK_{a,2}} = 7.21$) 3.5 pt

SOLUTION:

HA $=$ $H_2PO_4{}^-$, A^- $=$ $HPO_4{}^{2-}$

$\mathrm{pH} = \mathrm{pK_a} + \log \frac{c(\mathrm{A}^-}{\mathrm{HA}} = \mathrm{pK_a} + \log \frac{c(\mathrm{A}^-)}{(c_{tot}(\mathrm{A}) - c(\mathrm{A}^-))}$

$(c_{tot}(\mathrm{A}) - c(\mathrm{A}^-)) \times 10^{\mathrm{pH}-\mathrm{pK_a}} = c(\mathrm{A}^-)$

$c_{tot}(\mathrm{A}) \times 10^{\mathrm{pH}-\mathrm{pK_a}} = c(\mathrm{A}^-) \times (10^{\mathrm{pH}-\mathrm{pK_a}} + 1)$

$c(\mathrm{A}^-) = c_{tot}(A) \times \frac{10^{\mathrm{pH}-\mathrm{pK_a}}}{10^{\mathrm{pH}-\mathrm{pK_a}}+1} = 0.1\ \mathrm{mol\,L^{-1}} \times \frac{10^{7.5-7.21}}{10^{7.5-7.21}+1} = 0.0661\ \mathrm{mol\,L^{-1}}$

2.5 pts for correct mathematical reasoning, 1.0 pt for correct numerical result.

Redox Chemistry (7.5 points)

The Daniell cell (also called the Daniell element) is one of the first versions of a battery, which is used throughout the world as a practical introduction to electrochemistry and redox reactions. It is composed of two containers, one with a solution of zinc sulfate and a zinc plate suspended in the solution, the other with a solution of copper sulfate and a copper plate suspended in it. The two plates are connected with a conductive wire, while the two solutions are connected with a salt bridge. In redox chemistry, the standard reduction potentials are a measure of how easily ions in solution accept electrons. The standard reduction potential E^0_{red} for zinc and its ion is $E^0_{red}(\text{Zn}/\text{Zn}^{2+}) = -0.76\,\text{V}$, for copper and its ion it is $E^0_{red}(\text{Cu}/\text{Cu}^{2+}) = 0.34\,\text{V}$.

Important equations you will need for this problem:

Nernst equation for a half-cell:	$E = E^0 + \frac{RT}{zF} \ln \frac{c(Ox)}{c(Red)}$
Simplification of Nernst equation for a half-cell at 298.15 K:	$E = E^0 + \frac{0.059\,\text{V}}{z} \log \frac{c(Ox)}{c(Red)}$
Nernst equation for a full cell:	$\Delta E = \Delta E^0 + \frac{RT}{zF} \ln \frac{c(Products)}{c(Reactants)}$
Simplification of Nernst equation for a full cell at 298.15 K:	$\Delta E = \Delta E^0 + \frac{0.059\,\text{V}}{z} \log \frac{c(Products)}{c(Reactants)}$

6.1 Write down the two half-cell reactions occurring in the Daniell element. 1.0 pt

SOLUTION:

$\text{Zn (s)} \longrightarrow \text{Zn}^{2+}\text{ (aq)} + 2\,\text{e}^-$

$\text{Cu}^{2+}\text{ (aq)} + 2\,\text{e}^- \longrightarrow \text{Cu (s)}\downarrow$

0.5 pts per correct reaction equation.

6.2 Calculate the total cell potential / output voltage of the Daniell element. 1.0 pt

SOLUTION:

$\Delta E^0 = E^0_{red}(\text{Cu}/\text{Cu}^{2+}) - E^0_{red}(\text{Zn}/\text{Zn}^{2+}) = 0.34\,\text{V} - (-0.76\,\text{V}) = 1.10\,\text{V}$

6.3 How would you increase the total output voltage? Name two possible actions, without changing the chemical reaction that occurs. 2.0 pt

SOLUTION:

Possible answers: decrease c(Zn^{2+}), increase c(Cu^{2+}), increase temperature.

