

UNIVERSITY OF TORONTO
FACULTY OF ARTS AND SCIENCE

AUGUST EXAMINATIONS 2014
CHM 139H1 Summer

Name (print): _____

Student No: _____ Tutorial Section: _____

DURATION: 3 HOURS

TOTAL MARKS = 90

Calculators may be used but not shared. Programmable calculators may not be used. A **PERIODIC TABLE** and **USEFUL DATA** are attached to the back of the exam.

WHEN YOU RECEIVE YOUR EXAM PAPER AND COMPUTER ANSWER SHEET:

1. Write your name, student number and tutorial section on this page, **and** on the short answers page.
2. On the computer answer sheet:
 - a) Write your last name, your given name, and signature at the **front** (top left corner) and at the **back** (top) of the sheet.
 - b) **Blacken** the appropriate circles for your last name and initials.
 - c) **Write** your student number along the top of the student number box and **blacken** the circles which correspond to your student number.

YOUR ANSWERS ARE TO BE RECORDED ON THE COMPUTER ANSWER SHEET AND ON THIS PAPER, BOTH OF WHICH MUST BE HANDED IN AT THE END OF THE EXAM.

Part A (30 × 1.5 = 45 marks)

1. Clearly circle on the test paper the letter (a, b, c, or d) for the best answer you choose for each question.
2. Blacken the circle (below a, b, c, or d) on the computer sheet which corresponds to the answer you have chosen for each question. Make sure that only one answer is blackened.
3. Use soft pencil (No. 2 or softer). Do not use ink or ball point pen.
4. The computer sheet must be filled during the time allotted for the test.

Part B (3 questions = 45 marks) Clearly and concisely showing your work is essential in order to receive full marks.

AT THE END OF THE EXAM: Insert your computer answer sheet into your exam paper. Remain seated until all exam papers have been collected.

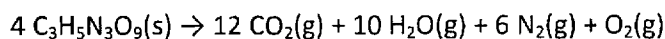
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MULTIPLE CHOICE QUESTIONS (1.5 marks each)

1) A 2.75-L container filled with CO₂ gas at 25°C and 225 kPa pressure springs a leak. When the container is re-sealed, the pressure is 185 kPa and the temperature is 10°C. How many moles of gas were lost?

- A) 3.39 mol
- B) 0.728 mol
- C) 0.0335 mol
- D) 0.882 mol

2) A 1.000 kg sample of nitroglycerine, C₃H₅N₃O₉, explodes and releases gases with a temperature of 1985°C at 1.100 atm. What is the total volume of gas produced?



- A) 4730 L
- B) 3525 L
- C) 742.2 L
- D) 5378 L

3) Which of the following compounds has the highest boiling point?

- A) H₂O
- B) NH₃
- C) HCl
- D) H₂S

4) Which of the following processes would result in a decrease in system entropy?

- A) a glass of cool lemonade warming in the sun
- B) evaporation of a puddle of gasoline
- C) sublimation of a moth ball
- D) melting of an ice cube
- E) condensation of water vapor on a cold windshield

5) A KCl solution is prepared by dissolving 20.0 g KCl in 250.0 g of water at 25°C. What is the vapor pressure of the solution if the vapor pressure of water at 25°C is 23.76 mm Hg?

A) 22.0 mm Hg

B) 24.6 mm Hg

C) 23.3 mm Hg

D) 22.9 mm Hg

6) In a sealed container, the rate of dissolving is equal to the rate of crystallization. Therefore we would expect

A) $\Delta G > 0$

B) $\Delta G = 0$

C) $\Delta S = 0$

D) $\Delta G < 0$

7) Which of the following quantities for an element has a value of zero in the standard state?

I) ΔH°_f

II) ΔG°_f

III) S°

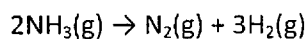
A) III only

B) I only

C) I and II

D) II only

8) The following reaction is endothermic.



