

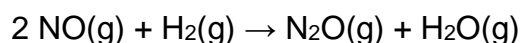
Problem X yy % of total points

										Problem 2	%
i	ii	iii	iv	v	vi	vii	viii	ix	x		
4	4	4	2	2	4	6	8	2	2		yy

Problem X: Reaction kinetics

Modified and adapted from 43rd IChO examination problem 1

NO reacts with H₂ at high temperatures to produce N₂O according to the following reaction:



The table below shows the initial rates for production of N₂O at a temperature of 820 °C, and with different partial pressures (*p*) as stated. Use pressure and time in seconds as units throughout this problem.

Experiment	Start pressure (atm)		Rate of formation N ₂ O ₂ (atm s ⁻¹)
	<i>p</i> _{NO}	<i>p</i> _{H₂}	
1	0,16	0,08	1,14 • 10 ⁻⁴
2	0,08	0,08	2,86 • 10 ⁻⁵
3	0,08	0,24	8,70 • 10 ⁻⁵

- i. Determine the experimental rate law and calculate the rate constant with units.

Rate law $r = k p_{\text{NO}}^x p_{\text{H}_2}^y$

Doubling of *p*_{NO} gives 3,98 (=4) times increase in rate *r*; hence *x* = 2.

Tripling of *p*_{H₂} gives 3,04 (=3) times increase in rate *r*; hence *y* = 1.

$r = k p_{\text{NO}}^2 p_{\text{H}_2}$

Use data from i.e. experiment 1 to calculate

$k = r p_{\text{NO}}^{-2} p_{\text{H}_2}^{-1} = 1,14 \cdot 10^{-4} \text{ atm s}^{-1} (0,16 \text{ atm})^{-2} (0,08 \text{ atm})^{-1} = 5,6 \cdot 10^{-2} \text{ atm}^{-2} \text{ s}^{-1}$

- ii. Estimate the time it takes to reduce the partial pressure of H_2 to 10% of its initial value if the reaction is started using $p_{\text{NO}} = 1,0 \text{ atm}$ and of $p_{\text{H}_2} = 0,002 \text{ atm}$.

$$r = k p_{\text{NO}}^2 p_{\text{H}_2}$$

$p_{\text{NO}, \text{start}} \gg p_{\text{H}_2, \text{start}}$, hence p_{NO} is constant during the experiment

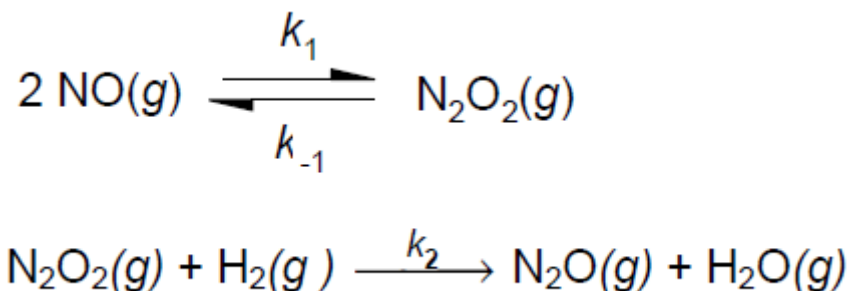
Rate law simplifies to

$$r = k_{\text{new}} p_{\text{H}_2} \text{ where } k_{\text{new}} = 5,6 \cdot 10^{-2} \text{ atm}^{-2} \text{ s}^{-1} \cdot (1,0 \text{ atm})^2 = 5,6 \cdot 10^{-2} \text{ s}^{-1}$$

Integrated form of first-order reaction: $p_{\text{H}_2}(t) = p_{\text{H}_2, \text{start}} \exp(-k_{\text{new}} t)$, which rearranges to $t = -k_{\text{new}}^{-1} \ln(p_{\text{H}_2}/p_{\text{H}_2, \text{start}})$

$$t = -(5,6 \cdot 10^{-2} \text{ s}^{-1})^{-1} \ln(1/10) = 41 \text{ s}$$

A proposed mechanism for this reaction is shown below.



A theoretical rate law can be calculated from this mechanism using some simple approximations. One method is called the pre-equilibrium method, while the steady-state approximation is more general. We will now explore these two methods to calculate a theoretical rate law.

The *pre-exponential method* assumes that the first step is the fastest step, and that the equilibrium is established before the second reaction starts.

- iii. Express the equilibrium constant K_{eq} for the first step using a) partial pressures, and b) rates k_1 and k_{-1} .

a)

$$K_{\text{eq}} = p_{\text{N}_2\text{O}_2} / p_{\text{NO}}^2$$

b)

$$K_{\text{eq}} = k_1 / k_{-1}$$

iv. Write the rate law (r_2) for the second step in the mechanism using partial pressures.

$$r_2 = k_2 p_{\text{N}_2\text{O}_2} p_{\text{H}_2}$$

v. What is the intermediate in this mechanism?



vi. Deduce the theoretical rate law from this mechanism using the *pre-equilibrium approximation* as stated above. The rate shall be expressed using partial pressures of reactants and/or products only, and rate constants k_1 , k_{-1} and k_2 .

The second step is the slow step, hence

$$r_{\text{total}} = r_2 = k_2 p_{\text{N}_2\text{O}_2} p_{\text{H}_2}$$

Substituting for $p_{\text{N}_2\text{O}_2}$ from the two expressions for K_{eq} gives

$$r_{\text{total}} = k_2 p_{\text{N}_2\text{O}_2} p_{\text{H}_2} = k_2 (p_{\text{NO}}^2 k_1 / k_{-1}) p_{\text{H}_2} = (k_1 / k_{-1}) k_2 p_{\text{NO}}^2 p_{\text{H}_2}$$

The *steady-state approximation* states that during the major part of a reaction, the concentration of any intermediate (here symbolized as B) is small and constant (i.e. $d[B]/dt_{\text{total}} = 0$). The steady-state approximation is more general than the pre-exponential modes since it *does not* assume that the first equilibrium is much faster than the second step (yet it still also assumes the same step as being the rate limiting step). We shall now use the steady-state approximation to calculate the theoretical rate law for the same reaction as above.

