19th – 29th July, 2018

Bratislava, SLOVAKIA

Prague, CZECH REPUBLIC

www.50icho.eu

**PREPARATORY PROBLEMS: THEORETICAL**

**SOLUTIONS**

|  |  |
| --- | --- |
|  | **50th IChO 2018**  International Chemistry Olympiad  SLOVAKIA & CZECH REPUBLIC  BACK TO WHERE IT ALL BEGAN |

NOT TO BE MADE ACCESSIBLE BEFORE 1st JUNE, 2018

Table of Contents

[Problem 1. Synthesis of hydrogen cyanide 2](#_Toc505852982)

[Problem 2. Thermochemistry of rocket fuels 3](#_Toc505852983)

[Problem 3. HIV protease 6](#_Toc505852984)

[Problem 4. Enantioselective hydrogenation 8](#_Toc505852985)

[Problem 5. Ultrafast reactions 9](#_Toc505852986)

[Problem 6. Kinetic isotope effects 13](#_Toc505852987)

[Problem 7. Designing a photoelectrochemical cell 14](#_Toc505852988)

[Problem 8. Fuel cells 16](#_Toc505852989)

[Problem 9. Acid-base equilibria in blood 18](#_Toc505852990)

[Problem 10. Ion exchange capacity of a cation exchange resin 20](#_Toc505852991)

[Problem 11. Weak and strong cation exchange resin 21](#_Toc505852992)

[Problem 12. Uranyl extraction 22](#_Toc505852993)

[Problem 13. Determination of active chlorine in commercial products 24](#_Toc505852994)

[Problem 14. Chemical elements in fireworks 25](#_Toc505852995)

[Problem 15. Colours of complexes 27](#_Toc505852996)

[Problem 16. Iron chemistry 29](#_Toc505852997)

[Problem 17. Cyanido- and fluorido-complexes of manganese 34](#_Toc505852998)

[Problem 18. The fox and the stork 37](#_Toc505852999)

[Problem 19. Structures in the solid state 39](#_Toc505853000)

[Problem 20. Cyclobutanes 41](#_Toc505853001)

[Problem 21. Fluorinated radiotracers 42](#_Toc505853002)

[Problem 22. Where is lithium? 44](#_Toc505853003)

[Problem 23. Synthesis of eremophilone 45](#_Toc505853004)

[Problem 24. Cinnamon all around 46](#_Toc505853005)

[Problem 25. All roads lead to caprolactam 48](#_Toc505853006)

[Problem 26. Ring opening polymerizations (ROP) 50](#_Toc505853007)

[Problem 27. Zoniporide 52](#_Toc505853008)

[Problem 28. Nucleic acids 54](#_Toc505853009)

Problem 1. Synthesis of hydrogen cyanide

1.1 Degussa process (BMA process):

Δr*H*m = − Δf*H*m(CH4) − Δf*H*m(NH3) + Δf*H*m(HCN) + 3 Δf*H*m(H2)

Δr*H*m = [− (−90.3) − (−56.3) + 129.0 + 3 × 0] kJ mol−1 = 275.6 kJ mol−1

Andrussow process:

Δr*H*m = − Δf*H*m(CH4) − Δf*H*m(NH3) − 3/2 Δf*H*m(O2) + Δf*H*m(HCN) + 3 Δf*H*m(H2O)

Δr*H*m = [− (−90.3) − (−56.3) − 3/2 × 0 + 129.0 + 3 × (−250.1)] kJ mol−1 = −474.7 kJ mol−1

1.2 An external heater has to be used in the Degussa process (BMA process) because   
the reaction is endothermic.

1.3

The result is in accordance with the Le Chatelier’s principle because the reaction is endothermic and therefore an increase in temperature shifts the equilibrium toward products (in other words, the equilibrium constant increases).

1.4 The equilibrium constant of the reaction in the Andrussow process decreases with   
an increase in temperature because the reaction is exothermic.

Problem 2. Thermochemistry of rocket fuels

Notation of indexes: 0M – hydrazine, 1M – methylhydrazine, 2M – 1,1-dimethylhydrazine

Standard conditions: *T*° = 298.15 K; *p*° = 101 325 Pa.

All values given below are evaluated from non-rounded intermediate results.

2.1 Calculation of the number of moles corresponding to 1 g of the samples: *ni* = *mi* / *Mi*

*M*0M = 32.05 g mol−1; *M*1M = 46.07 g mol−1; *M*2M = 60.10 g mol−1.

*n*0M = 31.20 mmol; *n*1M = 21.71 mmol; *n*2M = 16.64 mmol.

Calculation of combustion heat: *qi* = *C*cal × Δ*Ti*

*q*0M = 16.83 kJ; *q*1M = 25.60 kJ; *q*2M = 30.11 kJ.

Calculation of the molar internal energies of combustion: Δc*Ui* = −*qi* / *ni*

Δcomb*U*0M = −539.40 kJ mol−1; Δcomb*U*1M = −1 179.48 kJ mol−1;

Δcomb*U*2M = −1 809.64 kJ mol−1.

Bomb calorimeter combustion reactions with the stoichiometric coefficients added:

Hydrazine N2H4 (l) + O2 (g) → N2 (g) + 2 H2O (g)

Methylhydrazine N2H3CH3 (l) + 2.5 O2 (g) → N2 (g) + CO2 (g) + 3 H2O (g)

1,1-Dimethylhydrazine N2H2(CH3)2 (l) + 4 O2 (g) → N2 (g) + 2 CO2 (g) + 4 H2O (g)

Calculation of the molar enthalpies of combustion: Δc*Hi* = Δc*Ui* + Δc*n*(gas)*RT*std

Δcomb*H*0M = −534.44 kJ mol−1; Δcomb*H*1M = −1 173.29 kJ mol−1;

Δcomb*H*2M = −1 802.20 kJ mol−1.

2.2 Calculation of the molar enthalpies of formation:

Δform*H*0M = 2 Δform*H*H2O,g − Δcomb*H*0M = +50.78 kJ mol−1

Δform*H*1M = 3 Δform*H*H2O,g + Δform*H*CO2 − Δcomb*H*1M = +54.28 kJ mol−1

Δform*H*2M = 4 Δform*H*H2O,g + 2 Δform*H*CO2 − Δcomb*H*2M = +47.84 kJ mol−1

Rocket engines combustion reactions:

Hydrazine N2H4 (l) + 1/2 N2O4 (l) → 2 H2O (g) + 3/2 N2 (g)

Methylhydrazine N2H3CH3 (l) + 5/4 N2O4 (l) → CO2 (g) + 3 H2O (g) + 9/4 N2 (g)

1,1-Dimethylhydrazine N2H2(CH3)2 (l) + 2 N2O4 (l) → 3 N2 (g) + 4 H2O (g) + 2 CO2 (g)

Calculation of molar reaction enthalpies, related to one mole of hydrazine derivatives:

Δre*H*0M = (2 Δform*H*H2O,g − 1/2 Δform*H*N2O4 − Δform*H*0M) = −538.98 kJ mol−1

Δre*H*1M = (Δform*H*CO2 + 3 Δform*H*H2O,g − 5/4 Δform*H*N2O4 − Δform*H*1M) = −1 184.64 kJ mol−1

Δre*H*2M = (2 Δform*H*CO2 + 4 Δform*H*H2O,g − 2 Δform*H*N2O4 − 1 Δform*H*2M) = −1 820.36 kJ mol−1

2.3 Calculation of the standard molar reaction enthalpies, related to one mole of hydrazine derivatives:

Δre*H*°0M = Δre*H*0M − 2 Δvap*H*H2O = −620.28 kJ mol−1

Δre*H*°1M = Δre*H*1M − 3 Δvap*H*H2O = −1 306.59 kJ mol−1

Δre*H*°2M = Δre*H*2M − 4 Δvap*H*H2O = −1 982.96 kJ mol−1

Calculation of the standard molar reaction entropies, related to one mole of hydrazine derivatives:

Δre*S*°0M = (2 *S*H2O,l + 3/2 *S*N2 − 1/2 *S*N2O4 − *S*0M) = 200.67 J K−1 mol−1

Δre*S*°1M = (*S*CO2 + 3 *S*H2O,l + 9/4 *S*N2 − 5/4 *S*N2O4 − *S*1M) = 426.59 J K−1 mol−1

Δre*S*°2M = (2 *S*CO2 + 4 *S*H2O,l + 3 *S*N2 − 2 *S*N2O4 − *S*2M) = 663.69 J K−1 mol−1

Calculation of standard molar reaction Gibbs energies:

Δre*G*°0M = Δre*H*°0M − *T*° × Δre*S*°0M = −680.11 kJ mol−1

Δre*G*°1M = Δre*H*°1M − *T*° × Δre*S*°1M = −1 433.77 kJ mol−1

Δre*G*°2M = Δre*H*°2M − *T*° × Δre*S*°2M = −2 180.84 kJ mol−1

Estimation of the equilibrium constants for combustion reactions:

*Ki* = exp(−Δre*G*°*i* / (*RT*°))

*K*0M = e274.37 ≈ 1 × 10119

*K*1M = e578.41 ≈ 1 × 10251

*K*2M = e879.79 ≈ 1 × 10382

Equilibrium constants are practically equal to infinity; the equilibrium mixture of the outlet gases contains reaction products only.

