Topics in the June 2007 Exam Paper for CHEM1101

Click on the links for resources on each topic.

2007-J-2:

- Nuclear and Radiation Chemistry

2007-J-3:

- Wave Theory of Electrons and Resulting Atomic Energy Levels
- Filling Energy Levels in Atoms Larger than Hydrogen

2007-J-4:

- Lewis Structures
- VSEPR

2007-J-5:

2007-J-6:

- Thermochemistry
- First and Second Law of Thermodynamics

2007-J-7:

- Thermochemistry
- First and Second Law of Thermodynamics

2007-J-8:

- First and Second Law of Thermodynamics
- Chemical Equilibrium
- Types of Intermolecular Forces

2007-J-9:

- Gas Laws
- Chemical Equilibrium

2007-J-10:

- Chemical Equilibrium

2007-J-11:

- Electrochemistry

2007-J-12:

- Electrolytic Cells

Marks

- Balance the following nuclear reactions by identifying the missing nuclear particle or nuclide. **3**

$$^{55}_{26}\mathrm{Fe} + {}^{0}_{-1}\mathrm{e} \rightarrow \boxed{^{55}_{25}\mathbf{Mn}}$$

$$^{3}_{2}\mathrm{He} + {}^{3}_{2}\mathrm{He} \rightarrow 2\,{}^{1}_{1}\mathrm{p} + \boxed{^{4}_{2}\mathbf{He}}$$

$$^{15}_{7}\mathrm{N} + {}^{1}_{1}\mathrm{p} \rightarrow {}^{15}_{8}\mathrm{O} + \boxed{^{1}_{0}\mathbf{n}}$$

- Calculate the atomic mass of lead from the isotope information provided. **2**

Isotope	Mass of isotope (a.m.u.)	Relative abundance
^{204}Pb	203.97304	1.40%
^{206}Pb	205.97446	24.10%
^{207}Pb	206.97589	22.10%
^{208}Pb	207.97664	52.40%

The relative atomic mass of lead is the weighted average of the masses of its isotopes:

$$\text{atomic mass} = \left(203.97304 \times \frac{1.40}{100}\right) + \left(205.97446 \times \frac{24.10}{100}\right) + \left(206.97589 \times \frac{22.10}{100}\right) + \left(207.97664 \times \frac{52.40}{100}\right) = 207.2$$

(The relative abundances are given to 4 significant figures and limit the accuracy of the answer.)

Answer: **207.2**

- Calculate the molar activity of ^{11}C (in curie), given its half-life of 20.3 minutes. **3**

The molar activity is given by $A_{mol} = \lambda N_a$ where λ is the decay constant which is related to the half life $t_{1/2}$ by $\lambda = \frac{\ln 2}{t_{1/2}}$.

The half life = 20.3 minutes or 20.3 × 60 s = 1218 s. Hence the molar activity is:

$$A_{mol} = \left(\frac{\ln 2}{1218}\right) \times (6.022 \times 10^{23}) = 3.427 \times 10^{20}\ \text{Bq} = \frac{3.427 \times 10^{20}}{3.70 \times 10^{10}}\ \text{Ci} = 9.26 \times 10^{9}\ \text{Ci}$$

Answer: **9.26×10^{9} Ci**

- Provide a brief explanation of each of the following terms. (You may include an equation or a diagram where appropriate). **Marks 4**

(a) Pauli exclusion principle

No two electrons may occupy the same orbital with the same spin, thereby having the same set of quantum numbers, n, l, m_l, s and m_s.

(b) the Bohr model of the atom

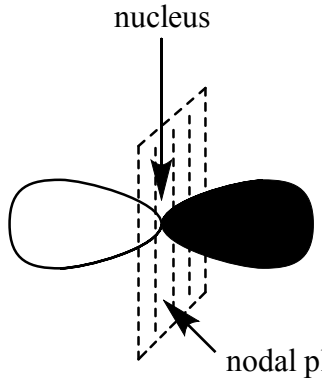
In the Bohr model, electrons in atoms occupy only discrete circular orbits. By being restricted to certain orbits, the energy of the electron can only have certain discrete values. The orbit occupied is labelled by a quantum number, n, which can only take integer values: n = 1, 2, 3….