The reaction:

- A) will be spontaneous at low temperature
- B) is spontaneous at all temperatures
- C) is not spontaneous at any temperature
- D) will be spontaneous at high temperature

9) Most chemical reactions are carried out in one of two ways

- I. in an open vessel at constant atmospheric pressure
- II. in a closed vessel

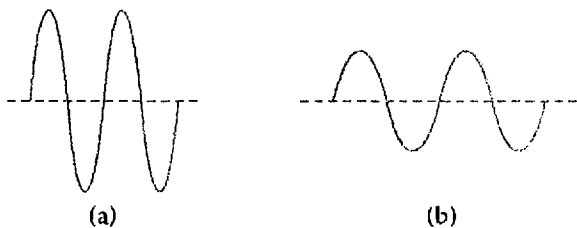
Which is true?

- A) $\Delta E = w$ for condition I and $\Delta H = w$ for condition II
- B) $\Delta H = w$ for condition I and $\Delta E = w$ for condition II
- C) $\Delta H = q$ for condition I and $\Delta E = q$ for condition II
- D) $\Delta E = q$ for condition I and $\Delta H = q$ for condition II

10) Consider the reaction of 10.00 moles of $\text{H}_2(\text{g})$ with 5.00 moles of $\text{O}_2(\text{g})$ forming 10.00 moles of $\text{H}_2\text{O}(\text{l})$ at 25°C and a constant pressure of 1.00 atm. If 683.0 kJ of heat are released during this reaction, and $P\Delta V$ is equal to -37.00 kJ, then the values of:

- A) $\Delta H^\circ = +683.0$ kJ and $\Delta E^\circ = +720.0$ kJ.
- B) $\Delta H^\circ = +683.0$ kJ and $\Delta E^\circ = +646.0$ kJ.
- C) $\Delta H^\circ = -683.0$ kJ and $\Delta E^\circ = -720.0$ kJ.
- D) $\Delta H^\circ = -683.0$ kJ and $\Delta E^\circ = -646.0$ kJ.

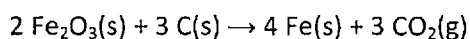
Two electromagnetic waves are represented below



13) Which of the following statements is **true** for wave (b):

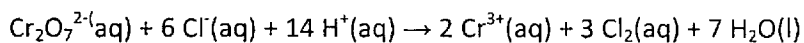
- A) lower amplitude and greater intensity than wave (a).
- B) lower amplitude and weaker intensity than wave (a).
- C) higher amplitude and greater intensity than wave (a).
- D) higher amplitude and weaker intensity than wave (a).

14) What is the oxidation number change for the iron atom in the following reaction?

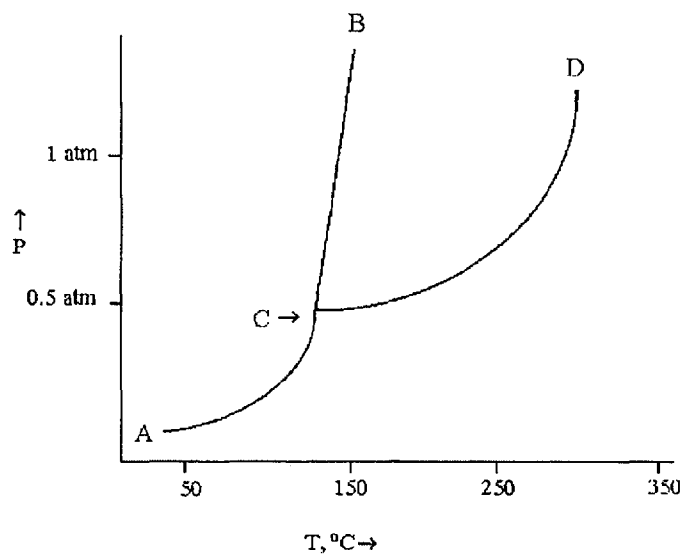


- A) -3
- B) -6
- C) +3
- D) +6

15) Which one is the oxidation half reaction in the following chemical reaction?