2.4 All reactions increase the number of the moles of gaseous species, so increasing the pressure will suppress the extent of the reaction (though negligibly for such values of *K*). All reactions are strongly exothermic, so increasing the temperature will affect the equilibrium in the same direction as pressure.

2.5 Summarizing the chemical equation representing the fuel mixture combustion:

N2H4 (l) + N2H3CH3 (l) + N2H2(CH3)2 (l) + 3.75 N2O4 (l) → 6.75 N2 (g) + 9 H2O (g) + 3 CO2 (g)

, solve for *T*f

*T*f = 4 288.65 K

2.6 Burning of 1,1-dimethylhydrazine with oxygen can be expressed as:

N2H2(CH3)2 (l) + 4 O2 (g) → N2 (g) + 2 CO2 (g) + 4 H2O (g)

, solve for *T*x

*T*x = 5 248.16 K

2.7 There is no temperature range of coexistence of both liquid oxygen and   
1,1-dimethylhydrazine, either 1,1-dimethylhydrazine is liquid and O2 is a supercritical fluid, or O2 is liquid and 1,1-dimethylhydrazine is solid.

2.8 Very high working temperatures maximize the temperature difference term in relation to the hypothetical efficiency of the Carnot engine. Assuming the low temperature equals *T*°, we get: *η* = (*T*f − *T*°) / *T*f = 93.0%.

Problem 3. HIV protease

3.1 Lopinavir binds most strongly, as illustrated by its smallest dissociation constant *K*D.

3.2 Apply Δ*G*° = −*RT* ln*K*D, and consider that the dissociation and the binding are opposite reactions. Thus, Δ*G*°(bind.) = −Δ*G*°(dissoc.) = *RT* ln*K*D, or in a slightly different way, Δ*G*°(bind.) = −*RT* ln*K*A = −*RT* ln[1 / *K*D] = *RT* ln*K*D. See below for the numerical results.

3.3 Consider Δ*G*° = Δ*H*° − *T*Δ*S*°. Thus, perform a linear regression of the temperature dependence of Δ*G*°. This can be done in at least two simplified ways: (i) Plot the dependence and draw a straight line connecting the four data points in the best way visually. Then, read off the slope and intercept of the straight line, which correspond to −Δ*S*° and Δ*H*°, respectively. (ii) Alternatively, choose two data points and set up and solve a set of two equations for two unknowns, which are Δ*S*° and Δ*H*°. The most accurate result should be obtained if the points for the lowest and highest temperatures are used. See below for the numerical results.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Temperature | | Amprenavir | | Indinavir | | Lopinavir | |
| °C | K | *K*D | Δ*G*° | *K*D | Δ*G*° | *K*D | Δ*G*° |
|  |  | nM | kJ mol−1 | nM | kJ mol−1 | nM | kJ mol−1 |
| 5 | 278.15 | 1.39 | −47.2 | 3.99 | −44.7 | 0.145 | −52.4 |
| 15 | 288.15 | 1.18 | −49.3 | 2.28 | −47.7 | 0.113 | −54.9 |
| 25 | 298.15 | 0.725 | −52.2 | 1.68 | −50.1 | 0.101 | −57.1 |
| 35 | 308.15 | 0.759 | −53.8 | 1.60 | −51.9 | 0.0842 | −59.4 |
| Δ*S*° | kJ K−1 mol−1 | | 0.228 |  | 0.239 |  | 0.233 |
| Δ*H*° | kJ mol−1 | | 16.3 |  | 21.5 |  | 12.4 |
| coeff. of determin. | | | 0.990 |  | 0.989 |  | 0.999 |

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Temperature | | Nelfinavir | | Ritonavir | | Saquinavir | |
| °C | K | *K*D | Δ*G*° | *K*D | Δ*G*° | *K*D | Δ*G*° |
|  |  | nM | kJ mol−1 | nM | kJ mol−1 | nM | kJ mol−1 |
| 5 | 278.15 | 6.83 | −43.5 | 2.57 | −45.7 | 0.391 | −50.1 |
| 15 | 288.15 | 5.99 | −45.4 | 1.24 | −49.1 | 0.320 | −52.4 |
| 25 | 298.15 | 3.67 | −48.1 | 0.831 | −51.8 | 0.297 | −54.4 |
| 35 | 308.15 | 2.83 | −50.4 | 0.720 | −53.9 | 0.245 | −56.7 |
| Δ*S*° | kJ K−1 mol−1 | | 0.236 |  | 0.273 |  | 0.218 |
| Δ*H*° | kJ mol−1 | | 22.4 |  | 29.8 |  | 10.5 |
| coeff. of determin. | | | 0.995 |  | 0.989 |  | 0.999 |

*Note 1*: Δ*S*° and Δ*H*° may also be obtained from a fit of *K*D or *K*A, without considering Δ*G*°. Here, a straight line would be fitted to the dependence:

ln *K*A = −ln*K*D = Δ*S*° / R − Δ*H*° / R × 1/*T*.

*Note 2*: It is evident that the binding is entropy-driven for all the inhibitors. The entropic gain stems from the changes in the flexibility of both the protease and the inhibitors, and also involves solvent effects. However, a molecular picture of those changes is rather complex.

3.4 The slowest dissociation is observed for the compound with the smallest dissociation rate constant, i.e. Saquinavir.

3.5 Using the relation for the dissociation constant *K*D = *k*D / *k*A and the data at 25 °C, we obtain for Amprenavir: *k*A = *k*D / *K*D = 4.76 × 10−3 s−1 / (0.725 × 10−9 mol L−1) = 6.57 × 106 L mol−1 s−1. Analogous calculations performed for the other inhibitors yield the following numerical results. The fastest association is exhibited by the compound with the largest association rate constant, i.e. Amprenavir.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
|  | Amprenavir | | Indinavir | Lopinavir | Nelfinavir | Ritonavir | Saquinavir |
| *k*A | 6.57 × 106 | 2.05 × 106 | | 6.48 × 106 | 0.59 × 106 | 3.12 × 106 | 1.43 × 106 |
| dm3 mol–1 s–1 |

3.6 The Arrhenius equation for the rate constant reads *k* = *A* × exp[−Δ*G*‡ / *RT*]. For two known rate constants of dissociation *k*1 and *k*2 determined at temperatures *T*1 and *T*2, respectively, we obtain a system of two equations,

*k*1 = *A* × exp[−Δ*G*‡ / *RT1*]

*k*2 = *A* × exp[−Δ*G*‡ / *RT2*],

from which the activation energy of dissociation results as Δ*G*‡ = (ln *k*1 / *k*2) / (1 / *RT*2 − 1  / *RT*1). Numerically, the activation energy is 8.9 kJ mol−1 for Lopinavir, 32.6 kJ mol−1 for Amprenavir (which has the fastest association rate constant) and 36.8 kJ mol−1 for Saquinavir (which has the lowest dissociation rate constant).

3.7 No, these are two different compounds. The strongest protease binder is not the same inhibitor as the one with the slowest dissociation. This observation may seem   
counter-intuitive if the distinction between thermodynamics (here, the strength of binding expressed by the equilibrium constant) and kinetics (the rate of binding represented by the rate constant or activation energy for dissociation) is not understood properly. While the equilibrium constant of dissociation captures the thermodynamic stability of the respective protein–inhibitor complex, the rate constant describes the kinetics of the process. These are two different sets of properties and they only become related if the rates of both dissociation and association are considered, *K*D = *k*D / *k*A.

Problem 4. Enantioselective hydrogenation

4.1 Structure:



4.2 => => s–1

4.3 From the previous question; at −40 °C . Substitute from the Arrhenius equation:

Therefore:

4.4 =>

At any given temperature *T*:

(‡) Therefore:

At this temperature, the reaction is likely to be really slow which would prevent its actual use.

4.5 The main difference is that **(*S*)-CAT** will provide the (*S*)-product. We will do all the calculations for **(*R*)-CAT** and just invert the sign at the end. It should be noted that the amount of catalyst does not influence the enantiomeric excess; it only accelerates the reaction.

From equation (‡):

=> *ee* = 85%

For 90% *ee*: [*α*]D20 (*c* 1.00, EtOH) = +45°,

which means [*α*]D20 (*c* 1.00, EtOH) = +42.5° for 85% *ee*

The same conditions are used for the measurement of the specific rotation, namely, the temperature, solvent, concentration and wavelength of the light used. Therefore, we can just invert the sign to obtain the result for the (*S*)-product:

[*α*]D20 (*c* 1.00, EtOH) = −42.5° = −43°

*Note*: The specific rotation should be formally stated in ° dm−1 cm3 g−1, but in most of the current scientific literature this is simplified to ° only.