0.5 pts per correct answer.

6.4 Calculate the total voltage for a modified Daniell element with c(Cu^{2+}) = 3.0 mol L^{-1} and c(Zn^{2+}) = 0.007 mol L^{-1} at a temperature of 20 °C. 3.0 pt

SOLUTION:

$\Delta E = \Delta E^0 - \frac{RT}{zF} \ln \frac{c(\text{Zn}^{2+})}{c(\text{Cu}^{2+})} = 1.10\,\text{V} - \frac{8.314\,\text{J}\,\text{mol}^{-1}\,\text{K}^{-1} \times 293.15\,\text{K}}{2 \cdot 96\,485\,\text{C}\,\text{mol}^{-1}} \ln \frac{0.007}{3} = 1.10\,\text{V} - (-0.076\,\text{V}) = 1.176\,\text{V}$

or: $\Delta E = \Delta E^0 + \frac{RT}{zF} \ln \frac{c(\text{Cu}^{2+})}{c(\text{Zn}^{2+})} = ... = 1.176\,\text{V}$

2.0 pts for correct mathematical reasoning, 1.0 pt for correct numerical result.

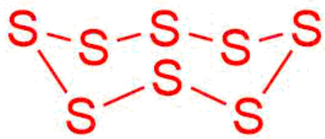
6.5	What happens to the cell potential if the mass of the copper electrode is doubled? Give a reason for your answer. **SOLUTION:** Nothing. The voltage is independent of the electrode's mass. 0.25 pts for correct answer, 0.25 pts for correct reasoning.	0.5 pt

Electrons two ways: VSEPR and Resonance (10.5 points)

Sulfur is an essential element to many life forms, in humans it is vital for the production of cysteine and methionine, performs vital metabolic reactions as part of Coenzyme A, and lets everyone in the train know you had broccoli and eggs for dinner yesterday. In addition, sulfur is an interesting element when it comes to VSEPR and its structures. In oxidation state zero, sulfur can exist as an octamer (sometimes called a sulfur crown due to its shape).

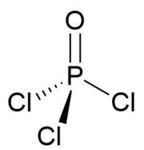
7.1 Draw the structure of the S_8 molecule, so that its 3D conformation is clearly visible. 1.0 pt

SOLUTION:



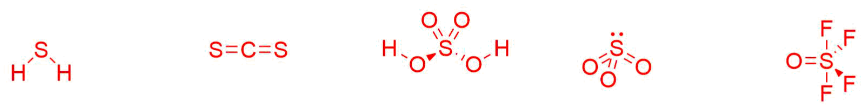
Once sulfur is not in an oxidation state of zero, however, things become more interesting.

7.2 Draw the correct 3D structures according to VSEPR for the following compounds: H_2S, CS_2, SO_3, H_2SO_4, OSF_4. Each of your drawings should look like this: 5.0 pt



$POCl_3$
Tetrahedral

SOLUTION:



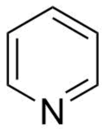
Hydrogen sulfide, Bent (92.1°) — Carbon disulfide, Linear — Sulfuric acid, Tetrahedral — Sulfur trioxide, Trig. pyr. — Thionyl tetrafluoride, Trig. bipyr.

0.5 pts per structure with correct bonding, 0.5 pts per correct geometry

For most inorganic compounds, only one structural formula correctly represents the actual shape of the compound. However, organic compounds are capable of something called resonance, where two or more structures describe different properties of the same compound, but no single structure can summarize them all.