- A) $2 \text{Cl}^-(\text{aq}) \rightarrow \text{Cl}_2(\text{aq}) + 2\text{e}^-$
- B) $\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14 \text{H}^+(\text{aq}) \rightarrow 2 \text{Cr}^{3+}(\text{aq}) + 7 \text{H}_2\text{O}(\text{l}) + 6\text{e}^-$
- C) $\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14 \text{H}^+(\text{aq}) + 6\text{e}^- \rightarrow 2 \text{Cr}^{3+}(\text{aq}) + 7 \text{H}_2\text{O}(\text{l})$
- D) $\text{Cl}_2(\text{aq}) + 2\text{e}^- \rightarrow 2 \text{Cl}^-(\text{aq})$



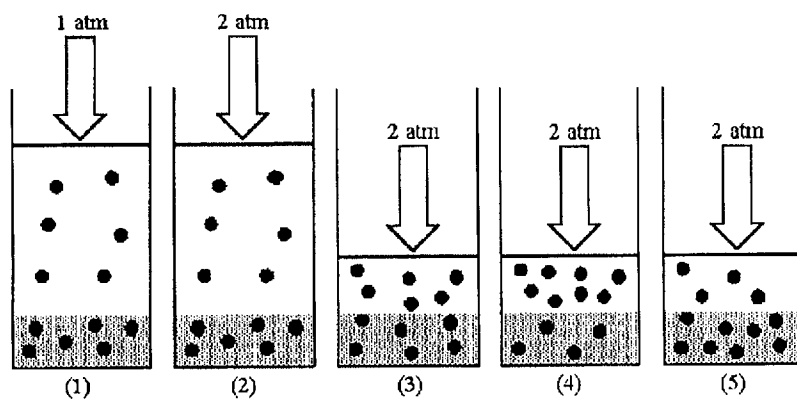
16) From the diagram above, determine if the solid phase of this substance

- A) is more dense than the liquid phase.
- B) is less dense than the liquid phase.
- C) is less dense than water.
- D) has the same density as the liquid phase.

17) Two aqueous solutions, **A** and **B**, are separated by a semipermeable membrane. The osmotic pressure of solution **A** immediately begins to decrease. Which of the following statements is **true**?

- A) The initial osmotic pressure of solution **B** is greater than that of solution **A**.
- B) The solvent molecules are moving from the solution of higher osmotic pressure to that of lower osmotic pressure.
- C) Solvent molecules are moving from solution **B** into solution **A**.
- D) Both **B** and **C** are true statements.

18) From the drawings below, **Drawing (1)** shows a system in which an equilibrium exists between dissolved and undissolved gas particles at $P = 1 \text{ atm}$. According to Henry's law, if the pressure is increased to 2 atm and equilibrium is restored, which one of the Drawing (2)-(5) best represents the equilibrium at 2 atm ?



- A) Drawing (2)
- B) Drawing (3)
- C) Drawing (4)
- D) Drawing (5)

19) For a reaction with rate law, $\text{Rate} = k[A][B]^2$, determine what will happen to the rate of the reaction if the concentration of **B** is increased by a factor of 2.00?

The rate will:

- A) Decrease by a factor of $1/2.00$.
- B) Increase by a factor of 4.00.
- C) Increase by a factor of 2.00.
- D) Decrease by a factor of $1/4.00$.

20) For a particular first-order reaction, it takes 48 minutes for the concentration of the reactant to decrease to 25% of its initial value. What is the value for rate constant (in s^{-1}) for the reaction?

A) $2.9 \times 10^{-2} s^{-1}$

B) $6.0 \times 10^{-3} s^{-1}$

C) $1.0 \times 10^{-4} s^{-1}$

D) $4.8 \times 10^{-4} s^{-1}$

21) Which of the following statements is **not true**?

A) A highly spontaneous process need not occur rapidly.

B) A spontaneous process always moves toward equilibrium.

C) A nonspontaneous process cannot be caused to occur.

D) The reverse of a spontaneous reaction is always nonspontaneous.

22) What is W in Boltzmann's formula, $S = k \ln W$?

A) The work times Avogadro's number

B) A number expressing randomness

C) A fraction indicating the probability of obtaining the state

D) The number of microstates corresponding to a particular the state

23) Which of the following gas molecules has the greatest standard molar entropy at 25°C ?

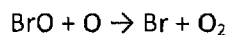
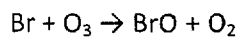
A) C_2H_2

B) CH_3CH_3

C) CH_2CH_2

D) All have the same entropy.