4.6 Since the product is crystalline, the easiest method would be recrystallization. Different chiral resolution methods can also be used, for examplecrystallization with a chiral agent or separation by HPLC with a chiral stationary phase.

Problem 5. Ultrafast reactions

*Note*: In all equilibrium constants considered below, the concentrations should be in principle replaced by activities, where we use the standard state for the solution . In all calculations we assume that and for clarity, we also ignore the unity factor. We also skip the units of quantities in the intermediate steps of the calculations to make the solution easier to follow.

5.1 The equilibrium constant of neutralization is given as

The constant *K* is related to the free energy change of the reaction:

Note that the Gibbs free energy change calculated in this way corresponds to the standard state for all species, including the water solvent. The Gibbs free energy change can be expressed via the enthalpy and entropy change for the reaction

from which

5.2 To estimate the pH of boiling water we need to evaluate *K*w at 373 K using the van ’t Hoff’s formula (alternatively, we could recalculate the constant *K*). Note that was defined for a reverse reaction, here we have to use . The temperature change is given as

After substitution

we get

which translates into proton concentration at the boiling point of water

or pH

5.3 pD is analogical to pH, i.e. pD = −log. The concentration of cations at 298 K is given as

and pD is given by

5.4

5.5 We start from the rate equation derived in 5.4

All concentrations can be expressed via the quantity *x*

Expanding the right hand side of the equation, we get

Using the equality of the backward and forward reaction rates at equilibrium

and neglecting the (small) quadratic term *x*2, we can rewrite the equation as

5.6 The relaxation time is given as

At equilibrium, the backward and forward reaction rates are the same. The concentration of heavy water is given as

The relaxation time is then given as

Substituting the values of all quantities

we get

We get *k*2 from the equilibrium constant *K*

5.7 The pH before irradiation is calculated from the dissociation constant of the ground state of 6-hydroxynaphthalene-2-sulfonate.

where is the concentration of 6-oxidonaphthalene-2-sulfonate and is the concentration of 6-hydroxynaphthalene-2-sulfonate.

The concentration of is equal to the concentration of due to electroneutrality and can be denoted as *y*. The equilibrium concentration of the undissociated acid is , where is the analytical concentration of the acid. The equilibrium constant is then given as

Because the amount of dissociated acid is very small, we can neglect *y* in the denominator

From which

During irradiation, 1 cm3 of sample absorbs 2.228 × 10−3 J of energy. 1 dm3 would thus absorb 2.228 J. The number of absorbed photons corresponds to the number of excited molecules of 6-hydroxynaphthalene-2-sulfonate.

One photon has energy

The number of absorbed photons in 1is

The number of moles of excited molecules of 6-hydroxynaphthalene-2-sulfonate is

The pH can again be calculated from the p in the excited state; the analytical concentration *c*\* of the excited acid is now

Let us denote by *x* the proton concentration and by *y\** the concentration of the   
6-oxidonaphthalene-2-sulfonate in the excited state . The electroneutrality condition implies

The two equilibrium constants are expressed as

where we assumed in the denominator of the last equation. These three equations constitute a system of equations from which we get

or

We can solve this equation e.g. with any on-line solver of cubic equations

Which corresponds to

It is possible to avoid solving cubic equations by an iterative solution. In the first step, we assume that . The equation for then transforms to

*y\** can be calculated from the quadratic equation

Next, we update the concentration of the anion in the ground state *y* from the corresponding equilibrium constant

From which *y* can be obtained by solving a quadratic equation

This again leads to the quadratic equation

The concentration of is

We could now repeat the whole cycle: with the first estimate of *x*, we would get a new value of and continue with these new values of *y* and *x* untilconvergence is reached. At the level of precision in our calculations, the concentration is already converged in the first iteration. Generally, more iterative cycles would be needed.

Problem 6. Kinetic isotope effects

6.1 Reduced mass:

Wavenumber:

Energies:

6.2 We are going to determine the atomic mass *A* of the lighter isotope of the element X.

*A* = 79.4 amu

*A* = 79; *A +* 2 = 81; *X* = Br

The second root of the quadratic equation 2.155, which would correspond to *A* = 2  
and *A +* 2 = 4, is unphysical.

6.3 The difference of the activation energies *E*a(H−C) − *E*a(D−C) is equal to the negatively taken difference of zero-point vibrational energies: − *E0*(H−C) + *E0*(D−C)

6.4 E2 elimination. The value of the kinetic isotope effect of 6.5 indicates that the C−H/D bond is broken in the rate-determining step of the reaction.

6.5 For a tertiary substrate, we can expect E1 elimination, where the C−H/D bond is not broken during the rate-determining step. Therefore, we observe only a small secondary kinetic isotope effect with the *k*H / *k*D ratio slightly larger than 1.0.

Problem 7. Designing a photoelectrochemical cell

7.1 Reduction potentials for reactions b), c), d), f) and h) are dependent on pH.

7.2 The potential dependence on pH is a linear function with intercept equal to *E*° and slope equal to:

7.3 Standard potential *E*°(**C**) is more positive than *E*°(**B**), hence substance **C** is a stronger oxidizer and will therefore oxidize substance **B** (a), and the standard reaction potential will be 0.288V (b):

c) using formula:

7.4 Reaction **E** is pH-dependent and its potential drop is 52 mV per pH unit (as can be calculated from formula derived in question 7.2: z = 1, n = 1, *T* = 262 K). The reaction potential *E*r= *E*E – *E*D is calculated from the equilibrium constant:

The potential for the reduction of substance **E** is *E*E = *E*D+ *E*r= 0.55 V + 0.28 V = 0.83 V. This value of potential is achieved at pH = 2.31. The two lines cross at pH = 7.7 (roughly); **D** will oxidize **E** in the pH range from 7.7 to 13.



7.5 Using the formula for electrolysis:

7.6 Only materials **G** and **I** can be used to catalyze the given reaction, because their HOMOs lie below *E*ox and their LUMOs are higher than *E*red. While material **G** can be irradiated only by UV light with a wavelength lower than 388 nm, material **I** can be irradiated by either visible or UV light, because the maximal wavelength that can be used to overcome the energy difference of 2 eV is equal to 620 nm.

Problem 8. Fuel cells

8.1 First, find the driving force, i.e., the Gibbs energy of the reaction H2 + ½ O2 → H2O

under standard conditions (298 K and 1 bar). Then, convert it to the EMF (voltage).

The standard reaction enthalpy and entropy are

The standard change of Gibbs energy is

The standard EMF is then

8.2 The solution is similar to the previous one with the difference of water state.

The standard change of Gibbs energy is

The standard EMF is then

8.3 The ideal thermodynamic efficiency is:

For both cells and for various temperatures, we get:

8.4 Cathode: O2 + 4 e− + 4 H+ → 2 H2O

Anode: C4H10 + 8 H2O → 4 CO2 + 26 H+ + 26 e−

8.5 The overall reaction is:

2 C4H10+ 13 O2 → 8 CO2 + 10 H2O

The reaction as accompanied by the transfer of 52 electrons. Hence, at standard temperature:

8.6 The ideal thermodynamic efficiency is determined as:

8.7 It is the same as in the previous answer. The overall reaction is the same.

8.8 Anode: CH3OH + H2O → 6 H+ + 6 e− + CO2

Cathode: O2 + 4 H+ + 4 e− → 2 H2O

Overall: 2 CH3OH + 3 O2 → 2 CO2 + 4 H2O

8.9 Nernst equation

Any answer with correctly expressed activities (e.g. using molar fractions) is assumed to be correct.

8.10 We use van ’t Hoff equation, in which we substitute EMFs for equilibrium constants. We obtain reaction enthalpy and Gibbs free energy changes, which we use to calculate the entropy change:

Problem 9. Acid-base equilibria in blood

9.1 CO2 concentration:

The initial concentration of bicarbonate in blood with no acid added, *c*(HCO3−, 37 °C):

pH after 10 mmol of acids were added to 1 dm3 of the buffer solution:

9.2

The buffering capacity of the bicarbonate buffer is higher when the system is open. However, pH is still outside the physiologic range (pH = 7.36–7.44). Non-bicarbonate buffers (e.g. albumin, phosphate, haemoglobin) that are present in blood additionally increase the overall buffering capacity of blood and help to keep pH within the physiologic range.

9.3 The van ’t Hoff’s equation will be used:

First, the integrated form is applied to calculate the reaction enthalpy from the p*K*a values at 37 °C and 25 °C.