- vii. Looking at the mechanism, write equations for a) rates of formation (i.e. positive contribution(s) to $d[B]/dt$), and b) rate of consumption (i.e. negative contribution(s) to $d[B]/dt$) for the intermediate, expressed using partial pressures and rate constants k_1 , k_{-1} and k_2 .

a)

$$d[B]/dt_{\text{formation}} = k_1 p_{\text{NO}}^2$$

b)

$$d[B]/dt_{\text{consumption}} = k_{-1} p_{\text{N}_2\text{O}_2} + k_2 p_{\text{N}_2\text{O}_2} p_{\text{H}_2}$$

- viii. Use the steady-state approximation to derive a theoretical rate law for the reaction. *Hint:* Start by using the definition for the reaction rate using dp_{H_2}/dt and the *second* step of the reaction mechanism. Use the steady-state approximation assuming $d[B]/dt_{\text{formation}} = d[B]/dt_{\text{consumption}}$, where B is the intermediate identified in v.

$r = dp_{\text{H}_2} / dt$ by definition since H_2 is a product, and the stoichiometric coefficient is 1

From $d[B]/dt_{\text{formation}} = d[B]/dt_{\text{consumption}}$ we get $k_1 p_{\text{NO}}^2 = k_{-1} p_{\text{N}_2\text{O}_2} + k_2 p_{\text{N}_2\text{O}_2} p_{\text{H}_2}$

Solving for the intermediate N_2O_2 we get

$$p_{\text{N}_2\text{O}_2} = k_1 p_{\text{NO}}^2 / (k_{-1} + k_2 p_{\text{H}_2})$$

Assuming that step 2 is the rate limiting step

$$r = dp_{\text{H}_2} / dt = k_2 p_{\text{N}_2\text{O}_2} p_{\text{H}_2}$$

and substituting for $p_{\text{N}_2\text{O}_2}$ from the steady-state assumption we get

$$r = dp_{\text{H}_2} / dt = k_2 [k_1 p_{\text{NO}}^2 / (k_{-1} + k_2 p_{\text{H}_2})] p_{\text{H}_2} = k_1 k_2 p_{\text{NO}}^2 p_{\text{H}_2} / (k_{-1} + k_2 p_{\text{H}_2})$$

- ix. Under which of the following conditions will the rate law for the steady-state approximation match up with the simpler pre-exponential approximation? Mark your answer with an X in the correct box.

$k_1 \gg k_2$

☐

$k_2 \gg k_1$

☐

$k_{-1} \gg k_2$

☒

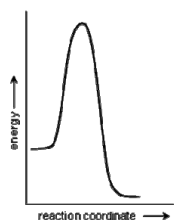
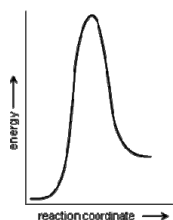
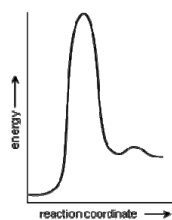
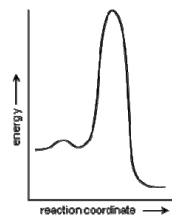
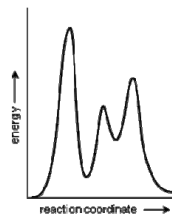
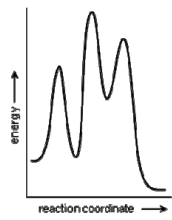
$k_{-1} \ll k_2$

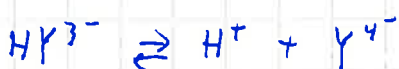
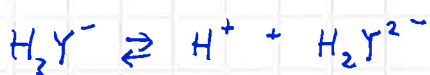
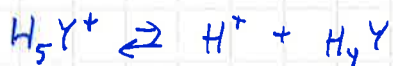
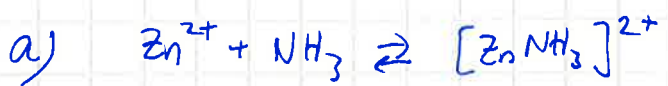
☐

$k_1 \approx k_2$

☐

- x. Which of the following energy profiles describes the reaction? Mark your answer with an X in the correct box.

☐☐☐☒☐☐



$$\beta_1 = \frac{[\text{Zn}(\text{NH}_3)]^{2+}}{[\text{Zn}^{2+}][\text{NH}_3]} = 10^{2,2}$$

$$\beta_2 = \frac{[\text{Zn}(\text{NH}_3)_2]^{2+}}{[\text{Zn}^{2+}][\text{NH}_3]^2} = 10^{4,50}$$

$$\beta_3 = \frac{[\text{Zn}(\text{NH}_3)_3]^{2+}}{[\text{Zn}^{2+}][\text{NH}_3]^3} = 10^{6,86}$$

$$\beta_4 = \frac{[\text{Zn}(\text{NH}_3)_4]^{2+}}{[\text{Zn}^{2+}][\text{NH}_3]^4} = 10^{8,89}$$

$$K_{a1} = \frac{[\text{H}^+][\text{H}_5\text{Y}^+]}{[\text{H}_6\text{Y}^{2+}]} = 10^{0,0}$$

$$K_{a2} = \frac{[\text{H}^+][\text{H}_4\text{Y}]}{[\text{H}_5\text{Y}^+]} = 10^{-1,5}$$