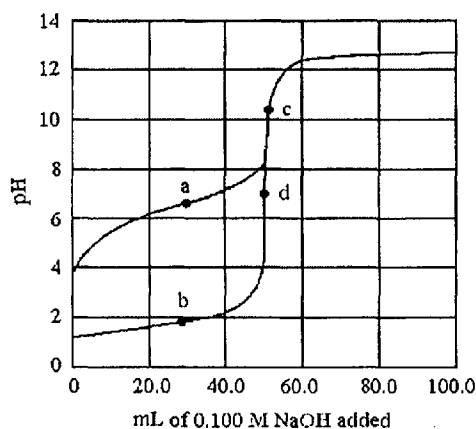
24) The decomposition of ozone in the stratosphere can occur by the following two-step mechanism:



Which species is a catalyst in this mechanism?

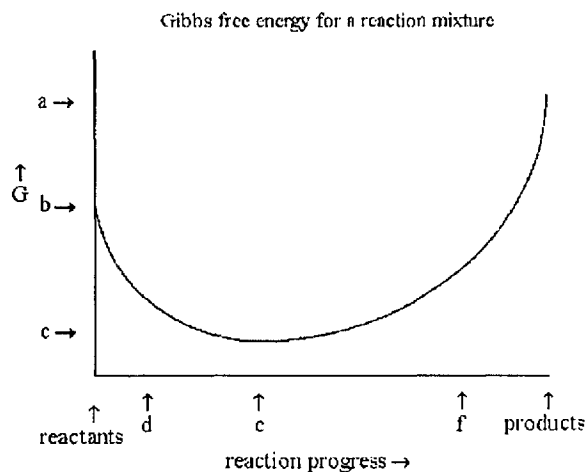
- A) BrO
- B) O
- C) Br
- D) O₃

The following plot shows two titration curves, each representing the titration of 50.00 mL of 0.100 M acid with 0.100 M NaOH.



25) Which of the points a-d represent the half-equivalence point (the middle point) and the equivalence point, respectively, for the titration of a weak acid?

- A) Points a and b
- B) Points a and c
- C) Points b and d
- D) Points c and d



26) According to the diagram above, the forward reaction is:

- A) Nonspontaneous at d, at equilibrium at e, and spontaneous at f.
- B) Spontaneous at d, at equilibrium at e, and nonspontaneous at f.
- C) Spontaneous at d, e, and f.
- D) Nonspontaneous at d and e, and spontaneous at f.

27) A salt bridge is used to:

- A) Provide reactants for the redox reaction.
- B) Allow the ion flow necessary for cell neutrality.
- C) Determine the direction of the cell reaction.
- D) Control whether the cell is electrolytic or galvanic.

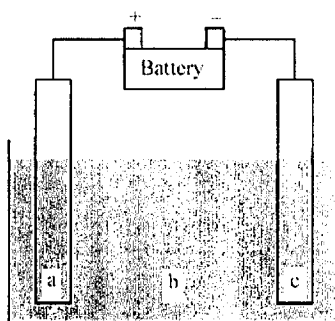
28) Doubling all the stoichiometric coefficients in the redox equation for the cell reaction:

- A) Doubles E° , but does not change ΔG° .
- B) Does not change E° or ΔG° .
- C) Doubles ΔG° , but does not change E° .
- D) Doubles both E° and ΔG° .

29) Which of the following statements concerning the rusting of iron is **false**?

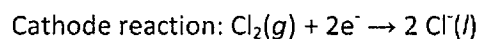
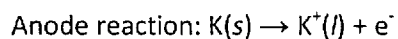
- A) Dissolved salt increases the rate of corrosion by providing ions to carry the current.
- B) The oxidation site can occur at a different place on the metal surface away from the reduction site.
- C) The metal is reduced.
- D) The rusting of iron requires both oxygen and water.

Shown below is an electrochemical cell with anode **a** and cathode **c**. Both the anode and the cathode are inert electrodes. The liquid shown in compartment **b** of the cell is molten potassium chloride, $KCl(l)$.

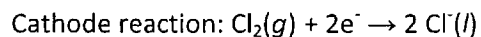
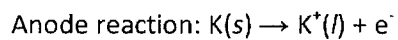


30) Determine whether this is a galvanic or an electrolytic cell and give the reaction occurring at the anode and the reaction occurring at the cathode.