Then, that same equation is used to calculate the p*K*a at 20 °C:

Henry’s solubility of CO2 is recalculated in an analogous way:

Finally, the pH of blood at 20 °C is obtained using these recalculated values:

9.4 In a working muscle, high oxygen supply is ensured by lowering the affinity towards oxygen in an acidic environment. In lungs, by contrast, CO2 is liberated from haemoglobin in red blood cells, which, in turn, binds oxygen with a greater affinity.

Problem 10. Ion exchange capacity of a cation exchange resin

10.1 The molecular formula of one unit of the catex polymer is C17H16O5S1, which corresponds to the molecular weight of 332.369 g mol−1. Mass percentage of an atom *w*x is

where *a*x and *A*x are the number of atoms and the atomic weight of an atom X, respectively.   
*M* is the molecular weight of one unit of the catex polymer. For sulfur (*a*S = 1,   
*A*S = 32.06 g mol−1) and carbon (*a*C = 17, *A*C = 12.011 g mol−1), the mass percentage is   
*w*S = 9.65% and *w*C = 61.43%, respectively.

10.2 The theoretical ion exchange capacity is the amount of exchange groups in one unit of the catex polymer per mass of the unit, i.e.

For -SO3H (one ion exchange group, *a*SO3H = 1) and -COOH (one ion exchange group   
*a*COOH = 1) we get *Q*m,SO3H = *Q*m,COOH = 3.01 mmol g−1.

10.3 The total ion exchange capacity is a sum of individual strong and weak exchange capacities. For *Q*m,SO3H = *Q*m,COOH = 3.01 mmol g−1 we get *Q*m,total = 6.02 mmol g−1.

10.4 The total ion exchange capacity in mmol cm−3 of a swollen resin *Q*V,total is

where *ε* and *ρ* are porosity and density, respectively, of a swollen resin and *w* is the mass ratio of water bound to the resin. For *Q*m,total = 6.02 mmol g−1, *ε* = 0.48, *ρ* = 1.28 g cm−3, and *w* = 0.45 we get *Q*V,total = 6.02 × (1 − 0.48) × 1.28 × (1 − 0.45) = 2.20 mmol cm−3.

Problem 11. Weak and strong cation exchange resin

11.1 At the beginning, all cation exchange sites are occupied with Na+ ions. Weak acetic acid exchanges all the weakly bound Na+ ions (weak cation exchange sites) and some of the strongly bound Na+ ions (strong cation exchange sites). The amount of Na+ in solution A is *n*1. When the resin is rinsed with a neutral solution of Mg2+ ions, all ions at the strong cation exchange sites are exchanged for Mg2+. Thus, solution B contains *n*2 moles of Na+ and *n*3 moles of H+.

The electrode potential is linearly proportional to the logarithm of concentration; i.e. for sodium ion selective electrode *E* = *k* + *S* log10[Na+]. Based on a two-point calibration, we get the following equations

−0.2283 = *k* + *S* log(0.0100) and −0.3466 = *k* + *S* log(0.00010)

Solving the system of equations, we get *k* = −0.1100 V and *S* = 0.05915 V.

The amounts of Na+ ions in solutions A (*V*A = 1 000 cm3) and B (*V*B = 500 cm3) are

mmol

mmol

The alkalimetric titration is based on 1:1 stoichiometry of the reaction of OH− (titration agent) and H+ (titrant). Then amount of H+ ions in solution B (*V*a is an aliquot of 100 cm3) is

mmol

Ion exchange capacities of the strong and weak ion exchange resins (*V*0 = 4 cm3)

mmol cm−3

mmol cm−3

11.2 The total ion exchange capacity is

mmol cm−3

Problem 12. Uranyl extraction

12.1 First, [HA]org is calculated:

The concentration of UO2A2 is omitted as recommended in the introductory text.

From the definition of *K*p,HA, *K*D,HA and *K*a,HA, [HA]org can be obtained by solving the quadratic equation

i.e.

Considering that the proton concentration corresponds to the analytic concentration of HNO3, [H+]aq = = 2.00 × 10−2 mol dm−3, we get [HA]org = 3.41 × 10−3 mol dm−3. Next, the uranyl ion distribution ratio, is expressed as:

Using , , and *βi* for [UO2(OH)*i*]2–*i* complexes, can be expressed as

The concentration of hydroxyl ions is obtained from the concentration of protons,

For [H+]aq = = 2.00 × 10−2 mol dm−3, we get

mol dm−3

Casting this value, [HA]org = 3.41 × 10−3 mol dm−3 and all the necessary constants into the expression for the distribution ratio, we obtain

Then, the yield *R* defined as

can be calculated, providing the final result of

12.2 For the conditions of [OH−] = = 2.00 × 10−4 mol dm−3, using the same calculation procedure, we get

[HA]org = 1.50 × 10−5 mol dm−3

and the yield *R* = 0.0121%.

Problem 13. Determination of active chlorine in commercial products

13.1 (i) Cl2 + H2O → HClO (**A**) + HCl (**B**)

(ii) NaClO + H2O → HClO (**A**) + NaOH (**C**)

In alkaline aqueous solution, hypochlorite ion (ClO−) will dominate.

13.2

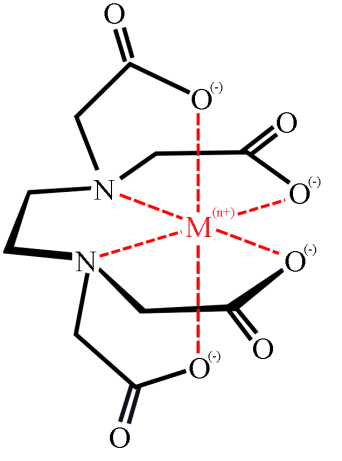
13.3 ClO− + 2 I− + 2 H+ → I2 + H2O + Cl−

I2 + 2 S2O32− → 2 I− + S4O62−

Problem 14. Chemical elements in fireworks

14.1 An aqueous sample is introduced to a hot, non-luminous flame, where the tested compound is partially evaporated, atomized and free atoms are excited. During de-excitation, the energy difference between the atomic energy levels is emitted as a photon of an appropriate wavelength, characteristic of the particular chemical element. In this case, all three wavelengths are in the visible region of the spectrum and the corresponding colours for sodium, barium and lithium are yellow, lime green and red, respectively.

14.2 The structure of a metal–EDTA complex is



*δ*(HY3−) = [HY3−] / *c*(EDTA) = *β*1 [H+] / (1 + *β*1 [H+] + *β*2 [H+]2 + *β*3 [H+]3**+ *β*4 [H+]4)

*δ*(Y4−) = [Y4−] / *c*(EDTA) = 1 / (1 + *β*1 [H+] + *β*2 [H+]2 + *β*3 [H+]3**+ *β*4 [H+]4),

where *β*1 = 1 / *K*a4, *β*2 = 1 / (*K*a4 *K*a3), *β*3 = 1 / (*K*a4 *K*a3 *K*a2), *β*4 = 1 / (*K*a4 *K*a3 *K*a2 *K*a1)

*δ*(HY3−) = 1.82 × 1010 × 10−10 / (1 + 1.82 × 1010 × 10−10 + 2.63 × 1016 × 10−20 + 1.23 × 1019 × 10−30 + + 1.23 × 1021 × 10−40) = 0.6453, i.e. 64.53%

*δ*(Y4−) = 1 / (1 + 1.82 × 1010 × 10−10 + 2.63 × 1016 × 10−20 + 1.23 × 1019 × 10−30 + 1.23 × 1021 × 10−40) = = 0.3546, i.e. 35.46%

*δ*(HY3−) + *δ*(Y4−) = 99.99% , hence other forms are present at molar ratios lower than 0.5%.

14.3 Ammonium buffer is a mixture of ammonia and ammonium chloride. Ions of alkaline earth metals form weak complexes with EDTA (log *K*MY between 7.7 and 10.7) and are present only in alkaline media (pH > 9).

14.4 Zn2+ + 4 CN− → [Zn(CN)4]2−

[Zn(CN)4]2− + 4 HCHO + 4 H2O → Zn2+ + 4 HOCH2CN + 4 OH−

14.5 2,3-Disulfanylpropan-1-ol is used for masking lead ions.

14.6 Step i: Zinc is masked in the cyanide complex, lead and magnesium react with EDTA

*n*(Pb) + *n*(Mg) = *n*1(EDTA)

Step ii: EDTA released from its complex with lead ions reacts with magnesium standard solution

*n*(Pb) = *n*std(Mg)

Step iii: Zinc released from cyanide complex reacts with EDTA

*n*(Zn) = *n*2(EDTA)

Masses of the elements in the sample (*m*1 = 1 g)

14.7 Complexation equation: Ca2+ + Y4− → CaY2−

Final analytical concentrations after dilution are:

The coefficient for EDTA side reactions

*α*(EDTA) = (1 + *β*1 [H+] + *β*2 [H+]2 + *β*3 [H+]3**+ *β*4 [H+]4)

(definitions of *βi* are in 14.2); for pH = 6

*α*(EDTA) = (1 + 1.82 × 1010 × 10−6 + 2.63 × 1016 × 10−12 + 1.23 × 1019 × 10−18**+ 1.23 × 1021 × 10−24) = = 4.45 × 104

The final concentration of free Ca2+ ions in the solution is:

Based on the mass balances

we get a quadratic equation with the following solution

Problem 15. Colours of complexes

15.1 Ground state: Excited state:

15.2 The wavenumber of 20 300 cm−1 corresponds to the wavelength of 493 nm which means the absorption of the blue-green light. The colour of the complex is the complementary one, i.e. orange-red.