- Write down the ground state electron configurations for the following elements. The configuration of lithium is given as an example. **2**

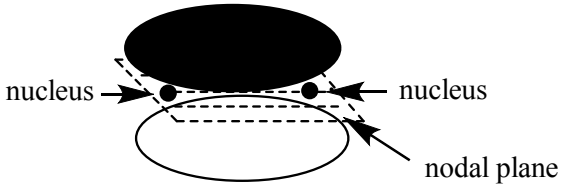
Li	$1s^2\ 2s^1$
Ne	**$1s^2\ 2s^2\ 2p^6$ or [He] $2p^6$**
Br	**$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^5$ or [Ar] $4s^2\ 3d^{10}\ 4p^5$**

- Sketch the following wave functions as lobe representations. Clearly mark all nodal surfaces and nuclear positions. **4**

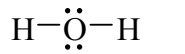
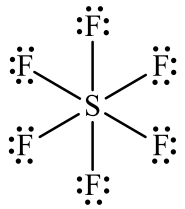
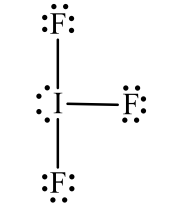
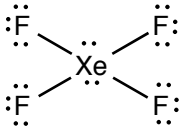
(a) a 2*p* orbital



(b) a π molecular orbital



• Complete the following table. Water is given as an example. **Marks 6**

Name	Lewis structure	Number of valence electron pairs on central atom	Geometric arrangement of valence electron pairs on central atom	Molecular shape
water		4	tetrahedral	bent
sulfur hexafluoride		**6**	**octahedral**	**octahedral**
iodine trichloride		**5**	**trigonal bipyramidal**	**T-shaped**
xenon tetrafluoride		**6**	**octahedral**	**square planar**

• A typical surface (skin) temperature of an adult human is 33.0 °C. Calculate the wavelength at which the most intense electromagnetic radiation is emitted from the human body. **3**

The wavelength, λ, is related to the absolute temperature, T, through the equation, $4.5k_BT = \frac{hc}{\lambda}$ or:

$$\lambda = \frac{hc}{4.5k_BT}$$

With $T = 33.0 + 273.0 = 306$ K,

$$\lambda = \frac{(6.626 \times 10^{-34})(2.998 \times 10^{8})}{(4.5)(1.381 \times 10^{-23})(306)} = 1.04 \times 10^{-6} \text{ m}$$

(As the temperature is given to 3 significant figures, this limits the accuracy of the answer to the same number of significant figures.)

Answer: **1.04×10^{-5} m**

Calculate the energy of a single photon of this radiation.

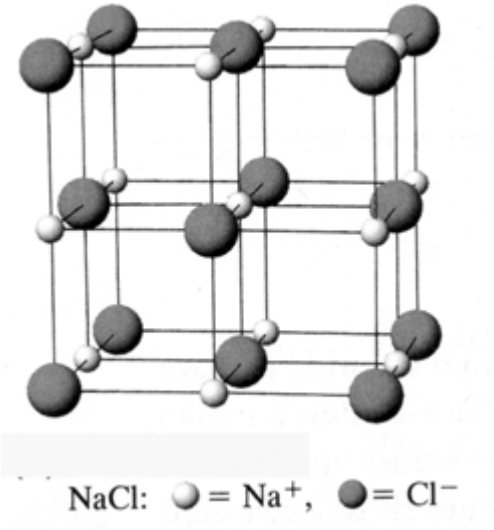
The energy is related to the wavelength through the equation, $E = \frac{hc}{\lambda}$. Hence:

$$E = \frac{(6.626 \times 10^{-34})(2.998 \times 10^{8})}{(1.04 \times 10^{-6})} = 1.90 \times 10^{-20}\ \text{J}$$

Answer: **1.90×10^{-20} J**

Marks 4

- A cartoon representation of the structure of *halite* (NaCl) is shown below. The structure arises from the closest possible packing of anions stabilized by cations in the interstices. From a density of 2.16 g cm^{-3}, a nearest neighbour distance of 282 pm was calculated.



Crystal structure	Madelung constant (*A*)
ZnS (wurtzite)	1.641
NaCl	1.748
CsCl	1.763

What is the molar lattice energy of *halite*?