$$K_{a3} = \frac{[\text{H}^+][\text{H}_3\text{Y}^-]}{[\text{H}_4\text{Y}]} = 10^{-2,00}$$

$$K_{a4} = \frac{[\text{H}^+][\text{H}_2\text{Y}^{2-}]}{[\text{H}_3\text{Y}^-]} = 10^{-2,69}$$

$$K_{a5} = \frac{[\text{H}^+][\text{HY}^{3-}]}{[\text{H}_2\text{Y}^{2-}]} = 10^{-6,273}$$

$$K_{a6} = \frac{[\text{H}^+][\text{Y}^{4-}]}{[\text{HY}^{3-}]} = 10^{-10,948}$$

$$b) \quad \alpha(\text{Zn}) = \frac{[\text{Zn}^{2+}] + [\text{Zn}(\text{NH}_3)]^{2+} + [\text{Zn}(\text{NH}_3)_2]^{2+} + [\text{Zn}(\text{NH}_3)_3]^{2+} + [\text{Zn}(\text{NH}_3)_4]^{2+}}{[\text{Zn}^{2+}]}$$

$$\alpha(\text{Y}) = \frac{[\text{H}_6\text{Y}^{2+}] + [\text{H}_5\text{Y}^+] + [\text{H}_4\text{Y}] + [\text{H}_3\text{Y}^-] + [\text{H}_2\text{Y}^{2-}] + [\text{HY}^{3-}] + [\text{Y}^{4-}]}{[\text{Y}^{4-}]}$$

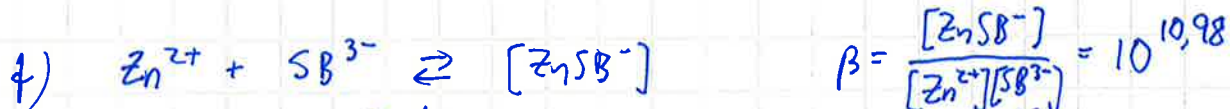
$$c) \quad \alpha(\text{Zn}) = \beta_3[\text{NH}_3]^3 + \beta_4[\text{NH}_3]^4 = 10^{6,86} \cdot 0,1^3 + 10^{8,89} \cdot 0,1^4 = 8,487 \cdot 10^4$$

$$\alpha(\text{Y}) = \frac{[\text{HY}^{3-}]}{[\text{Y}^{4-}]} + 1 = \frac{[\text{H}^+]}{K_{a6}} + 1 = \frac{10^{-10}}{10^{-10,948}} + 1 = 9,872$$

$$d) \quad \text{Zn}^{2+} + \text{Y}^{4-} \rightleftharpoons [\text{ZnY}]^{2-} \quad K = \frac{[\text{ZnY}^{2-}]}{[\text{Zn}^{2+}][\text{Y}^{4-}]} = 10^{18,0} \quad (1)$$

$$e) \quad C(\text{Zn}) = [\text{ZnY}^{2-}] + \alpha(\text{Zn})[\text{Zn}^{2+}] = 0,00100 \text{ M} \quad (2)$$

$$C(\text{Y}) = [\text{ZnY}^{2-}] + \alpha(\text{Y})[\text{Y}^{4-}] = 0,001 \text{ X} \quad (3)$$



$$\Leftrightarrow [\text{Zn}^{2+}] = \frac{[\text{ZnS}^{0}]}{\beta [\text{S}^{3-}]} \stackrel{i)}{=} \frac{10^{-11}}{10^{10,98} \cdot 10^{-11}} = 10^{-9,98} = 1,047 \cdot 10^{-10} \text{ M} \stackrel{ii)}{=} \frac{10^{-11}}{10^{10,98} \cdot 10^{-11}} = 10^{-11,98} = 1,047 \cdot 10^{-12} \text{ M}$$

g) i) The titration error is approximated negative, i.e. $\alpha(Y)[Y^{4-}]$ is approximated negligible in (3).

$$(2) \Rightarrow [ZnY^{2-}] = C(Zn) - \alpha(Zn)[Zn^{2+}] = 0,001 - 8,487 \cdot 10^4 \cdot 1,047 \cdot 10^{-10} = 9,911 \cdot 10^{-4} M$$

$$(3) \Rightarrow X = \frac{[ZnY^{2-}]}{C(Zn)} = \frac{9,911 \cdot 10^{-4}}{0,001} = 0,9911 \quad \text{Titration error} = X - 1 = \underline{\underline{-0,8887\%}}$$

ii) Now also the error is negative. Like above, $[ZnY^{2-}] = 9,99911 \cdot 10^{-4} M$

$$\Rightarrow X = 0,999911 \Rightarrow \text{Titration error} = \underline{\underline{-0,0089\%}}$$

(No points are deducted, if a positive titration error is calculated, because the error is below 0,025% anyway.)

h) i) $20X = \underline{\underline{19,82 \text{ ml}}}$ ii) $20X = \underline{\underline{20,00 \text{ ml}}}$

i) ii)

j) i) $[Mg^{2+}] = 10^{-4,67}$ The error is negative, $[MgY^{2-}] = 9,786 \cdot 10^{-4} M$

$$\Rightarrow X = 0,9786 \Rightarrow \text{Titration error} = \underline{\underline{-2,138\%}}$$

ii) $[Mg^{2+}] = 10^{-6,67}$ Now the error is positive, so $[Mg^{2+}]$ is approximated negligible in (2).

$$(1) \Rightarrow [Y^{4-}] = \frac{[MgY^{2-}]}{[Mg^{2+}] K} = \frac{0,001}{10^{-6,67} \cdot 10^{8,79}} = 7,586 \cdot 10^{-6} M$$

$$(3) \Rightarrow X = \frac{[MgY^{2-}] + \alpha(Y)[Y^{4-}]}{C(Mg)} = \frac{0,001 + 9,872 \cdot 7,586 \cdot 10^{-6}}{0,001} = 1,07488$$

$$\text{Titration error} = X - 1 = \underline{\underline{+7,488\%}}$$

k) i) $20X = \underline{\underline{19,57 \text{ ml}}}$ ii) $20X = \underline{\underline{21,50 \text{ ml}}}$

l) iv)

m) v) vi)

Instructions:

Add bragg's law p 31 in PP to equations... They also need to know nm and Å by heart (or have it in a table)

Problem x. Perovskite solar cells (PSC)

Perovskite solar cells is a promising emerging technology for obtaining energy from the sun. They have a light harvesting efficiency up toward 25 % making them almost as efficient as the expensive solid state silicon solar cells.