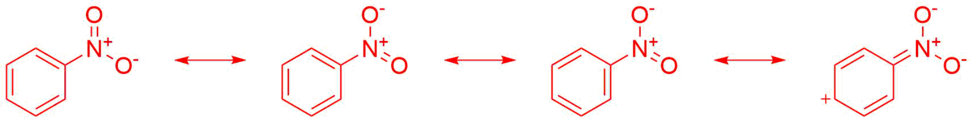
7.3 Draw at least three resonance structures for each of the following compounds: nitrobenzene (Ph—NO_2), 4-dimethylaminopyridine (Py—$N(CH_3)_2$), and succinate ($^-OOC-CH_2-CH_2-COO^-$). **4.5 pt**

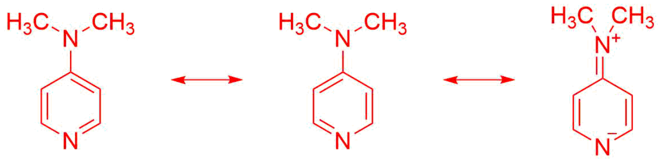
For reference:

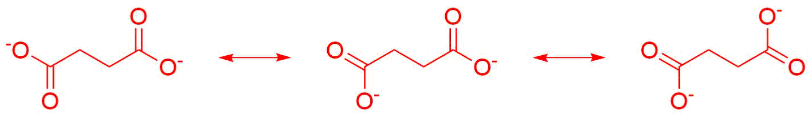


Pyridine

SOLUTION:







0.5 pts for each correct resonance structure.

Explosions and maybe Fire (14.0 points)

Gunpowder (sometimes referred to as black powder) is the oldest explosive known to humanity. First referred to in a 9th century Chinese text, it allowed for the development of the first true gun: the hand cannon. Gunpowder derives its literal kaboom from the mixing of saltpeter (potassium nitrate) with sulfur and charcoal. When ignited, it combusts rapidly according to the following reaction equation:

$$10\,KNO_3\,(s) + 3\,S\,(s) + 8\,C\,(s) \longrightarrow 2\,K_2CO_3\,(s) + 3\,K_2SO_4\,(s) + 6\,CO_2\,(g)\uparrow + 5\,N_2\,(g)\uparrow$$

As you might know, gunpowder also has a less militaristic use case: fireworks. You as a chemist are now tasked with creating the ultimate fireworks rocket. Please do not blow yourself up in the process, the cleanup might be difficult.

In a physical chemistry textbook, you find the following thermodynamic data:

Compound	ΔH_f^0 / kJ mol^{-1}	S^0 / J mol^{-1} K^{-1}
KNO_3	-494.6	133.1
S	0.0	32.1
C	0.0	5.7
K_2CO_3	-1151.0	155.5
K_2SO_4	-1437.8	175.6
CO_2	-393.5	213.8
N_2	0.0	191.6

Thermodynamic data for various compounds at 100 000 Pa and 298.15 K.

8.1 First things first: Calculate the standard reaction enthalpy and standard reaction entropy for the reaction mentioned in the introduction. Express your results in kJ mol^{-1} and J mol^{-1} K^{-1}, respectively, rounding to one decimal place. 4.0 pt

SOLUTION:

$\Delta_r H^0 = (2\times(-1151.0\,\text{kJ mol}^{-1}) + 3\times(-1437.8\,\text{kJ mol}^{-1}) + 6\times(-393.5\,\text{kJ mol}^{-1}) + 5\times 0.0\,\text{kJ mol}^{-1}) - (10\times(-494.6\,\text{kJ mol}^{-1}) + 3\times 0.0\,\text{kJ mol}^{-1} + 8\times 0.0\,\text{kJ mol}^{-1}) = -4030.4\,\text{kJ mol}^{-1}$

$\Delta_r S^0 = (2\times 155.5\,\text{J mol}^{-1}\,\text{K}^{-1} + 3\times 175.6\,\text{J mol}^{-1}\,\text{K}^{-1} + 6\times 213.8\,\text{J mol}^{-1}\,\text{K}^{-1} + 5\times 191.6\,\text{J mol}^{-1}\,\text{K}^{-1}) - (10\times 133.1\,\text{J mol}^{-1}\,\text{K}^{-1} + 3\times 32.1\,\text{J mol}^{-1}\,\text{K}^{-1} + 8\times 5.7\,\text{J mol}^{-1}\,\text{K}^{-1}) = 1605.7\,\text{J mol}^{-1}\,\text{K}^{-1}$

3.0 pts for correct formulas used (-1.0 pt if reactants and products are switched*), 1.0 pt for correct numerical results.