The molar lattice energy is given by the equation, $E = -A\frac{e^2}{4\pi\varepsilon_0 r}N_a$ where A is the Madelung constant and r is the separation of the ions which is equal to the nearest neighbour distance. With r = 282 pm = 282 × 10^{-12} m and A = 1.748 for the NaCl structure from the table:

$$E = -(1.748) \times \frac{(1.602 \times 10^{-19})^2}{(4)\times(3.142)\times*8.8524\times10^{-12})\times(282\times10^{-12})} \times (6.022 \times 10^{23})$$

= 859000 J mol^{-1} = 859 kJ mol^{-1}

Answer: **859 kJ mol^{-1}**

What would be the Madelung constant of lithium chloride given that it does not adopt the wurtzite structure? Explain your answer.

As the lattice energy is proportional to the Madelung constant, a salt will adopt the structure with the maximum *possible* Madelung constant. The Madelung constant is related to the number of anions surrounding each cation (and vice versa). Thus, the ZnS, NaCl and CsCl structures have 4, 6 and 8 anions around each cation respectively. The number of anions is limited by the radius ratio rules: the anions must physically fit around the cation.

Na^+ is large enough to fit 6 Cl^- around it but not large enough to fit 8 Cl^- and thus adopts the NaCl structure. Li^+ is smaller than Na^+ so is definitely also too small to fit 8 Cl^- around it. As the question states that it does not adopt the ZnS (wurtzite) structure, it must therefore adopt the NaCl structure so has A = 1.748.

Marks 5

- The current "petrochemical economy" is based on the combustion of fossil fuels, of which octane is a typical example.

$$2C_8H_{18}(l) + 25O_2(g) \rightarrow 16CO_2(g) + 18H_2O(l)$$

Calculate the heat of combustion of octane using the supplied heat of formation data.

Data: $C_8H_{18}(l)$: –249.9 kJ mol^{-1}; $CO_2(g)$: –393.5 kJ mol^{-1}; $H_2O(l)$: –285.8 kJ mol^{-1}

Using $\Delta_{rxn}H^o = \sum m\Delta_f H^o(\text{products}) - \sum n\Delta_f H^o(\text{reactants})$, the heat of the reaction as written is:

$$\begin{aligned}\Delta_{rxn}H^o &= [16\Delta_f H^o(CO_2(g)) + 18\Delta_f H^o(H_2O(l))] - [2\Delta_f H^o(C_8H_{18}(l))] \\ &= [(16 \times -393.5) + (18 \times -285.8)] - [(2 \times -249.9)] \\ &= -10940\ \text{kJ mol}^{-1}\end{aligned}$$

where $\Delta_f H^o(O_2(g)) = 0$ has been used for the formation of an element in its standard state.

The enthalpy of combustion is defined per mole of fuel. The above reaction is for the combustion of two moles of C_8H_{18}.

Hence, $\Delta_{comb}H^o$ = ½ × -10940 = -5470 kJ mol^{-1}

Answer: **-5470 kJ mol^{-1}**

How much energy is released when 1.00 L of octane is burned?

Data: Density of octane is 0.67 kg L^{-1}

As density = $\frac{\text{mass}}{\text{volume}}$, 1.00 L corresponds to:

mass = density × volume = 0.67 × 1.00 = 0.67 kg = 670 g.

The molar mass of octane, C_8H_{18}, is 8 × 12.01 (C) + 18 × 1.008 (H) = 114.224. This mass of octane therefore corresponds to:

$$\text{number of moles} = \frac{\text{mass}}{\text{molar mass}} = \frac{670}{114.224} = 5.9\ \text{mol}$$

From above, 1 mole releases 5470 kJ mol^{-1}. Therefore, this amount release:

energy released = 5.9 × 5470 = 32 × 10^3 kJ = 32 MJ

Answer: **32 × 10^3 kJ or 32 MJ**

Marks 3

- The so-called "hydrogen economy" is based on $H_2(g)$ produced from water by solar energy. The gas is then burned as fuel:

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l) \qquad \Delta H_r = -571.6 \text{ kJ mol}^{-1}$$

Calculate the volume of H_2 gas at 25 °C and 1 atm required to produce 1.0×10^4 kJ of heat.