A perovskite is a cubic crystal structure on the form ABX_3 , where A and B are cations, often of different size, occupying different sites/holes and **X is an anion**, often oxygen or a halide. One of the most popular perovskites used in solar cells is $CH_3NH_3PbI_3$ or $MAPbI_3$, where lead is **cation B** and the methylammonium ion (MA) is **cation A**. The perovskite crystal structure can be seen below.

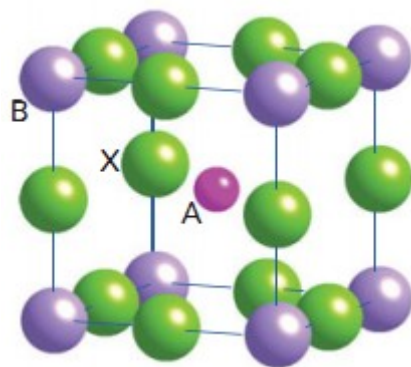


Figure 1. A unit cell of the cubic perovskite structure.

1. State the number of atoms of each element (A, B, X) in the unit cell in figure 1. Show the calculations.

Answer: $A=1$, $B=8 \cdot 1/8=1$, $X=12 \cdot 1/4=3$

2. Which of the statements below are correct?

- a) Figure 1 shows a primitive unit cell for the perovskite structure
- b) The structure in figure 1 is face centred cubic (FCC) with respect to X
- c) The structure in figure 1 is body centred cubic (BCC) with respect to A
- d) The structure in figure 1 is body centred cubic (BCC) with respect to A AND B (if A and B was the same element)
- e) The structure in figure 1 is simple cubic (SC) with respect to A
- f) The sides of the structure in figure is of different size
- g) The A atoms coordination number to the X atoms is 4
- h) The unit cell in figure 1 contains 8 lattice points

Answer: a) yes it contains 1 A, 1 B and 3 X and is a unit cell=repeats itself,

b) no

c) no

d) yes

e) yes

f) no, it is a cubic structure

g) no 12

h) no 1 lattice point (since it is primitive, $(8 \text{ points} \times 1/8 = 1 \text{ lattice point})$)

3.

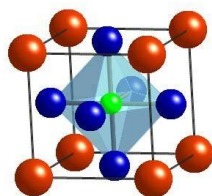
a) Draw the cubic unit cell (of the same size as figure 1) that is obtained if the lattice in figure 1 is translated/shifted so that the A atom in the center of the cell ends up in the forward lower left corner of the unit cell.

Note. Indicate the elements with different shapes/nuances/colour or by marking them A, B and X.

b) The B atoms can be seen as occupying holes formed by the oxygen atom. What is the geometry of the holes (can be solved independent of 3a)?

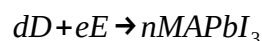
☐ Icosahedral ☐ Decahedral ☐ Octahedral ☐ Cubic ☐ Tetrahedral

Answer: 3b = octahedral



(blue = X = I = green_{fig1}, red = A = MA = pink_{fig1}, green = B = Pb = purple_{fig1}.)

To synthesise MAPbI₃, two precursor solutions containing the chemicals D and E are made and mixed together in a 3:1 D:E molar ratio by stirring overnight in DMF. The excess material is washed off the MAPbI₃ crystals. The unbalanced reaction is written below.



The D and E mixture contains 50.85 mass percent D before the solvent is added. During a chemical analysis of this mixture it was discovered that it consisted of 67.65 mass percent of I and 10.26 mass percent of MA. State the composition of D and E. The solution only contains MA, Pb and I and no other chemicals (before adding the solvent DMF).

Hint 1. calculate the elements individual molar masses first or 2. the molar mass divided to the molar mass of MA₃PbI₅.... Skip the hints?

Answer: The molar ratios are:

Pb=1

MA=3

I=5

We have 3 D for each E. 1. start by assuming we have 3 MA, 5I and 1 Pb. The total molar mass is then 937.91 g/mol. The relative molar mass of D is $937.91 \times 0.5085/3 = 158.97 \rightarrow$ if the assumption is correct then it can not contain Pb. 2. Assume D contains one I, $158.97 - 126.9 = 32.08 \rightarrow$ one MA. If D is MAI, then E is PbI₂, that would give the mass percentage of 49.15 % \rightarrow It is a valid guess of

D and E.

I.e. D is MAI, E is PbI₂.

The synthesised crystals were examined with XRD (X-ray diffraction) and the size of the unit cell of the crystal was determined to $a = 6.13 \text{ \AA}$ by seeing that the (114) plane diffracted light at the angle 32.3° .

4. What wavelength of light was used in this XRD experiment? Give your answer in nm.

Answer: 0.154 nm

Atomic radius's can be estimated using crystal structures.

5. Calculate the maximum theoretical radius of the I⁻ ions, using the hard sphere model where the iodine atoms touch each other.