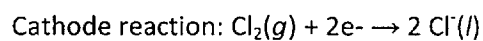
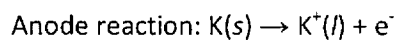
A) Galvanic cell



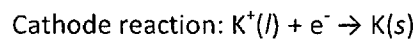
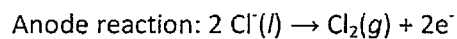
B) Galvanic cell



C) Electrolytic cell



D) Electrolytic cell



Name: _____ Student Number: _____ Tutorial: T _____

PG1:	/12
PG2:	/16
PG3:	/17
Total:	/45

SHORT ANSWER QUESTIONS: Be sure to show your work.

1. (12 marks) A 1.50 L sample of gaseous HI with density of 0.0101 g/cm^3 is heated at 410°C . As time passes, the HI decomposes to gaseous H_2 and I_2 .

The rate law is: $-\Delta [\text{HI}] / \Delta t = k [\text{HI}]^2$, where $k = 0.031 \text{ M}^{-1}\text{s}^{-1}$ at 410°C .

a. Write the balanced equation of the reaction. Calculate the initial concentration of HI, and the initial rate of production of I_2 in M/min

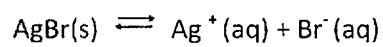
b. Calculate the concentration of HI after a reaction time of 8 hours.

c. Calculate the partial pressure of H_2 after a reaction time of 8 hours.

Continued ...

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2. (16 points) Consider the dissolution of AgBr in water at 25°C:



Relevant data:

$\text{Ag}^+(aq)$: $\Delta H_f^\circ = 105.6 \text{ kJ/mol}$; $S^\circ = 72.7 \text{ J/(K mol)}$; $\Delta G_f^\circ = 77.1 \text{ kJ/mol}$

$\text{Br}^-(aq)$: $\Delta H_f^\circ = -121.5 \text{ kJ/mol}$; $S^\circ = 82.4 \text{ J/(K mol)}$; $\Delta G_f^\circ = -104.0 \text{ kJ/mol}$

$\text{AgBr}(s)$: $\Delta H_f^\circ = -100.4 \text{ kJ/mol}$; $S^\circ = 107.1 \text{ J/(K mol)}$; $\Delta G_f^\circ = -96.9 \text{ kJ/mol}$

a. calculate $\Delta G_{\text{rxn}}^\circ$ for this process of dissolution at 25 °C.

b. Calculate K_{sp} for AgBr at 25 °C.

c. Calculate ΔG for the dissolution of AgBr at 25 °C when $[\text{Ag}^+] = [\text{Br}^-] = 1.00 \times 10^{-5} \text{ M}$.

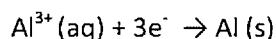
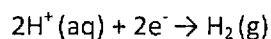
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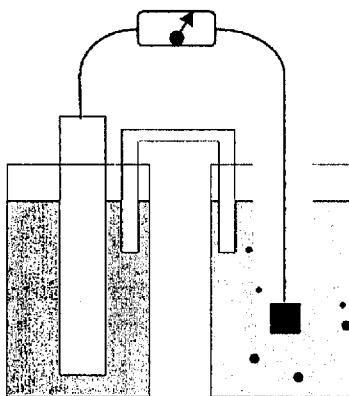
d. analyze in two - three sentences the values for ΔG and Q calculated in c. and the value for K_{sp} calculated in b. and compare them. Are these data consistent and why?

Make sure that your writing is legible.

3. (17 marks) Consider a galvanic cell that uses the following half-reactions:



NaNO_3 has been used as solution in one of the compartments.



a. On the picture above identify in writing:

- the anode, its sign, and the material it is made of;
- the cathode, its sign, and the material it is made of;
- the direction of the electrons;
- the kind of the ions in each compartment and the direction of the ion flow.

Make sure that your writing is legible.

b. write the balanced redox equation and calculate the standard cell potential.

c. calculate the cell potential at 25 °C if the ion concentrations are 0.10 M and the partial pressure of H₂ is 10.0 atm.

d. Calculate ΔG° in kJ and the equilibrium constant K for the cell reaction at 25 °C.

e. Calculate the mass change (in grams) of the aluminum electrode after the cell has supplied a constant current of 10.0 A for 25.0 min.