15.3 The complex absorbs visible light in the range from 493 to 575 nm, i.e. blue-green to   
yellow-green. The complex is purple.

15.4 Electron configurations:



15.5 Equations:

(1) 2 CoCl2 + 3 F2 → 2 CoF3 + 2 Cl2

(2) CoF3 + 3 KF → K3[CoF6]

(3) 4 CoF3 + 2 H2O → 4 HF + 4 CoF2 + O2

15.6 Equation:

(4) 4 CoCl2 + 4 NH4Cl + 20 NH3 + O2 → 4 [Co(NH3)6]Cl3 + 2 H2O

15.7 The wavenumbers correspond to the wavelengths of 475 nm (blue light) and 340 nm (UV region). The second band has no effect on the observed colour and the complex is orange. Luteus means yellow in Latin (it refers to the yellow-orange colour of the complex).

15.8 Due to their position in the spectrochemical series, fluoride ions (F−) cause only small splitting, which leads to a high-spin configuration with four unpaired electrons. Ammonia molecules (NH3) cause greater splitting, which means that all the electrons in the t2g orbitals pair up and a low-spin configuration is formed

15.9 Electron configurations:



15.10 The wavenumbers correspond to the wavelengths of 877 nm (IR region) and 690 nm (red light). The first band has no effect on the observed colour and the complex is   
blue-green.

Problem 16. Iron chemistry

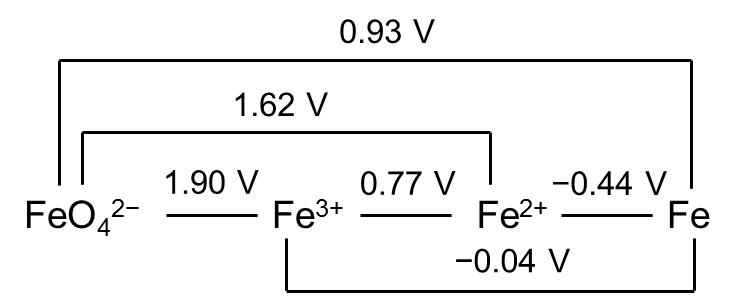
16.1 The requested potentials are calculated as follows, (1)–(3):

*E*°(FeO42−,H+/Fe2+) = (3 × 1.90 + 1 × 0.77) / 4 V = 1.62 V (1)

*E*°(FeO42−,H+/Fe) = (3 × 1.90 + 1 × 0.77 + 2 × (−0.44)) / 6 V = 0.93 V (2)

*E*°(Fe3+/Fe) = (1 × 0.77 + 2 × (−0.44)) / 3 V = −0.04 V (3)

The corresponding Latimer diagram is depicted in Figure 1.



**Figure 1.** Latimer diagram for iron species in water (pH 0).

16.2 The voltage equivalent is defined as a product of the formal oxidation state *N* and the standard redox potential *E*° (4) for the reduction of the particular species to the elemental state. The Frost diagram (Figure 2) then plots voltage equivalents versus oxidation state.

Voltage equivalent = *N* × *E*°(species/element) (4)

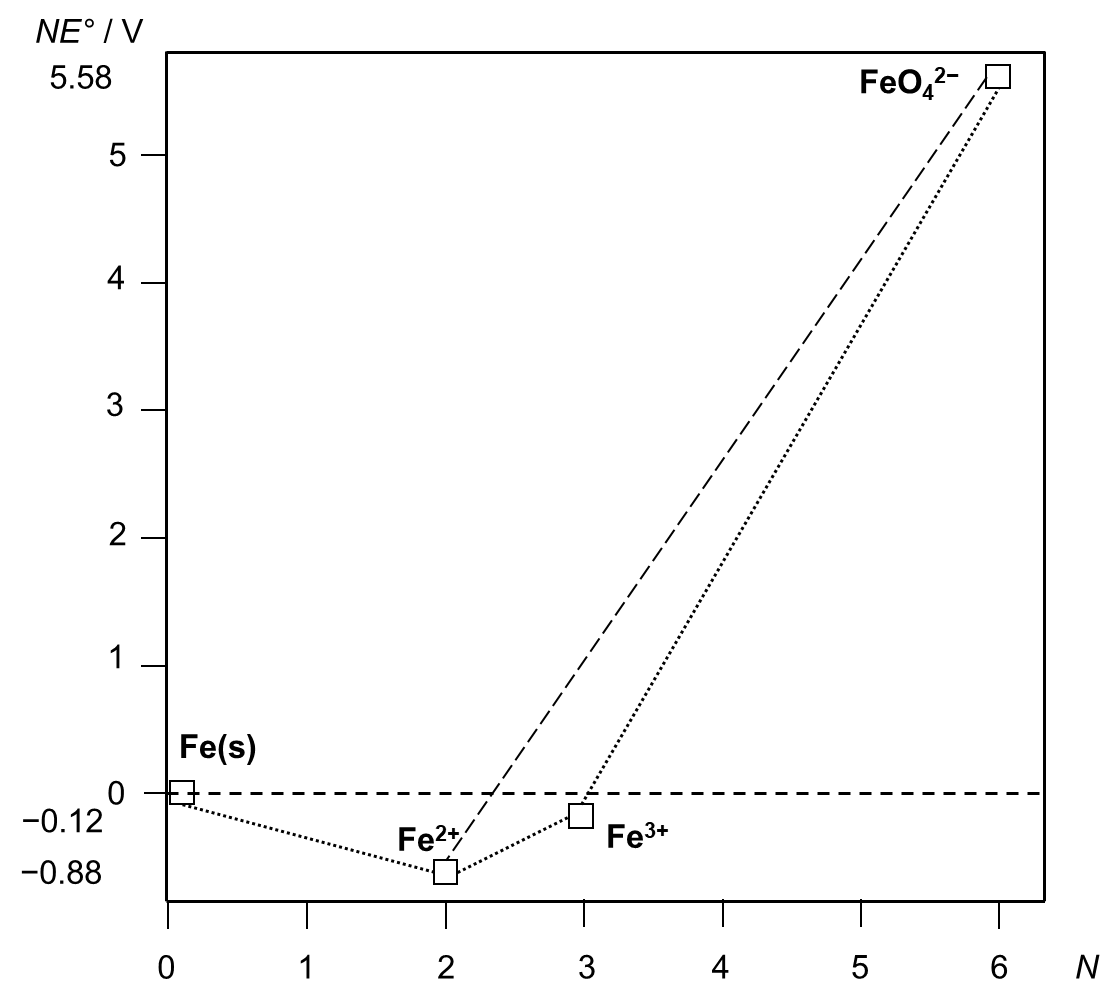
The individual voltage equivalents are calculated from the data above (5)–(8).

Voltage equivalent (Fe) = 0 × 0 V (def.) = 0 V (5)

Voltage equivalent (Fe2+) = 2 × (−0.44) V = −0.88 V (6)

Voltage equivalent (Fe3+) = 3 × (−0.04) V = −0.12 V (7)

Voltage equivalent (FeO42−) = 6 × 0.93 V = 5.58 V (8)