Answer: $r_I = 2.17 \text{ \AA}$

The Goldschmidt tolerance factor (t) can be used to predict the structure for perovskites. If $t = 1$ then it is probable that the perovskite crystallizes in a cubic structure. The formula for the Goldschmidt tolerance factor is written below.

$$t = \frac{r_{MA} + r_I}{\sqrt{2}(r_{Pb} + r_I)}$$

6. Estimate the radius of iodine using the Goldschmidt tolerance. The radius of Pb = 1.19 \AA and the radius for MA = 2.57 \AA , and the fact that MAPbI₃ crystallizes in a cubic structure.

Answer: $r_I = 2.14 \text{ \AA}$

7. A 1.229 \mu g crystal was used in the solar cell. How many unit cells from figure 1 ($a = 6.13 \text{ \AA}$) does that correspond to?

Answer: $2022 \cdot 10^{12} \text{ unit cells}$.

Another name for a solar cell is a photovoltaic device. Solar cells function similar to batteries but instead of creating an electric current/energy from chemical reactions, the current/energy comes from the adsorption of light.

In the PSC a photon from the sun is absorbed by the perovskite and as a result an electron is excited from the highest occupied/filled orbital (HOMO) to the lowest unoccupied/empty orbital (LUMO). For this excitation to occur the energy of the photon must be equal to the energy difference between the HOMO and LUMO orbitals. This electron is then transported from the solar cell to an electrical circuit and can be used to charge electrical devices. The difference in energy between the HOMO and LUMO decides what wavelength of light that is absorbed. The HOMO LUMO energies can be tuned by slightly changing the crystal structure or size of the perovskite.

8. Calculate the wavelength of the light absorbed by the solar cell if the energy of the HOMO is $E_{\text{HOMO}} = -8.88 \cdot 10^{-19} \text{ J}$ and $E_{\text{LUMO}} = -6.15 \cdot 10^{-19} \text{ J}$. State what colour of visible light that approximately corresponds to.

☐ Blue ☐ Green ☐ Red

Answer: 728 nm (red).

The photon conversion efficiency (PCE) states how much of the absorbed photon energy that is converted into an electric current i.e. how efficient the solar cell is.

9. Assume that the PCE is 25.45 % for the solar cell in question 8 and that 20 % of the incident photons are absorbed by the solar cell. Calculate how many photons that are needed to generate the average energy used by one household in Iceland in a year ($1.74 \cdot 10^{11}$ J).

Answer: $n_{\text{photons}} = E_{\text{household}} / (E_{\text{photon}} \cdot \text{PCE} \cdot \text{incident photon efficiency}) = 1.25 \cdot 10^{31}$ photons.

[illegible]

Modified and adapted from IChO 48th preparatory problem 3

Redox potential diagram for Chromium in acidic solution. The diagram shows two rows of species connected by horizontal lines representing standard reduction potentials. The top row includes $\text{Cr}_2\text{O}_7^{2-}$, Cr(V) , Cr(IV) , Cr^{3+} , Cr^{2+} , and Cr . The bottom row includes CrO_4^{2-} , Cr(OH)_3 , and Cr(OH)_4^- . Vertical lines connect the species in the two rows, and horizontal lines connect species within the same row. Numerical values for the potentials are provided along the lines.

Species	Reduction Potential (V)
$\text{Cr}_2\text{O}_7^{2-} \rightarrow \text{Cr(V)}$	0.55
$\text{Cr(V)} \rightarrow \text{Cr(IV)}$	0.95
$\text{Cr(IV)} \rightarrow \text{Cr}^{3+}$	2.10
$\text{Cr}^{3+} \rightarrow \text{Cr}^{2+}$	-0.42
$\text{Cr}^{2+} \rightarrow \text{Cr}$	-0.74
$\text{Cr}_2\text{O}_7^{2-} \rightarrow \text{Cr}^{3+}$	1.72
$\text{CrO}_4^{2-} \rightarrow \text{Cr(OH)}_3$	-0.11
$\text{Cr(OH)}_3 \rightarrow \text{Cr(OH)}_4^-$	-1.33
$\text{CrO}_4^{2-} \rightarrow \text{Cr(OH)}_4^-$	-0.72

- $$\text{Cr(V)} - \text{Cr(IV)} = 2 \cdot 0,95 - 0,55 = 1,35$$

- ii. Are Cr(V) and Cr(IV) stable with respect to disproportionation? Tick off your answer in the appropriate answer boxes. If **not**, write a reaction equation (only balanced with respect to chromium) and support your answer by calculating the standard cell potential E^0_{cell} .

Cr (V): No, it will form Cr(VI) and Cr^{3+}

Yes

☐

No

☒


$$E^0_{\text{cell}} = 1,72 - 0,55 = 1,18 \text{ V} > 0$$

(spontaneous)

Cr (IV): No, it will form Cr(VI) and Cr^{3+}

Yes

☐

No

☒


$$E^0_{\text{cell}} = 2,10 - 0,95 = 1,15 \text{ V} > 0$$

(spontaneous)

- iii. Write the **balanced** equation for the disproportionation of Cr^{2+} , and calculate the equilibrium constant at 298K for the reaction.



$$E^0_{\text{cell}} = -0,9 - (-0,42) = -0,48 \text{ V}$$

$$\Delta G = -n F E^0_{\text{cell}} = -2 \cdot 96485 \cdot (-0,48) = 92,625 \text{ kJ/mol}$$

$$K = \exp(-\Delta G/RT) = \exp(-92625 / (8,314 \cdot 298)) = \exp(-37,386) = 5,8 \cdot 10^{-17}$$

- iv. Write down the reactions for *reduction* of Cr(OH)_3 and Cr^{3+} in basic and acidic solutions, respectively. Combine these two half reactions into a single reaction with positive E^0_{cell} . Use this information, and the fact that the solubility of Cr(OH)_3 , i.e. a saturated solution of Cr(OH)_3 in equilibrium with solid precipitate, describes a system at equilibrium, to calculate the solubility constant (K_{sp}) for Cr(OH)_3 .