* Wrong numerical values in future tasks arising from this will carry no additional penalty (Folgefehler).

8.2 From your results in 8.1, calculate the Gibbs free energy in kJ for the reaction mentioned in the introduction, assuming that 3 mol of KNO_3 react. The reaction occurs at a temperature of 1700 °C and standard pressure. If you couldn't solve problem 8.1, assume $\Delta_r H^0 = -4300\,\text{kJ mol}^{-1}$ and $\Delta_r S^0 = 2000\,\text{J mol}^{-1}\,\text{K}^{-1}$. 2.0 pt

SOLUTION:

$\Delta_r G = -4\,030\,400\,\text{J} - (1973.15\,\text{K} \times 1605.7\,\text{J K}^{-1}) = -7\,198\,686.95\,\text{J mol}^{-1} = -7198.7\,\text{kJ mol}^{-1}$

Adjusting to 3 mol of KNO_3 reacting: $\Delta_r G' = -7\,198\,686.95\,\text{J mol}^{-1} 10 \times 3\,\text{mol} = -2\,159\,606.09\,\text{J} = -2159.6\,\text{kJ}$

If student used provided values: $\Delta_r G = -4\,300\,000\,\text{J} - (1973.15\,\text{K} \times 1605.7\,\text{J K}^{-1}) = -7\,468\,286.95\,\text{J mol}^{-1} = -7468.3\,\text{kJ mol}^{-1}$

Adjusting to 3 mol of KNO_3 reacting: $\Delta_r G' = -7\,468\,286.95\,\text{J mol}^{-1} 10 \times 3\,\text{mol} = -2\,240\,486.09\,\text{J} = -2240.5\,\text{kJ}$

1.0 pt for correct formula used, 0.5 pts for adjustment of $\Delta_r G$, 0.5 pts for correct numerical result.

Based on these results, we can see that this reaction has enormous explosive power. Let's harness it!

Your supervisor wants you to formulate a recipe for 10 kilograms of gunpowder that will react properly (no leftovers except for lots of gas, potassium carbonate, and potassium sulfate).

8.3 Calculate the amounts of reactants you need to weigh in to create the 10 kg of gunpowder. Express your results in grams, rounding to one decimal place. 4.0 pt

SOLUTION:

$m_{tot} = 10\,000\,\text{g}$, stoichiometric ratio of reactants is 10:3:8, so 21 total parts to the mixture

Weighted average molar mass: $\tilde{M} = \frac{10 \cdot M(\text{KNO}_3) + 3 \cdot M(\text{S}) + 8 \cdot M(\text{C})}{21} = \frac{10 \cdot 101.32\,\text{g mol}^{-1} + 3 \cdot 32.065\,\text{g mol}^{-1} + 8 \cdot 12.011\,\text{g mol}^{-1}}{21} = 57.404\,\text{g mol}^{-1}$

Number of "moles of gunpowder": $\tilde{n} = \frac{m_{tot}}{\tilde{M}} = \frac{10\,000\,\text{g}}{57.40\,\text{g mol}^{-1}} = 174.204\,\text{mol}$

$n(\text{KNO}_3) = \frac{174.204\,\text{mol}}{21} \times 10 = 82.954\,\text{mol}$

$n(\text{S}) = \frac{174.204\,\text{mol}}{21} \times 3 = 24.886\,\text{mol}$

$n(\text{C}) = \frac{174.204\,\text{mol}}{21} \times 8 = 66.363\,\text{mol}$

$m(\text{KNO}_3) = 82.954\,\text{mol} \times 101.32\,\text{g mol}^{-1} = 8404.9\,\text{g}$

$m(\text{S}) = 24.886\,\text{mol} \times 32.065\,\text{g mol}^{-1} = 797.3\,\text{g}$

$m(\text{C}) = 66.363\,\text{mol} \times 12.011\,\text{g mol}^{-1} = 797.1\,\text{g}$

3.0 pts for correct mathematical reasoning, 1.0 pt for correct numerical result.