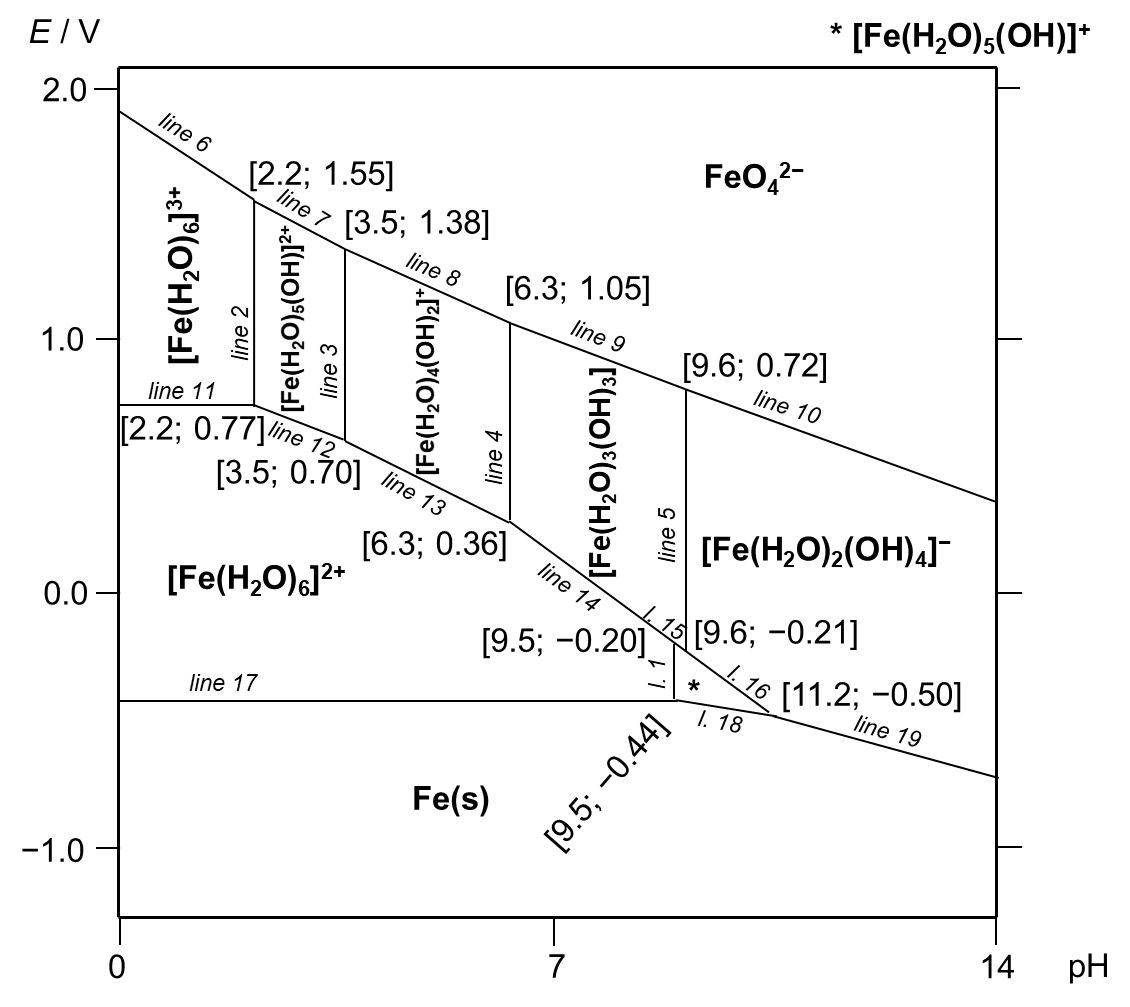
**Figure 2.** Frost diagram for iron species (pH 0).

Since the imaginary line connecting both the requested oxidation states (FeO42− and Fe2+, dashed line in Figure 2) lies above the Fe3+ point in the diagram, a synproportionation will be favoured, (9):

FeO42− + 3 Fe2+ + 8 H+ → 4 Fe3+ + 4 H2O (9)

16.3

1. The individual zone labels follow the successive uptake of electrons (from up to down) and hydroxide anions as ligands (from left to right). The identity of any zone can be checked by comparing the appropriate borderline definitions. The answers are displayed in Figure 3.



**Figure 3.** Pourbaix diagram for dissolved iron species and metallic iron.

It should be noted that this type of Pourbaix diagram would be valid only in highly diluted solutions of iron species. The increase in concentration will lead to the precipitation of insoluble (first ferric, then ferrous) oxides/hydroxides as well as the formation of polynuclear hydroxido complexes.

1. Each borderline is drawn with the assumption that the activities of both participating species are equal. The equations which refer to *lines 11* and *17*, respectively, can be derived from the corresponding forms of the Nernst–Peterson equation (10) and (11) assuming the equilibrium conditions [Fe3+] = [Fe2+] and [Fe2+] = *a*(Fe,s). Because there is no term which depends on pH, the results are horizontal constant lines numerically equal to the standard redox potentials, see Figure 3.

*line 11* (Fe3+/Fe2+): *E* = *E*° − 0.059 × log([Fe2+] / [Fe3+]), thus *E* = 0.77 (10)

*line 17* (Fe2+/Fe): *E* = *E*° − (0.059 / 2) × log(*a*(Fe,s) / [Fe2+]), thus *E* = −0.44 (11)

The conditions for *lines 2* and *5* are [Fe3+] = [Fe(OH)2+] and [Fe(OH)3] = [Fe(OH)4−], respectively, i.e. the expressions imply constant lines again, but in this case vertical ones, since there is no connection with the redox potential. The analytical expressions are represented by equations (12) and (13).

*line 2* (Fe3+/[Fe(OH)]2+): pH = p*K*w − log*β*1, thus pH = 2.2 (12)

*line 5* ([Fe(OH)3]/[Fe(OH)4]−): pH = p*K*w + log*β*3 − log*β*4, thus pH = 9.6 (13)

1. The analytic expression of *line 6* (14) is also derived from the Nernst–Peterson equation under the assumption [FeO42−] = [Fe3+].

*line 6* (FeO42−/Fe3+): *E* = *E*° − (0.059 / 3) × log{[Fe3+] / ([FeO42−] × [H+]8)},

thus *E* = 1.90 − 0.157 × pH (14)

The first coordinate of the intersection of *lines 2*, *6* and *7* is obviously pH = 2.2. The second coordinate can be calculated by substituting for pH = 2.2 in equation (14), i.e. *E* = 1.55.

Although it was not required to derive the expressions for all the lines, they are given in the following list for completeness, (15)–(28), and shown in Figure 3.

*line 1* (Fe2+/[Fe(OH)]+): pH = 9.5 (15)

*line 3* ([Fe(OH)]2+/[Fe(OH)2]+): pH = 3.5 (16)

*line 4* ([Fe(OH)2]+/[Fe(OH)3]): pH = 6.3 (17)

*line 7* (FeO42−/[Fe(OH)]2+): *E* = 1.86 − 0.138 × pH (18)

*line 8* (FeO42−/[Fe(OH)2]+): *E* = 1.79 − 0.118 × pH (19)

*line 9* (FeO42−/[Fe(OH)3]): *E* = 1.66 − 0.098 × pH (20)

*line 10* (FeO42−/[Fe(OH)4]−): *E* = 1.48 − 0.079 × pH (21)

*line 12* ([Fe(OH)]2+/Fe2+): *E* = 0.90 − 0.059 × pH (22)

*line 13* ([Fe(OH)2]+/Fe2+): *E* = 1.11 − 0.118 × pH (23)

*line 14* ([Fe(OH)3]/Fe2+): *E* = 1.48 − 0.177 × pH (24)

*line 15* ([Fe(OH)3]/[Fe(OH)]+): *E* = 0.92 − 0.118 × pH (25)

*line 16* ([Fe(OH)4]−/[Fe(OH)]+): *E* = 1.48 − 0.177 × pH (26)

*line 18* ([Fe(OH)]+/Fe): *E* = −0.16 − 0.030 × pH (27)

*line 19* ([Fe(OH)4]−/Fe): *E* = 0.38 − 0.079 × pH (28)

1. Ferrate ion can only be produced in a very basic solution by strong oxidizing agents (stronger than elemental oxygen under these conditions), e.g. hypochlorite (32). This will overcome *line 10* and produce some ferrate ions.

2 [Fe(OH)4]− + 3 ClO− + 2 OH− → 2 FeO42− + 3 Cl− + 5 H2O (32)

Other possibilities are for example oxidation in a mixture of melted sodium nitrate with sodium hydroxide or analogous reactions in melts.

16.4 From the viewpoint of "Hard and Soft Acid-Base" (HSAB) theory, Fe2+ is an intermediary hard, Fe3+ hard and imaginary "Fe6+" would be an extremely hard acid (the hardness correlates with the ionic radii and the surface charge density). Hard acids prefer hard bases and soft acids prefer soft bases. In aqueous solutions, H2O, OH− and O2− are available (although the oxide ion is not present in water at all, it can be at least formally "extracted" by e.g. a precipitation process). Therefore, the tendency to attract harder OH− ions is higher for Fe3+ than for Fe2+ which leads to a higher proton acidity of the hexaaquaferric ion and easier hydrolysis to the corresponding hydroxido species. For the Fe6+ centre, only a similarly extremely hard base is acceptable, i.e. O2− ion (although only formally, since there are covalent bonds between Fe(VI) and O atoms). Therefore, iron in the oxidation state +6 exists only in an anionic form.

16.5 The answers are summarized in Table 1.

**Table 1**: Electronic and magnetic properties of selected iron species.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Species | Conf. | Spin state | | Magn. | LFSE |
| [Fe(H2O)6]2+ | d6 | high- | t2g4eg2 | para- | −0.4Δo + P |
| [Fe(CN)6]4− | d6 | low- | t2g6eg0 | dia- | −2.4Δo + 3P |
| [Fe(H2O)6]3+ | d5 | high- | t2g3eg2 | para- | 0 |
| [Fe(H2O)5OH]2+ | d5 | high- | (t2g3eg2)\* | para- | 0 |
| [Fe(CN)6]3− | d5 | low- | t2g5eg0 | para- | −2.0Δo + 2P |

Remark: \* not Oh symmetry.