From the chemical equation, burning of two moles of $H_2(g)$ produces 571.6 kJ. so one mole produces ½ × 571.6 = 285.8 kJ mol.

To produce 1.0×10^4 kJ therefore requires:

$$\text{amount of } H_2(g) \text{ required} = \frac{1.0 \times 10^4}{285.5} = 35 \text{ mol}$$

At 25 °C and 1 atm, 1 mole of an ideal gas has a volume of 24.5 L. This amount therefore has a volume of:

volume = 35 × 24.5 = 860 L

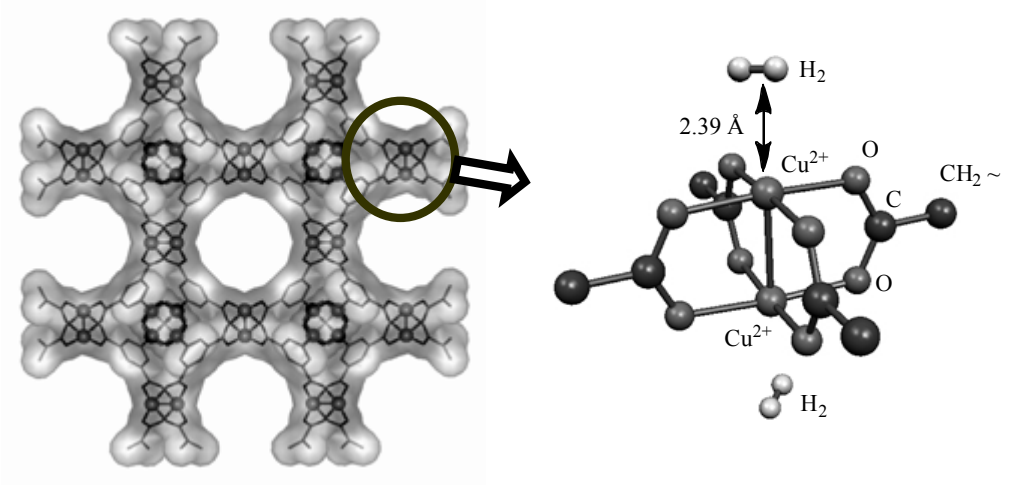
Alternatively, and entirely equivalently, the ideal gas law PV = nRT can be used:

$$V = \frac{nRT}{P} = \frac{(35) \times (0.08206) \times (25 + 273)}{(1)} = 860\,L$$

Answer: **860 L**

Marks 5

A major disadvantage of hydrogen as a fuel is that it is a gas, and therefore hard to store. There is an enormous world-wide effort, including research performed in the University of Sydney, to develop novel chemical structures in which H_2 can be stored much more efficiently. One of the structures being tested in the School of Chemistry is shown below.



What type of intermolecular force (or forces) are responsible for the binding between the Cu^{2+} and the H_2?

There are ion-induced dipole forces between Cu^{2+} and the H_2 molecules as well as weak dispersion (London or induced dipole-induced dipole) forces.

In order that such a material be useful for fuel storage, the binding of the H_2 must be reversible:

$$\text{cage(s)} + H_2(g) \rightleftharpoons \text{cage}\cdot H_2(s)$$

One simple way to reverse the binding is to increase the temperature, so that at low temperature the equilibrium lies to the right and at high temperature to the left. Use this information, plus any chemical knowledge or intuition to infer the sign of ΔG, ΔH and ΔS at "low" and "high" temperatures. (You may assume that ΔH and ΔS do not change greatly with temperature.)

At low temperature, the equilibrium lies to the right favouring products: $\Delta G < 0$. At high temperature, it lies to the left favouring reactants: $\Delta G > 0$.

The reaction involves formation of a solid from a solid and a gas. There is therefore a decrease in the entropy: $\Delta S < 0$. This is true at all temperatures.

The forward reaction becomes less favourable as the temperature is increased. Le Chatelier's principle therefore suggests that the reaction is exothermic: $\Delta H < 0$. This is true at all temperatures. (If the temperature is increased, the equilibrium shifts to remove heat by increasing the backward reaction.)