You have weighed in your chemicals and carefully transferred them into an explosion-proof container. Now your supervisor wants an estimate of how much force this explosion generates. The container can be described as an upside-down cylinder of 5 L volume, with its circular opening being placed onto the ground. The opening measures 10 cm in diameter, and the combustion is started remotely. Your (American) textbook indicates that the reaction will reach a sizzling 3300 degrees Fahrenheit, which you convert to 1815.556 °C. Assume that only the gases produced during the reaction contribute to the force.

8.4 What will be the force applied to the ground when the charge ignites, assuming your 10 kg of gunpowder combust completely? 4.0 pt

SOLUTION:

Example answer: $p = \frac{F}{A} \implies F = p \cdot A$

$A = r^2 \times \pi = \frac{d^2}{4} \times \pi$

Insert ideal gas law: $p = \frac{nRT}{V} \implies F = \frac{nRT \cdot A}{V}$

Split in two for N_2 and CO_2: $F_{tot} = F_1 + F_2 = \frac{(n(\mathrm{N_2}) + n(\mathrm{CO_2}) \cdot RT \cdot A)}{V}$

174.204 mol of gunpowder being burned produces $\frac{174.204\,\mathrm{mol}}{16} \times 6 = 65.327\,\mathrm{mol CO_2}$ and $\frac{174.204\,\mathrm{mol}}{16} \times 5 = 54.439\,\mathrm{mol N_2}$

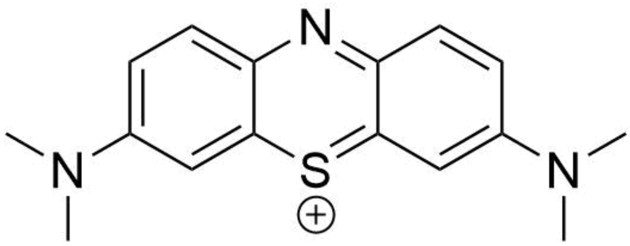
$F_{tot} = \frac{(54.439\,\mathrm{mol} + 65.327\,\mathrm{mol}) \times 8.314\,\mathrm{J\,mol^{-1}\,K^{-1}} \times 2088.706\,\mathrm{K} \times \pi \times 25\,\mathrm{cm^2})}{5\,\mathrm{dm^3}} = \frac{(54.439\,\mathrm{mol} + 65.327\,\mathrm{mol}) \times 8.314\,\mathrm{J\,mol^{-1}\,K^{-1}} \times 2088.706\,\mathrm{K} \times \pi \times 0.0025\,\mathrm{m^2})}{0.005\,\mathrm{m^3}} = 3.27 \times 10^6\,\mathrm{N}$

3.0 pts for mathematical reasoning, 1.0 pt for correct numerical result.

A tremendous amount of force indeed! Luckily, nobody got hurt when the container took off and hit the ceiling. Next time, maybe perform the blast test outdoors...

Kinetics of Methylene Blue Discoloration (9.0 points)

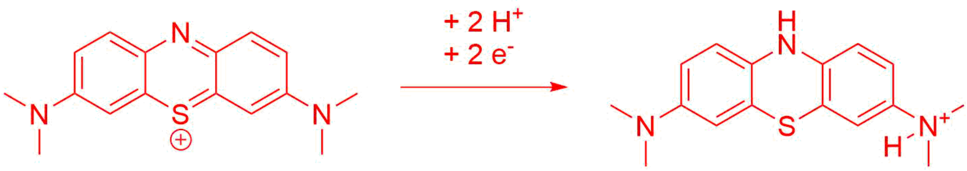
Methylene blue is a cationic dye that can be used as a redox indicator. It is blue in its oxidised form (see structure below). This form of the indicator has its absorption maximum λ_{max} at 665 nm.