Combining these two to get a reaction with $E_{\text{cell}}^0 > 0$ gives



This reaction is the opposite reaction of the solubility of $\text{Cr(OH)}_3 (\text{s})$

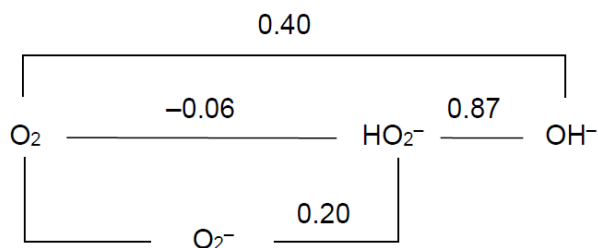
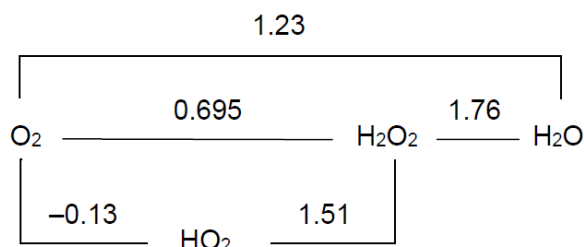


At equilibrium, $E_{\text{cell}} = 0$, hence from the Nernst equation we get

$$0 = E_{\text{cell}}^0 = 0,59 \text{ V} - (0,0592 / n) \cdot \log (K) \quad \text{with } K = 1 / ([\text{Cr}^{3+}] \cdot [\text{OH}^-]^3) = 1 / K_{\text{sp}}$$

$$\text{Solving } 0 = 0,59 \text{ V} - (0,0592 / 3) \cdot \log (1/K_{\text{sp}}) \text{ gives } K_{\text{sp}} = 1,26 \cdot 10^{-30}$$

The following information is given for the hydrogen peroxide compound at pH 0 (upper diagram) and pH 14 (lower diagram):



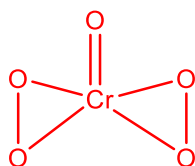
- v. Write a balanced equation and the corresponding standard cell potential showing what happens if Cr(VI), Cr(III) and H₂O₂ are mixed at pH = 0

Largest possible voltage for a reaction involving these three species is $E^{\circ}_{\text{cell}} = 1,33\text{V} - 0,695\text{V} = 0,635\text{V}$ for the reduction of Cr(VI) to Cr(III) and oxidation of H_2O_2 :



The reaction mentioned in the previous question actually takes place in two steps, with formation of a chromium compound called *chromium(VI) oxide peroxide*, with the molecular formula CrO_5 . In this compound, the central atom forms bonds with different valences to oxygen (in order to still have the formal oxidation state +VI), and as the name suggests, it contains two copies of the peroxide unit $-\text{O}-\text{O}-$.

vi. Draw the molecular structure of CrO_5 .



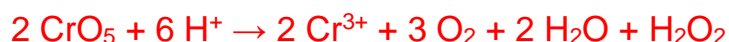
Write down balanced equations for the two steps mentioned above when dichromate reacts with hydrogen peroxide to form CrO_5 as a short-lived intermediate. *Hint*. The first step is **not** a redox reaction, just a substitution reaction where peroxide units bind to chromium as shown in the molecular structure of CrO_5 . The second step is the redox step that eventually forms the final products.

vii. Next

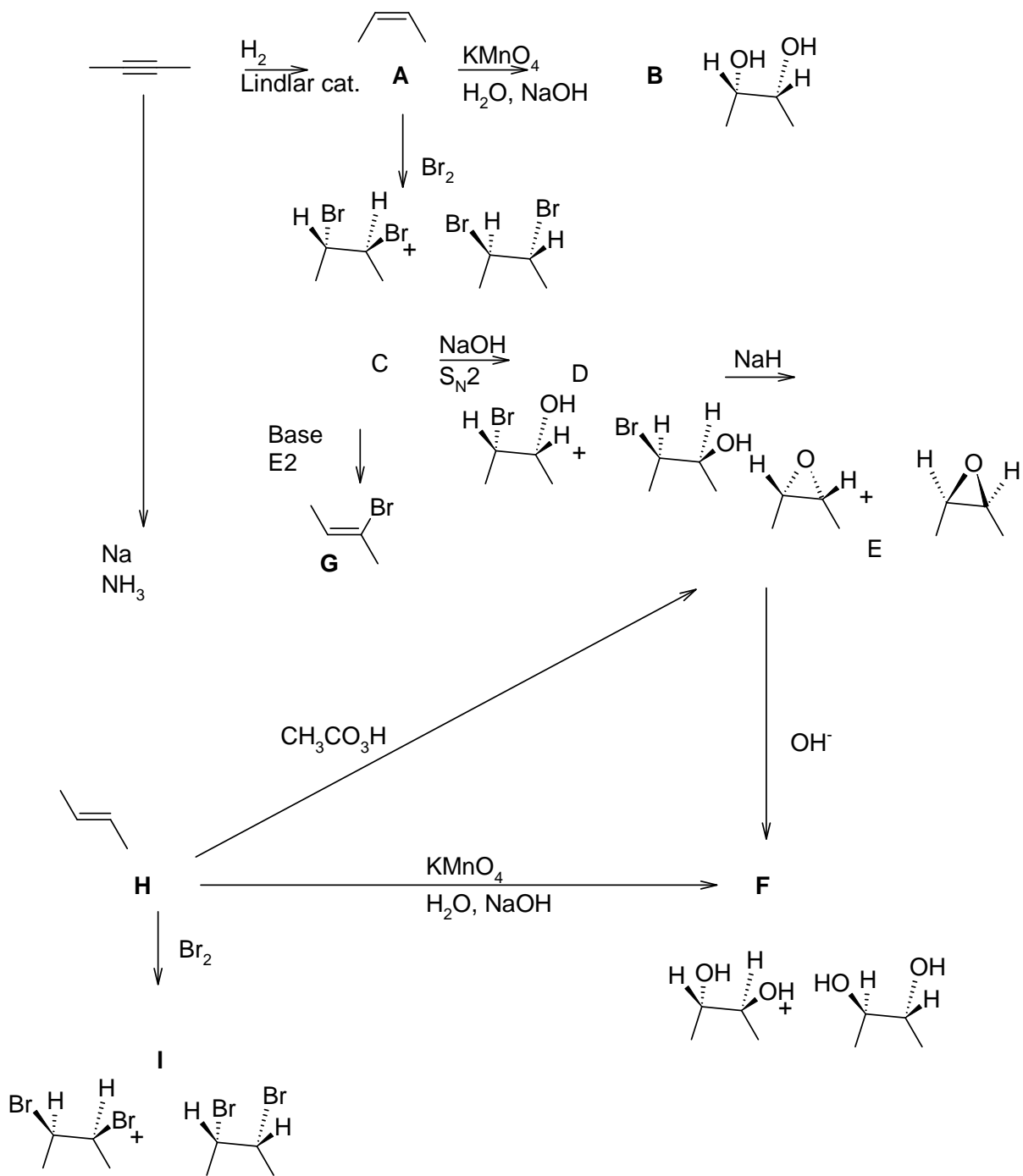
Starting with $\text{Cr}_2\text{O}_7^{2-}$ forming 2 units of CrO_5 each with two peroxide units coordinated to the central Cr(VI) is as follows:



The second redox reaction then becomes



Adding these two, gives the balanced reaction in part (v)



Add nm and Å to equations

Problem y. Unknown sample

A scientist was cleaning out a lab and found an unnamed bottle containing a white salt (A) with the total volume 1.3 cm^3 . She tried to dissolve it in a small amount of water with little progress by using a magnetic stirrer, without success. But when she added concentrated hydrochloride it directly started to dissolve forming a colorless solution (B). When she came back after lunch she found that the solution had turned brown. She stopped the stirrer and the brown parts settled leaving a clear blue-green solution (C).

She scooped out the brown metallic powder and heated it to over $1\,000\text{ }^\circ\text{C}$ in an oxygen free environment until it started to melt and obtained a solid brownish metal (D). By measuring the very low resistance of the material she could confirm that the metal consisted of only one element and what that element was.

By adding silver nitrate to solution C the solution turned clear blue (E) and a white precipitate (F) was formed directly and settled at the bottom of the container. After removing the precipitate and adding sodium chloride to the blue solution E, it turned back to blue-green and after adding some more sodium chloride it turned to green (G).

1. What was the element “M” of metal D?

☐ Silver ☐ Iron ☐ Brass ☐ Copper ☐ Zink ☐ Aluminium

The M^+ ions of element M disproportionate spontaneously in water solutions. When an element disproportionate the same element is oxidized and reduced in the same reaction.

2a. Write down the oxidation and reduction reactions when M^+ disproportionates to a brown metal and a blue water solution. Include electrons if needed to balance the reactions.

Reaction 1, reduction of M^+ :

Reduction 2, oxidation of M^+ :

Answer: Ox: $\text{M}^+ \rightarrow \text{e}^- + \text{M}^{2+}$, red: $\text{M}^+ + \text{e}^- \rightarrow \text{M}$ **or** Ox: $\text{Cu}^+ \rightarrow \text{e}^- + \text{Cu}^{2+}$, red: $\text{Cu}^+ + \text{e}^- \rightarrow \text{Cu(s)}$, aggregation state is not necessary, but if it is included it must be correct.

2b. The E^0 value for the reduction in reaction 1 is 0.153 V and for the reduction in reaction 2 it is 0.521 V . Calculate E^0 for the full disproportionation reaction in solution B.

Answer: 0.368 V

3a. What is the white precipitate F?

3b. Write the chemical equation for the reaction when solution C reacts with AgNO_3 and forms precipitate F, include spectator ions and aggregation state.

Answer: silver chloride, AgCl(s) . $\text{CuCl}_2(\text{aq}) + 2\text{AgNO}_3(\text{aq}) \rightarrow \text{Cu(NO}_3)_2(\text{aq}) + 2\text{AgCl(s)}$ **or** $\text{CuCl}_2(\text{aq}) + 2\text{AgNO}_3(\text{aq}) \rightarrow 2\text{Cu}^{2+}(\text{aq}) + 2\text{NO}_3^-(\text{aq}) + 2\text{AgCl(s)}$

The unit cell of the original white salt A, is cubic with a lattice constant of 0.542 nm, and can be seen below.

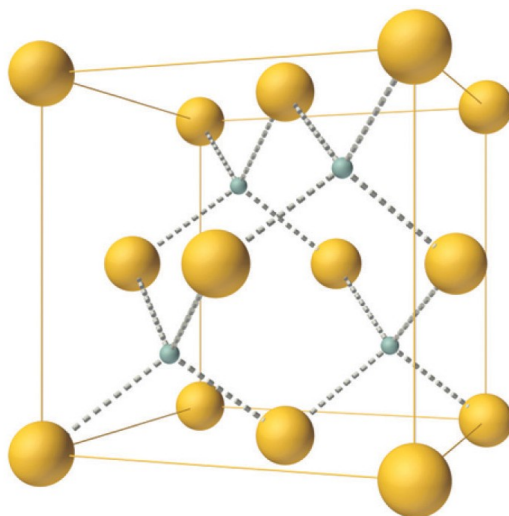


Figure 1. The unit cell of the white salt A. The height of the cubic cell is $a = 0.542 \text{ nm}$.