PHYSICAL AND CHEMICAL CONSTANTS

Atomic mass unit	$1 \text{ a.m.u.} = 1.6605402 \times 10^{-27} \text{ kg}$
Mass of an electron	$m_e = 9.109 \times 10^{-31} \text{ kg}$
Mass of a neutron	$m_n = 1.674 \times 10^{-27} \text{ kg}$
Mass of a proton	$m_p = 1.672 \times 10^{-27} \text{ kg}$
Avogadro's number	$N_A = 6.0221367 \times 10^{23} \text{ mole}^{-1}$
Boltzmann's constant	$k_B = 1.380658 \times 10^{-23} \text{ J K}^{-1}$
Faraday's constant	$F = 9.6485309 \times 10^4 \text{ C mole}^{-1}$
Fundamental unit charge	$e = 1.60217733 \times 10^{-19} \text{ C}$
Gas constant	$R = 8.314510 \text{ J mole}^{-1} \text{ K}^{-1} = 0.082058 \text{ L atm mole}^{-1} \text{ K}^{-1}$
Heat capacity of water	$S = 4.184 \text{ J g}^{-1} \text{ K}^{-1} = 75.4 \text{ J mole}^{-1} \text{ K}^{-1}$
Planck's constant	$h = 6.6260755 \times 10^{-34} \text{ J s}$
Rydberg's constant	$R_H = 2.1798 \times 10^{-18} \text{ J}$ $= 1.097 \times 10^{-2} \text{ nm}^{-1}$
Speed of light	$c = 2.99792458 \times 10^8 \text{ m s}^{-1}$
Zero point	$0^\circ\text{C} = 273.15 \text{ K}$
K_w of H_2O at 25°C	$K_w = 1.00 \times 10^{-14}$
Pi	$\pi = 3.1415927$

CONVERSION FACTORS

$2.54 \text{ cm} = 1 \text{ inch}$
$1 \text{ N} = 1 \text{ kg m s}^{-2}$
$1 \text{ kg} = 2.205 \text{ pounds (lbs)}$
$1 \text{ nm} = 10^{-9} \text{ m}$
$1 \text{ \AA} = 10^{-10} \text{ m}$
$1 \text{ Watt} = 1 \text{ Joule sec}^{-1}$
$1 \text{ Amp} = 1 \text{ C/s}$
$1 \text{ atmosphere (atm)} = 1.01325 \times 10^5 \text{ Pa (N m}^{-2}\text{)} = 760.0 \text{ mm Hg (torr)} = 1.01325 \text{ bar}$
$1 \text{ calorie (cal)} = 4.184 \text{ joules (J)}$
$1 \text{ debye (D)} = 3.335617 \times 10^{-30} \text{ C m}$
$1 \text{ eV/particle} = 96.485 \text{ kJ mole}^{-1} = 23.061 \text{ kcal mole}^{-1}$
$1 \text{ eV} = 1.602 \times 10^{-19} \text{ J} = 8067 \text{ cm}^{-1}$
$1 \text{ kcal mole}^{-1} = 4.184 \text{ kJ mole}^{-1} = 349.73 \text{ cm}^{-1}$
$1 \text{ kJ mole}^{-1} = 0.23901 \text{ kcal mole}^{-1} = 83.591 \text{ cm}^{-1}$
$1 \text{ L atm} = 101.325 \text{ J} = 24.217 \text{ cal}$
$\ln x = 2.3026 \log x$

USEFUL EQUATIONS

$$E = h\nu \quad \lambda = c/\nu \quad \lambda = h/mv \quad E_{\text{photon}} = h\nu_0 + E_k \quad E_n = -R_H Z^2/n^2$$

$$PV = nRT \quad (P + n^2 a/V^2)(V - nb) = nRT$$

$$KE = \frac{1}{2} m u^2 = 3RT/(2N_A) \quad u_{\text{rms}} = (3RT/M)^{1/2}$$

$$\Delta T_b = K_b m \quad \Delta T_f = K_f m \quad \Pi = MRT \quad P_{\text{solution}} = X_{\text{solvent}} P_{\text{solvent}}$$

$$ax^2 + bx + c = 0 \quad x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \quad \ln(ab) = \ln(a) + \ln(b) ; \quad \ln(a/b) = -\ln(b/a)$$