Methylene blue, oxidised form.

9.1 Methylene blue can be reduced by ascorbic acid. In this reaction, methylene blue formally takes up two electrons and two protons from the reducing agent. Draw the reaction scheme for the reduction of methylene blue; it is sufficient to only draw the structures of methylene blue in its oxidised and reduced forms. 2.0 pt

SOLUTION:



1.5 pts for correct structure of reduced form, 0.5 pts for including protons and electrons in reaction scheme.

9.2 Upon reduction, methylene blue loses its characteristic blue colour. Give an explanation for this phenomenon. 1.0 pt

SOLUTION:

The blue colour arises from the large π-electron system. Upon reduction, this system is broken up.

9.3 To determine the molecular extinction coefficient, you prepare a 1×10^{-5} mol L^{-1} solution of methylene blue. You fill 1 mL of your solution into a cuvette of 1 cm length and determine an absorbance of 0.7402. Calculate the molar extinction coefficient ϵ_{max}. 1.0 pt

SOLUTION:

$A = \epsilon \times c \times d$

$\epsilon = \frac{A \times d}{c} = \frac{0.7402 \times 1\,\text{cm}}{1 \times 10^{-5}\,\text{mol L}^{-1}} = 74\,020\,\text{L mol}^{-1}\,\text{cm}^{-1}$

9.4 You perform experiments to observe the discolouration kinetics at different concentrations of methylene blue and ascorbic acid. You observe the following reaction rates ν_i (i being the number of the experiment you conducted). Determine the reaction orders with regard to methylene blue (MB^+) and to ascorbic acid (AsA). 3.0 pt

Experiment no.	$c(MB^+)$ / mol L^{-1}	$c(\mathrm{AsA})$ / mol L^{-1}	ν / mol L^{-1} s^{-1}
1	1.8×10^{-5}	0.023	1.12×10^{-6}
2	1.3×10^{-5}	0.023	7.93×10^{-7}
3	8.9×10^{-6}	0.023	5.66×10^{-7}
4	3.5×10^{-6}	0.023	2.14×10^{-7}
5	1.3×10^{-5}	0.011	3.97×10^{-7}
6	1.3×10^{-5}	0.046	1.59×10^{-6}
7	1.3×10^{-5}	0.101	3.46×10^{-6}
8	1.3×10^{-5}	0.399	1.38×10^{-5}

SOLUTION:
1^{st} order regarding methylene blue, 1^{st} order regarding ascorbic acid.
1.5 pts per correct reaction order.

9.5 Write down the correct rate law for the reaction. 1.0 pt

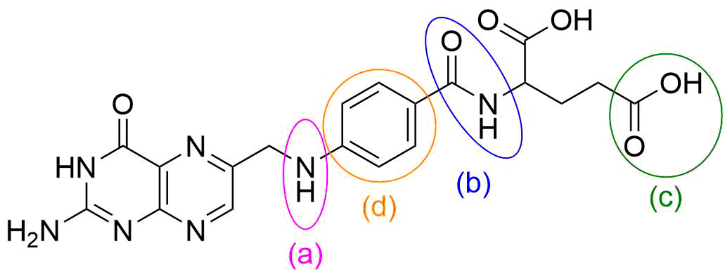
SOLUTION:
$\nu = k \cdot c(\mathrm{MB}^+) \cdot c(\mathrm{AsA})$

9.6 For experiment no. 5, calculate the absorbance right at the beginning of the reaction. If you couldn't solve problem 9.3, assume the molecular extinction coefficient to be 70 000 L mol^{-1} cm^{-1}. 1.0 pt

SOLUTION:
$A = \epsilon \times c \times d = 74020\ \mathrm{L\,mol^{-1}\,cm^{-1}} \times 1.3 \times 10^{-5}\ \mathrm{mol\,L^{-1}} \times 1\ \mathrm{cm} = 0.962$
If student used the provided value: $A = \epsilon \times c \times d = 70000\ \mathrm{L\,mol^{-1}\,cm^{-1}} \times 1.3 \times 10^{-5}\ \mathrm{mol\,L^{-1}} \times 1\ \mathrm{cm} = 0.910$

Organic Chemistry (6.0 points)

10.1 Identify the highlighted functional groups (a) - (c) in the molecule below. 1.5 pt



Structure of folic acid.