16.6 a) FeCl3, b) Fe4[Fe(CN)6]3.

Problem 17. Cyanido- and fluorido-complexes of manganese

17.1 (1) 2 Mn + 12 NaCN + 2 H2O → 2 Na5[Mn(CN)6] + H2 + 2 NaOH

17.2 Diagram – low-spin configuration d6:



17.3 Diagram – high-spin configuration d5:



The complex has five unpaired electrons.

17.4 Diagram – low-spin configuration d5:



17.5 Equations:

(2) 4 Mn2+ + O2 + 24 CN− + 2 H2O → 4 [Mn(CN)6]3− + 4 OH−

(3) 2 [Mn(CN)6]4− + H2O2 → 2 [Mn(CN)6]3− + 2 OH−

(4) 3 MnCl2 + HNO3 + 3 H3PO4 → 3 MnPO4↓ + NO + 6 HCl + 2 H2O

(5) MnPO4 + 6 KCN → K3[Mn(CN)6] + K3PO4

17.6 Diagram – low-spin configuration d4:



17.7 (6) 4 MnO2 + 12 KHF2 → 4 K3[MnF6] + O2 + 6 H2O

17.8 Diagram – high-spin configuration d4:



17.9 Sharing 1 bridging F atom between 2 neighbouring octahedral units corresponds to the stoichiometry [MnF5]2−:



17.10 The stoichiometry [MnF4]− could be achieved in a chain structure having 2 bridging F atoms between 2 neighbouring octahedral units:



However, the structure is a 2D-anionic layer, so it is necessary to extend the structure to 2 dimensions – to have 4 bridging F atoms for each octahedral unit:



17.11 Diagram – configuration d3:



17.12 Since the magnitude of splitting in tetrahedral crystal field is about a half of octahedral (exactly Δtet =  Δoct; the negative sign refers to the inverse order of split d-orbitals with respect to the octahedral crystal field), it is always lower than electron pairing energy (Δtet < *P*) which leads to high-spin configurations in tetrahedral complexes.

Diagram – high-spin configuration d5:



17.13 (7) 2 KMnO4 + 3 H2O2 + 2 KHF2 + 8 HF → 2 K2[MnF6] + 3 O2 + 8 H2O

17.14 Manganese(IV) complexes have a configuration of d3. Since these three electrons occupy the t2g level only, low- and high-spin configurations cannot form regardless of the magnitude of the crystal field splitting.

17.15 (8) K2[MnF6] + 2 SbF5 → 2 K[SbF6] + MnF2 + F2

Problem 18. The fox and the stork

**Large stones**

18.1 Each layer consists of one sphere only: *n* = 50 / (2 × 5) = 5

18.2 The volume of 5 spheres:

The volume of cylinder:

The fraction of volume: *f* = 2 618 / 3 927 = 0.667, i.e. 66.7 %

18.3 The free volume: *V*free = 3 927 − 2 618 = 1 309 cm3

**Pebbles**

18.4 Radius: *r* = 10 / 6 = 1.667 cm

18.5 Number of layers: *N* = 50 / (2 × 1.667) = 15

18.6 Number of spheres: *n* = 15 × 7 = 105

18.7 The volume of 105 spheres:

The fraction of volume: *f* = 2 036 / 3 927 = 0.518, i.e. 51.8 %

18.8 The free volume: *V*free = 3 927 − 2 036 = 1 891 cm3



18.9 The interlayer distance can be calculated as a height of a regular tetrahedron formed by 4 spheres with edge *a* = 2 × *r* (the formula can be simply derived from the Pythagorean theorem):

The distance of the first and the last layer from the bases of the cylinder will be at minimum equal to *r*. Thus the maximum number of layers:

*N* = (50 − 2 × *r*) / *h* + 1 = (50 − 2 × 1.667) / 2.722 + 1 = 18.14 ⇒ 18 layers

18.10 The total number of spheres: each of the 9 odd layers contains 7 spheres, each of the 9 even layers contains 3 spheres, the total number is:

*n* = 9 × 7 + 9 × 3 = 90

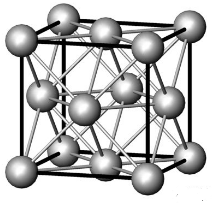
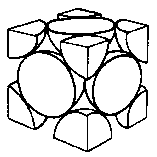
18.11 The volume of 90 spheres:

The fraction of volume: *f* = 1 745 / 3 927 = 0.444, i.e. 44.4 %

18.12 The free volume: *V*free = 3 927 − 1 745 = 2 182 cm3

**Sand**

18.13 The situation corresponds to the theoretical maximum possible space filling by spheres known as “close-packing of equal spheres”. The limiting fraction is , i.e.  74.05 %. There are many ways to derive this ratio. The derivation from a face centered cubic (fcc) elementary cell is shown.

The lattice constant is . Then the volume of the elementary cell is:

The number of spheres belonging to the elementary cell is:

Thus the fraction volume occupied by the spheres is:

18.14 The free volume: *V*free = 3 927 × (1 − 0.7405) = 1 019 cm3

Problem 19. Structures in the solid state

19.1 It is obvious from the picture that:

*a*(NaCl) = 2 × *r*(Na+) + 2 × *r*(Cl−), and therefore:

*r*(Cl–) = ½ × (5.64 − 2 × 1.16) Å = 1.66 Å.

19.2 The density of KCl is:

*ρ*(KCl) = *m* / *V* = [4 × *M*(KCl)] / [*N*A × *a*(KCl)3], and therefore:

*a*(KCl) = {[4 × *M*(KCl)] / [*N*A × *ρ*(KCl)]}⅓ = [(4 × 74.55) / (6.022 × 1023 × 1.98)]⅓ cm =

= 6.30 × 10−8 cm = 6.30 Å

*r*(K+) = ½ × [*a*(KCl) − 2 × *r*(Cl−)] Å = ½ × (6.30 − 2 × 1.66) Å = 1.49 Å.

19.3 The ratio of ionic radii of Li+ to Cl− is:

*r*(Li+) / *r*(Cl−) = 0.90 / 1.66 = 0.54. It is higher than the relative size of the octahedral cavity (0.41), which is a critical value for an ion to occupy this cavity. Thus, occupying this cavity by Li+ ion will result in a stable arrangement and LiCl should crystallize in the NaCl type of structure.

(Taking into account the smaller size of Li+ compared to Na+, it is not necessary to consider the upper limit of an ion size for a stable arrangement. However, for completeness, one can assume that the relative size of a cation with respect to an anion higher than 0.73 should lead to the change of the coordination sphere and enforce a cubic coordination environment and the structure type of CsCl. In fact, the ratio for KCl is somewhat above this limiting value, but KCl still adopts the structural type of NaCl as stated above.)

19.4 *ρ* (PbS) = *m* / *V* = [4 × *M*(PbS)] / [*N*A × *a*(PbS)3] = (4 × 239.3) / (6.022 × 1023 × 5.943) g Å−3 = = 7.58 g cm−3

19.5 Due to total electro-neutrality, one can derive:

2(1 − *x*) + 1*x* = 2*y*, and thus:

*y* = 1 − ½*x*

A general formula of silver-containing galena is thus Pb1–*x*Ag*x*S1–½*x*.

19.6 *ρ*(Pb1−*x*Ag*x*S1−½*x*) = *m* / *V* = [4 × *M*(Pb1−*x*Ag*x*S1−½*x*)] / [*N*A × *a*(Pb1−*x*Ag*x*S1−½*x*)3], and therefore:

*M*(Pb1−*x*Ag*x*S1−½*x*) = *ρ*(Pb1−*x*Ag*x*S1−½*x*) × *N*A × *a*(Pb1−*x*Ag*x*S1−½*x*)3 / 4 =

*=* [7.21 × 6.022 × 1023 × (5.88 × 10−8)3] / 4 g mol−1 = 220.7 g mol−1, and thus:

207.2(1 − *x*) + 107.9*x* + 32.1(1 − ½*x*) = 220.7, and *x* = 0.16

19.7 Four.

19.8 According to the crystal structure type, the bond distance of Ge–Ge corresponds to one fourth of the body diagonal of the unit cell and, thus, atomic radius is equal to one eighth of the body diagonal. Thus, the lattice parameter *a*(Ge) is:

*a*(Ge) = 8 × *r*(Ge) / √3 = 8 × 1.23 / √3 Å = 5.68 Å,

giving the density:

*ρ*(Ge) = *m* / *V* = [8 × *M*(Ge)] / [*N*A × *a*(Ge)3] = (8 × 72.6) / (6.022 × 1023 × 5.683) g Å−3 = 5.26 g cm−3

(Alternatively, substituting the *a*(Ge) by the term 8 × *r*(Ge) / √3 in the latter equation gives the following formula:

*ρ*(Ge) = *m* / *V* = [3√3 × *M*(Ge)] / [64 × *N*A × *r*(Ge)3] = 5.26 g cm−3

without the need to calculate the lattice parameter. However, the similarity of the lattice constant of Ge with that of the isoelectronic GaAs [*a*(GaAs) = 5.65 Å] is emphasized by the previous approach.)