- 4a. How many yellow and how many gray atoms are there per unit cell?
 4b. Based on your answer in question 1, 3 and 4a, what is the chemical formula for the white salt A?
 4c. If the unit cell only consisted of the yellow atoms, what would the name/class of the unit cell be?
 4d. The small gray atoms can be seen as occupying some of the holes formed by the yellow atoms. What is the name of the shape of those holes?

Answer: 4a. 4 yellow, 4 grey. 4b. CuCl . 4c. FCC, face centered cubic. 4d. Tetrahedral holes.

- 5a. Assuming that the yellow atoms are packed as close to each other as possible. What is the maximum radius of the yellow atoms? Show your calculations.
 5b. Using your answer in 5a, what is the maximum radius of the gray atoms? Show your calculations.

Answer: 5a. Shortest distance for the yellow spheres is along the side-diagonal.

$$4r_{\text{yellow}} = \sqrt{(2 \cdot 0.542)^2} \Rightarrow r = 0.192 \text{ nm}$$

5b. This can be calculated with right angle triangles/pythagoras or cosine-rule. The yellow-yellow-gray triangles have the base " $2r_{\text{yellow}}$ " and the height $a/4$.

$$r_{\text{yellow}} + r_{\text{grey}} = \sqrt{(r^2 + (a/4)^2)} = \sqrt{(0.192^2 + (0.542/4)^2)} = 0.235 \text{ nm}$$

$$r_{\text{grey}} = 0.235 \text{ nm} - r_{\text{yellow}} = 0.043 \text{ nm}$$

If you didn't solve the chemical formula of salt A from problem 4b, use $M_{\text{yellow}} = 44.8 \text{ g/mol}$ and $M_{\text{grey}} = 54.2 \text{ g/mol}$ for problem 6 and 7.

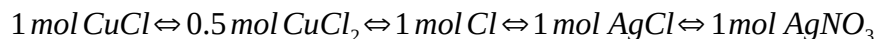
6. Use the unit cell to calculate the density of salt A. Answer in g/cm^3 and show your calculations. Show your calculations.

$$\text{Answer: } \rho = \frac{m}{V} = \frac{4 \cdot M_{\text{Cu}} + 4 \cdot M_{\text{Cl}}}{a^3 \cdot N_a} = \frac{4 \cdot 63.5 + 4 \cdot 35.5}{(0.542 \cdot 10^{-9})^3 \cdot 6.022 \cdot 10^{23}} = 4.13 \text{ g/cm}^3$$

7a. If the white salt A had a volume of 1.3 cm^3 , how many grams of AgNO_3 needs to be added to solution C to form 7.20 g of the precipitate F? $K_{sp} = 1.77 \cdot 10^{-10}$ for salt F. Show your calculations.

Answer: $m = \rho \cdot V = 4.13 \text{ g/cm}^3 \cdot 1.3 \text{ cm}^3 = 5.239 \text{ g}$

$$n = m/M = 5.239 / (63.5 + 35.5) = 0.0529 \text{ mol}$$



If 7.20 g precipitates:

$$n_{\text{Cl}^- (\text{aq})} = n_{\text{Cl, tot}} - n_{\text{AgCl}} = n_{\text{Cl, tot}} - m_{\text{AgCl}} / M_{\text{AgCl}} = 0.0529 - 7.20 / 143.32 = 0.00266 \text{ mol}$$

$$K_{sp} = c_{\text{Cl}} \cdot c_{\text{Ag}}$$

Giving $n_{\text{Ag}^+ (\text{aq})} = K_{sp} / n_{\text{Cl}} = 6.647 \cdot 10^{-8} \text{ mol}$

$$n_{\text{Ag}} = n_{\text{Ag}^+ (\text{aq})} + n_{\text{AgCl} (\text{s})} = 6.647 \cdot 10^{-8} + 7.20 / 143.32 = 0.0502 \text{ mol}$$

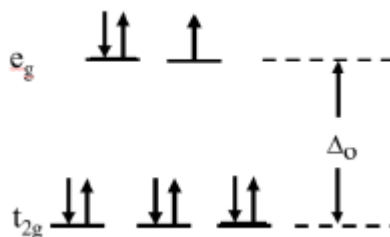
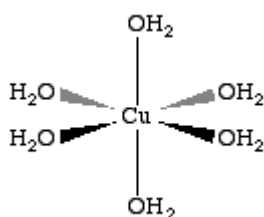
$$m = M \cdot n = (107.87 + 14.01 + 3 \cdot 16.00) \cdot 0.0502 = 8.53 \text{ g}$$

The metal M^{x+} in solution E had a d^9 orbital occupation in its valence shell and has formed an octahedral complex with water.

8a. Draw the complex, with correct geometry.

8b. Draw the configuration of the d-electrons in this complex indicating which orbitals that are e_g and which are t_{2g} and the octahedral splitting Δ_o .

Answer:



In solution G the M^{x+} ion have formed a tetrahedral complex with the chloride ions.

9a. Write the chemical formula for the tetrahedral complex, using sodium ions as counter ions.

9b. Draw the d-electron configuration of the tetrahedral complex given that H_2O is a weak field ligand. Indicating which orbitals that are d_{xy} , $d_{x^2-y^2}$, d_{xz} , d_{yz} and d_{z^2} .

9c. Draw the d-electron configuration if a strong field ligand was used instead.

Answer: $[\text{CuCl}_4]\text{Na}_2$ **or** $[\text{CuCl}_4]^{2-} \cdot 2\text{Na}^+$