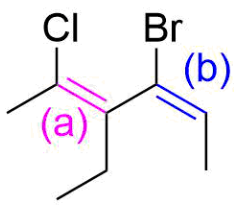
SOLUTION:
(a) Secondary amine
(b) Secondary amide
(c) Carboxylic acid

0.5 pts per correctly identified functional group (-0.25 pts if student wrote "amine" instead of "secondary amine", -0.25 pts if student wrote "amide" instead of "secondary amide").

10.2 Name the substitution pattern of the benzene ring (d) in the folic acid structure (see above). 0.5 pt

SOLUTION:
Ring is *para*-substituted.

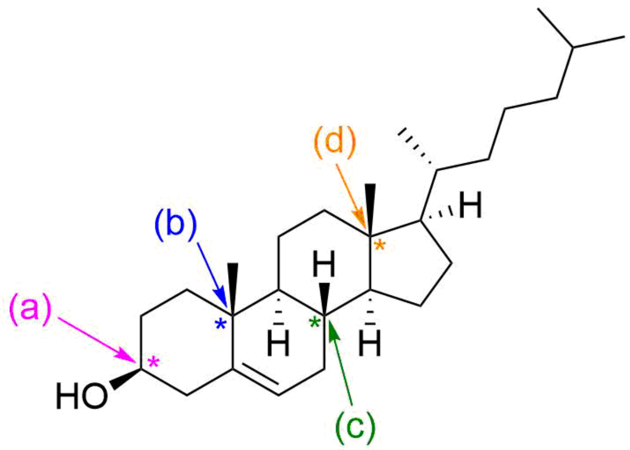
10.3 Give the correct descriptors for the double bonds (a) and (b) in the following molecule. 1.0 pt



SOLUTION:
(a) (*Z*)
(b) (*E*)

0.5 pts per correct assignment, *cis* (a) and *trans* (b) were also accepted as correct

10.4 Assign the correct descriptors for the marked chiral centres (a) to (d) of cholesterol, according to the CIP nomenclature. 2.0 pt



SOLUTION:

(a) (*S*)
(b) (*R*)
(c) (*S*)
(d) (*R*)

0.5 pts per correct assignment

10.5 How many chiral centres does cholesterol have in total? How many stereoisomers of cholesterol could potentially exist, based on this information? 1.0 pt

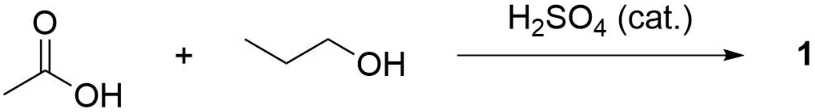
SOLUTION:

8 chiral centres, so $2^8 = 256$ theoretically possible stereoisomers.

0.5 pts per correct answer.

Assorted Organic Reactions (9.0 points)

11.1 Draw the product **1** of the reaction shown below. 0.5 pt



SOLUTION:

Full marks if student only draws ester.

11.2 Give the name of the reaction in problem 11.1. 0.5 pt

SOLUTION:

Fischer esterification.

0.25 pts if student wrote "Fischer reaction", 0.25 pts if student wrote "esterification".

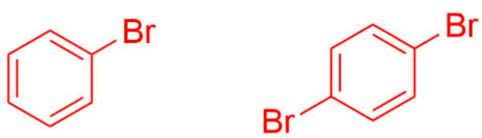
11.3 Identify the type of reaction in problem 11.1. Choose from the following: condensation reaction, hydrolysis, nucleophilic substitution, elimination, neutralisation. 0.5 pt

SOLUTION:

Condensation reaction.