19.9 According to the crystal structure type, the bond distance of Ga–As (and Ga–P) corresponds to one fourth of the body diagonal of the unit cell. Thus:

*d*(Ga–As) = (5.65 × √3) / 4 Å = 2.45 Å

*d*(Ga–P) = (5.45 × √3) / 4 Å = 2.36 Å

The radius of phosphorus in these types of compounds is 0.09 Å smaller than the radius of arsenic.

Problem 20. Cyclobutanes

20.1 and 20.2



Note that the two carbon atoms marked with a double asterisk (\*\*) are pseudo-asymmetric. They have two constitutionally identical ligands which differ in configuration.

20.3



20.4



Problem 21. Fluorinated radiotracers

21.1 18O (18-fluorine is synthesized by the following reaction: 18O + p → 18F + n)

21.2 (18F) = 6 586 s

*k* = ln 2 / (6 586 s) = 1.052 × 10−4 s−1

*n* = *N* / *N*A = 300 MBq / (1.052 × 10−4 s−1 × 6.022 × 1023 mol−1) = 4.73 × 10−12 mol

21.3 Heat of combustion of glucose = 2 800 kJ mol−1

Chemical energy of one glucose molecule: *E*c = 2 800 kJ / *N*A = 4.650 × 10−18 J

Energy of γ-photons per one glucose molecule: *E*p = 2 × *m*e × *c*2 = 1.637 × 10−13 J

Calculation of time:

Total chemical energy of 18O-glucose=Totalenergy of not yet released γ‑photons

*E*c × *N*(glucose) = *E*p × *N*(18F)

*E*c × [*N*0(18F) − *N*(18F)] = *E*p × *N*(18F)

*E*c × *N*0(18F) × (1 − e−*kt*) = *E*p × *N*0(18F) × e−*kt*

*E*c = *E*p × e−*kt* + *E*c × e−*kt*

*E*c / (*E*c + *E*p) = e−*kt*

ln [*E*c / (*E*c + *E*p)] = − *k* × *t*

*t* = ln [(*E*c + *E*p) / *E*c] × (1 / *k*) = ln (35 213) / (1.052 × 10−4 s−1) = 9.95 × 104 s = 27 h 38 min

21.4 See structures below. **X** can be any K+ chelator (e.g. 18-crown-6 ether), not only [2.2.2]cryptand shown below.



21.5



21.6









21.7



Problem 22. Where is lithium?

22.1 The formation of organolithium reagents involves a radical pathway.



22.2 The structures of intermediates **A**, **B**, **C**, and **D**:



22.3 Reaction scheme for the haloform reaction:



Other reagents, such as NaOH + I2 or NaClO can also be used.

Problem 23. Synthesis of eremophilone

23.1



23.2 This reaction is called the Claisen rearrangement.



23.3



Problem 24. Cinnamon all around

24.1



24.2 Direct UV irradiation (313 nm, acetonitrile). A conformationally mobile biradical is formed. Under these conditions, **B** and **A** are obtained in a 79 : 21 ratio.

Alternatively, UV irradiation with sensitizers (e.g. riboflavin), or reagents such as diphenyldiselenide, hydrogen peroxide etc. can be used.

24.3 Arbuzov reaction with 2-bromoacetic acid and tribenzyl phosphite:



24.4



24.5



24.6 The carboxylic acid functional group reacts with DCC to form an *O*-acylisourea, which serves as the reactive intermediate in reactions with nucleophiles (e.g. alcohols or amines) in acyl nucleophilic substitutions.



24.7 The starting compound is (*E*)-cinnamic acid methyl ester.

24.8



24.9 The two isomers **Q** and **R** are diastereoisomers (diastereomers).

24.10 The acidic hydrogens of the OH groups would decompose the organolithium compound.

24.11



24.12 The reaction is named after Prof. Mitsunobu.

Problem 25. All roads lead to caprolactam

25.1



25.2 d)

25.3









25.4



25.5 Gas **E** (NOCl) is orange. Therefore, the optimal wavelength would be below 530 nm (green and blue light).

25.6 Beckmann rearrangement.



Problem 26. Ring opening polymerizations (ROP)

26.1



26.2











26.3



26.4 Ten grams of sodium ethoxide correspond to 10 / (2 × 12 + 5 × 1 + 1 × 23) = 0.1923 mol. Two kilograms consumed with 83% conversion means 2 000 × 0.83 = 1 660 g embedded into polymer. Each molecule of the initiator initiates one chain, so the number-average molecular weight is 1 660 / 0.1923 = 8 632 g mol−1. After rounding to two digits, we get the number-average molecular weight of 8 600 g mol−1.

26.5



26.6



26.7



26.8



26.9 A single wrong enantiomer of an amino acid in the protein structure causes loss of activity. Glycine is not chiral, so there are 129 − 12 = 117 chiral amino acids in lysozyme. The overall yield is (1/2)117 × 100% = 6.02 × 10−34%.

*Theoretically, in the “world behind the mirror” the all-d-protein would be active against the all-chiral reversed proteoglycan. However, this does not meet the condition that only the enzyme digesting native peptidoglycan is considered functional.*

26.10 The amount of enzyme (120 mg = 0.000 12 kg) obtained with 6.02 × 10−34% yield (see the the answer in 26.9) would require the production of 0.00012 / ((1/2)117) = 1.99 × 1031 kg of material. As the Earth weighs 5.972 × 1024 kg, this corresponds to 1.99 × 1031 / 5.972 × 1024 =   
= 3.34 × 106 times the mass of the Earth.

Problem 27. Zoniporide

27.1



27.2 Ammonia (NH3), carbon dioxide (CO2) and hydrogen (H2)

27.3 and 27.4



27.5



27.6 **Mechanism 2**

From a) the KIE is >> 1 which indicates that the C2–H bond is being cleaved during the rate determining step (RDS). For **Mechanism 1** the RDS would have to be **E** → **3**, for **Mechanism 2** the RDS would be the concerted **2** → **3** transformation.

From b) we know that electron withdrawing groups (EWGs) on the heterocyclic core speed up the reaction. This indicates that the RDS involves either buildup of negative charge on the quinoline ring (e.g. by a nucleophilic attack) or loss of positive charge from the ring (e.g. by deprotonation). In **Mechanism 1**, this is true for the **2** → **E** step (an electron rich nucleophile adds to the quinoline core) but not for the **E** → **3** step (expulsion of a hydride nucleophuge is disfavoured in the presence of EWGs). This contradiction disproves **Mechanism 1**; therefore, the correct answer is **Mechanism 2**.

27.7 Hydrogen peroxide (H2O2)

27.8

27.9



Problem 28. Nucleic acids

28.1



28.2





28.3

Unknown sample (**1**) transmittance: *T*1 = 0.11

Known sample (**2**) transmittance: *T*2 = 1 − 0.57 = 0.43

Using Lambert–Beer law: −log10 *T* = *ε l c*

(−log10 *T*2) / c2 = (−log10 *T*1) / *c*1

*c*1 = *c*2 × (−log10 *T*1) / (−log10 *T*2) = 27 [μmol dm−3] (−log10 0.11) / (−log10 0.43) = 106 μmol dm−3

28.4

1. **True.** According to the Lambert–Beer law, absorbance is directly proportional to concentration (as long as the cuvette length and the molar absorption coefficients are assumed equal). The higher absorbance of DNA1 actually means that the concentration of dsDNA1, which absorbs less radiation than ssDNA1, is lower.
2. **False.** Thermodynamic stability is described in terms of *Tm*, which can be read as the inflexion point of the sigmoidal curve; here *Tm*(DNA1) ~ 315 K and *Tm*(DNA2) ~ 340 K.
3. **False.** Since *Tm*(DNA1) ~ 315 K and *Tm*(DNA2) ~ 340 K, dsDNA2 is more stable than dsDNA1 with respect to their single-stranded forms.
4. **Cannot be answered.** The thermodynamic stability of a DNA double helix depends on both its length (i.e. the number of nucleobase pairs) and its sequence (roughly, the content of G–C nucleobase pairs). Since no information about the G–C pairs content is given, no conclusions about the DNA lengths can be drawn.

28.5 cDNA: 5′-ACCTGGGG-3′, mRNA: 5′-CCCCAGGU-3′

28.6 Each position of the 8-nucleobase sequence can be occupied by one of the four nucleobases (A, C, G, U). Hence, there are 48 = 65 536 theoretically possible   
single-stranded octanucleotides.