Temperature	ΔG	ΔS	ΔH
low	< 0	< 0	< 0
high	> 0	< 0	< 0

Marks 5

- $N_2(g)$ and $O_2(g)$ react with each other to a small extent if a catalyst is present to form nitric oxide, NO(g), according to the following equation.

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$

The equilibrium constant, K_p, for this reaction is 4.35×10^{-35} at 298 K and 2.75×10^{-20} at 500 K. Is the reaction exothermic or endothermic? Give reasons for your answer.

The reaction is favoured at higher temperatures (*i.e.* increasing the temperature increases the amount of product). Le Chatelier's principle therefore suggests that the reaction is endothermic: $\Delta H > 0$

The partial pressures of $O_2(g)$ and $N_2(g)$ in air are 0.210 atm and 0.780 atm respectively. If air at atmospheric pressure is sealed in a 1.00 L container containing the catalyst at 298 K, what will be the partial pressure of NO(g) and the total pressure inside the container at equilibrium?

Two moles of NO are produced for every mole of O_2 and N_2 that is lost.

partial pressures	O_2	N_2	NO
start	0.21	0.78	0
change	-x	-x	+2x
equilibrium	0.21-x	0.78-x	2x

The equilibrium constant in terms of partial pressures is then:

$$K_p = \frac{(p_{NO})^2}{(p_{O_2})(p_{N_2})} = \frac{(2x)^2}{(0.21-x)(0.78-x)} = 4.35\times10^{-35}$$

As K_p is *very* small, x will be tiny so that (0.21-x) ~ 0.21 and (0.78-x) ~ 0.78 to a very good approximation. Substituting these approximations in gives:

$$4x^2 = (4.35\times10^{-35})\times(0.21)\times(0.78) \Rightarrow x = 1.33\times10^{-18}$$

The partial pressure of NO is twice this value = 2.67×10^{-18} atm

The overall number of moles of gas does not change during the reaction so neither does the total pressure. The pressure at equilibrium = 1.00 atm

Pressure of NO(g): **2.67×10^{-18} atm**	Total pressure: **1.00 atm**

THIS QUESTION CONTINUES ON THE NEXT PAGE.

Marks 6

Oxidation of NO(g) to produce the pollutant $NO_2(g)$ is favoured at higher temperatures, such as those in a car exhaust:

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$

The equilibrium constant, K_p, for this reaction is 1.3×10^{4} at 500 K. What is the value of K_c at 500 K?

K_p and K_c are related through the equation $K_p = K_c\,(RT)^{\Delta n}$ where Δn is the change in the number of moles of gas during the reaction. As three moles go to two moles in the reaction, $\Delta n = -1$ and hence:

$$\mathbf{K_p = K_c (RT)^{-1}}$$

$$\mathbf{K_c = K_p \times (RT) = (1.3 \times 10^4) \times (0.08206 \times 500) = 5.3 \times 10^5}$$

K_c = **5.3×10^5**

Using this value and the equilibrium constant for the formation of NO(g) from the previous page, calculate the value of K_c for the formation of $NO_2(g)$ from $N_2(g)$ and $O_2(g)$ at 500 K according to the following equation.

$$N_2(g) + 2O_2(g) \rightleftharpoons 2NO_2(g)$$

From 2007-J-9, $K_p = 2.75 \times 10^{-20}$ for the reaction $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$. For this reaction, $\Delta n = 0$ and hence $K_p = K_c\,(RT)^0$ or $K_c = K_p$. This reaction and the one above can be combined:

$\mathbf{N_2(g) + O_2(g) \rightleftharpoons 2NO(g)}$	$\mathbf{K_c = 2.75 \times 10^{-20}}$
$\mathbf{2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)}$	$\mathbf{K_c = 5.3 \times 10^{5}}$
$\mathbf{N_2(g) + 2O_2(g) \rightleftharpoons 2NO_2(g)}$	$\mathbf{K_c = (2.75 \times 10^{-20}) \times (5.3 \times 10^{5}) = 1.5 \times 10^{-14}}$

K_c = **1.5×10^{-14}**

	Marks
• Give balanced ionic equations for the reactions that occur in each of the following cases.	**3**

Potassium metal is added to excess water.