$$K_p = K_c(RT)^{\Delta n} ; \quad \Delta n = c + d - (a + b) \quad \text{Arrhenius equation: } k = Ae^{-E_a/RT} \quad \ln\left(\frac{k_2}{k_1}\right) = \left(\frac{-E_a}{R}\right)\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\text{First order reaction: } \ln\{[A]_0/[A]\} = kt \quad t_{1/2} = 0.693/k$$

$$\text{Second order reaction: } 1/[A] - 1/[A]_0 = kt \quad t_{1/2} = 1/k[A]_0$$

$$\text{Zero order reaction: } [A] = -kt + [A]_0$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] \quad \text{pOH} = -\log[\text{OH}^-] \quad \text{pH} + \text{pOH} = 14 \quad K_a \times K_b = K_w$$

$$q = nC\Delta T \quad w = -P\Delta V \quad \Delta E = q + w \quad \Delta H = \Delta E + P\Delta V$$

$$S = k \ln W \quad \Delta S = \frac{q}{T} \quad \Delta S_{\text{univ}} = \Delta S + \Delta S_{\text{surr}}$$

$$\Delta H^\circ = \sum \text{coeff}_p \Delta H_f^\circ(\text{pds}) - \sum \text{coeff}_r \Delta H_f^\circ(\text{rcts})$$

$$\Delta S^\circ = \sum \text{coeff}_p S^\circ(\text{pds}) - \sum \text{coeff}_r S^\circ(\text{rcts})$$

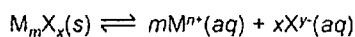
$$\Delta G^\circ = \sum \text{coeff}_p \Delta G_f^\circ(\text{pds}) - \sum \text{coeff}_r \Delta G_f^\circ(\text{rcts})$$

$$\Delta G = \Delta H - T\Delta S \quad \Delta G = \Delta G^\circ + RT \ln Q \quad \Delta G^\circ = -RT \ln K$$

$$E = E^\circ - \frac{RT}{nF} \ln Q \quad I = \frac{nC}{t} \quad \Delta G = -nFE$$

Overall Reaction Order	Units for k
Zeroth order	M/s or M s ⁻¹
First order	1/s or s ⁻¹
Second order	1/(M s) or M ⁻¹ s ⁻¹
Third order	1/(M ² s) or M ⁻² s ⁻¹

$$\text{pH} = \text{p}K_a + \log \frac{[\text{conjugate base}]}{[\text{acid}]}$$



$$K_{\text{sp}} = [M^{n+}]^m [X^{y-}]^x$$

Standard Reduction Potentials (in Volts), 25°C

Reaction	E°(V)
$\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Cl}^-$	+1.36
$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$	+1.23
$\text{Br}_2 + 2\text{e}^- \rightarrow 2\text{Br}^-$	+1.07
$\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$	+0.77
$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$	+0.80
$\text{I}_2 + 2\text{e}^- \rightarrow 2\text{I}^-$	+0.54
$\text{Cu}^+ + \text{e}^- \rightarrow \text{Cu}$	+0.52
$\text{Fe}(\text{CN})_6^{3-} + \text{e}^- \rightarrow \text{Fe}(\text{CN})_6^{4-}$	+0.36
$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$	+0.34
$\text{Cu}^{2+} + \text{e}^- \rightarrow \text{Cu}^+$	+0.15
$\text{Sn}^{4+} + 2\text{e}^- \rightarrow \text{Sn}^{2+}$	+0.15
$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$	0.00
$\text{Fe}^{3+} + 3\text{e}^- \rightarrow \text{Fe}$	-0.04
$\text{Pb}^{2+} + 2\text{e}^- \rightarrow \text{Pb}$	-0.13
$\text{Ni}^{2+} + 2\text{e}^- \rightarrow \text{Ni}$	-0.26
$\text{Fe}^{2+} + 2\text{e}^- \rightarrow \text{Fe}$	-0.41
$\text{Cr}^{3+} + 3\text{e}^- \rightarrow \text{Cr}$	-0.74
$\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}$	-0.76
$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^-$	-0.83
$\text{V}^{2+} + 2\text{e}^- \rightarrow \text{V}$	-1.18
$\text{Mn}^{2+} + 2\text{e}^- \rightarrow \text{Mn}$	-1.18
$\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}$	-1.66
$\text{Mg}^{2+} + 2\text{e}^- \rightarrow \text{Mg}$	-2.37

Continued ...