11.4 Draw the products **2** and **3** of the reaction shown below. Hint: Both products are aromatic. 1.0 pt

SOLUTION:

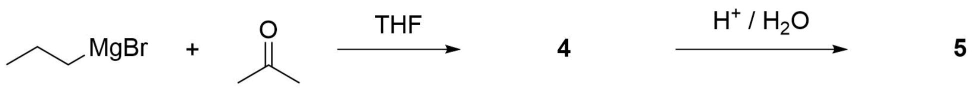


2 **3**

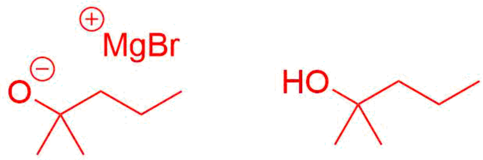
0.5 pts per correctly identified product.

11.5	Identify the type of reaction in problem 11.4. Choose from the following: nucleophilic substitution, nucleophilic aromatic substitution, electrophilic substitution, electrophilic aromatic substitution. **SOLUTION:** Electrophilic aromatic substitution.	0.5 pt

11.6 Draw the intermediate **4** and the product **5** of the Grignard reaction shown below. — 1.0 pt



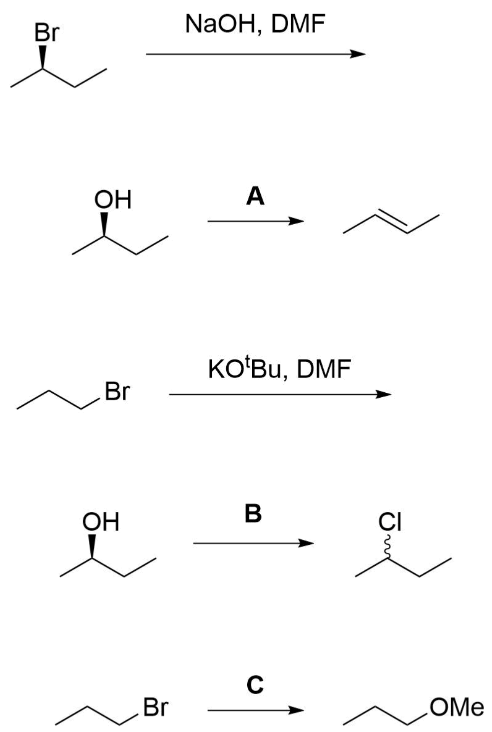
SOLUTION:



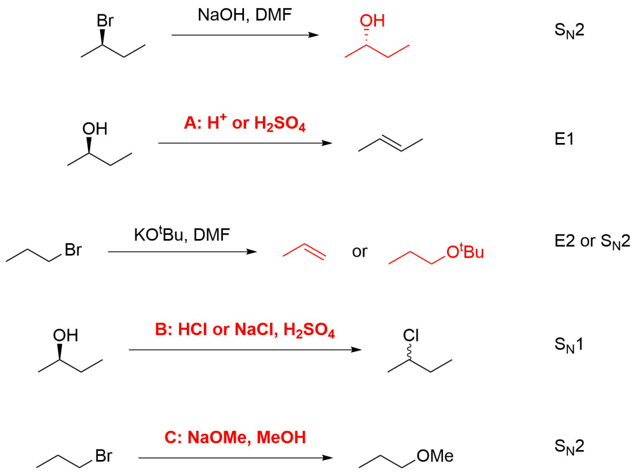
4 5

0.5 pts per correct compound.

11.7 For each of the following reactions, copy the reaction scheme to your answer sheet and fill in the missing product(s) or reagent(s). In addition, write down for each reaction whether it proceeds according to an S_N1, S_N2, E1, or E2 mechanism. 5.0 pt



SOLUTION:



0.5 pts per correct structure or reagent, 0.5 pts per correct assignment of S_N1 / S_N2 / E1 / E2.