When added to water, potassium produces an alkaline solution and hydrogen gas which is ignited by the exothermicity of the reaction:

$2K(s) + 2H_2O(l) \rightarrow 2K^+(aq) + 2OH^-(aq) + H_2(g)$

Solutions of zinc nitrate and sodium phosphate are mixed.

A white precipitate is produced (Table E2-3 in the Laboratory Manual). The zinc ion has a +2 charge and phosphate, PO_4^{3-}, has a -2 charge:

$3Zn^{2+}(aq) + 2PO_4^{3-}(aq) \rightarrow Zn_3(PO_4)_2(s)$

Solid strontium carbonate is dissolved in dilute nitric acid.

Carbonates produce $CO_2(g)$ when treated with acid:

$SrCO_3(s) + 2H^+(aq) \rightarrow Sr^{2+}(aq) + CO_2(g) + H_2O(l)$

• Explain why the voltage of the lead acid battery ($E°$ = 2.05 V) decreases when it discharges, whereas the zinc/silver button battery ($E°$ = 1.6 V) does not.	**2**

$$Pb(s), PbSO_4(s) \mid H^+(aq), HSO_4^-(aq) \parallel H^+(aq), HSO_4^-(aq) \mid PbO_2(s), PbSO_4(s)$$

$$Zn(s), ZnO(s) \mid OH^-(aq) \parallel OH^-(aq) \mid Ag_2O(s), Ag(s)$$

The overall reaction for the zinc/silver button battery is:

$Zn(s) + Ag_2O(s) \rightarrow ZnO(s) + 2Ag(s)$

All components are solids and hence do not enter in to equilibrium constant expression for the reaction or into the Nernst equation for the cell. The voltage will remain constant as concentrations of all products and reactants remains constant.

In contrast, the overall reaction for the lead acid battery is:

$PbO_2(s) + Pb(s) + 2H^+(aq) + 2HSO_4^-(aq) \rightarrow 2PbSO_4(s) + 2H_2O$

Here the concentrations of $H^+(aq)$ and $HSO_4^-(aq)$ decrease as the battery discharges and hence the voltage drops.

- If 1.00 tonne (10^3 kg) of aluminium metal is produced by the electrolysis of molten Al_2O_3, how many tonnes of carbon dioxide are emitted by oxidation of the carbon electrodes?

Marks 3

The overall reaction is:

$2Al_2O_3(l) + 3C(s) \rightarrow 4Al(s) + 3CO_2(g)$

3 moles of CO_2 are produced for every 4 moles of Al(s). The atomic mass of aluminium is 26.98 so the amount of aluminium in 10^3 kg = 10^6 g is:

$$\text{amount of aluminium} = \frac{\text{mass}}{\text{atomic mass}} = \frac{(1.00 \times 10^6)}{(26.98)} = 37100 \text{ mol}$$

Therefore the amount of CO_2 produced is (¾ × 37100 mol) = 27800 mol.

The molar mass of CO_2 is (12.01 (C)) + (2 × 16.00) = 44.01. Hence, this amount of CO_2 corresponds to a mass of:

mass = molar mass × number of moles = (27800) × (44.01) = 1.22×10^6
= 1.22 tonnes

Answer: **1.22 tonnes**

- The electrolysis of aqueous sodium chloride produces $H_2(g)$ and $Cl_2(g)$. Circle the choice that correctly finishes each of the following statements about this process.

4

The $Cl_2(g)$ is produced at the ……..	**anode**	cathode
In the aqueous salt solution, the sodium ions migrate towards the electrode that produces…...	$Cl_2(g)$	**$H_2(g)$**
As the electrolysis proceeds the pH of the aqueous salt solution……	**increases**	decreases
If the process were being run with a battery, the positive electrode of the battery would be connected to the electrode that produces ……	**$Cl_2(g)$**	$H_2(g)$

The two half cells are:

$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$ **reduction (always occurs at the cathode)**
$2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$ **oxidation (always occurs at the anode)**

The cathode is negatively charged so $Na^+(aq)$ migrate to the cathode where H_2O is preferentially reduced to $H_2(g)$.

$OH^-(aq)$ is produced at the cathode so the pH increases.

The anode is positively charged with the positive electrode of the battery is connected to it. $Cl_2(g)$ is produced at the anode.