

# GEOCHEMISTRY

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KP CLASSES

# CHAPTER 1 INTRODUCTION TO ELEMENTS

## 1.1 Properties of Elements

An element is a substance whose atoms all have the same number of protons or atomic number.

- Ionization potential- The First Ionization Potential of an atom is the energy required to the least tightly bound electron. The Second Ionization Potential is the energy required to remove a second electron.
- Electron affinity- It is defined as the change in energy (in kJ/mole) of a neutral atom when an electron is added to the atom to form a negative ion. It is the energy given up in reactions.
- Electronegativity- It is a measure of an atom's ability to attract the shared electrons of a covalent bond to itself. If atoms bonded together have the same electronegativity, the shared electrons will be equally shared. It quantifies the tendency of an element to attract a shared electron when bonded to another element.

## 1.2 Atomic Structure

The 92 naturally occurring chemical elements (90, in fact, because promethium and technetium are no longer found in their natural state on Earth) are composed of a nucleus of subatomic nucleons orbited by negatively charged electrons.

- Nucleons are positively charged protons and neutral neutrons. As an atom contains equal numbers of protons and electrons with equal but opposite charges, it carries no net electrical charge. The mass of a proton is 1836 times that of an electron.
- The chemical properties of elements are largely, although not entirely, determined by the way their outermost shells of electrons interact with other elements. Ions are formed when atoms capture surplus electrons to give negatively charged anions or when they shed electrons to give positively charged cations.
- A nuclide is an atomic nucleus characterized by the number  $Z$  of its protons and the number  $N$  of its neutrons regardless of its cloud of electrons. The mass number  $A$  is the sum of the nucleons  $N + Z$ .
- Two nuclides with the same number  $Z$  of protons but different numbers  $N$  of neutrons will be accompanied by the same suite of electrons and so have very similar chemical properties; they will be isotopes of the same element.
- An isotope is radioactive if its nucleus undergoes spontaneous change such as occurs, for instance, when alpha particles (two protons and two neutrons) or electrons are emitted. It changes into a different isotope, referred to as radiogenic, by giving out energy, usually in the form of gamma radiation, some of which is harmful for humans.
- The vast majority of natural isotopes of naturally occurring elements are stable, i.e. the number of their protons and neutrons remains unchanged, simply because most radioactive isotopes have vanished over the course of geological time.

## 1.3 The Periodic Table

- The atomic number of an element is equal to the number of its protons. We have seen before that the atom's mass number is equal to the number of particles making up its nucleus.

- Dimitri Mendeleev’s great discovery in 1871 was to demonstrate the periodic character of the properties of elements when ordered by ascending atomic number.
- Melting point, energy of formation, atomic radius, and first ionization energy all vary periodically as we work through Mendeleev’s table. The geochemical properties of elements are reflected by their position in this table.
- The alkali metals (Li, Na, K, Rb, Cs), alkaline-earth metals (Be, Mg, Ca, Sr, Ba), titanium group elements (Ti, Zr, Hf), but also the halogens (F, Cl, Br, I), inert gases (He, Ne, Ar, Kr, Xe), rare-earths (lanthanides), or actinides (uranium family) all form groups sharing similar chemical properties.

I		II				III		IV		V		VI		VII		VIII																			
1	H																2																		
3	Li	4	Be					5	6	7	8	9	10	11	12		13																		
11	Na	12	Mg					13	14	15	16	17	18	19	20		21																		
19	K	20	Ca	21	Sc	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36															
37	Rb	38	Sr	39	Y	40	Zr	41	Nb	42	Mo	(Tc)	44	Ru	45	Rh	46	Pd	47	Ag	48	Cd	49	In	50	Sn	51	Sb	52	Te	53	I	54	Xe	
55	Cs	56	Ba	57	La*	72	Hf	73	Ta	74	W	75	Re	76	Os	77	Ir	78	Pt	79	Au	80	Hg	81	Tl	82	Pb	83	Bi	84	Po	85	At	86	Rn
87	Fr	88	Ra	89	Ac**																														
*Lanthanides				57	58	59	60	61	62	63	64	65	66	67	68	69	70	71																	
**Actinides				89	90	91	92	93	94																										

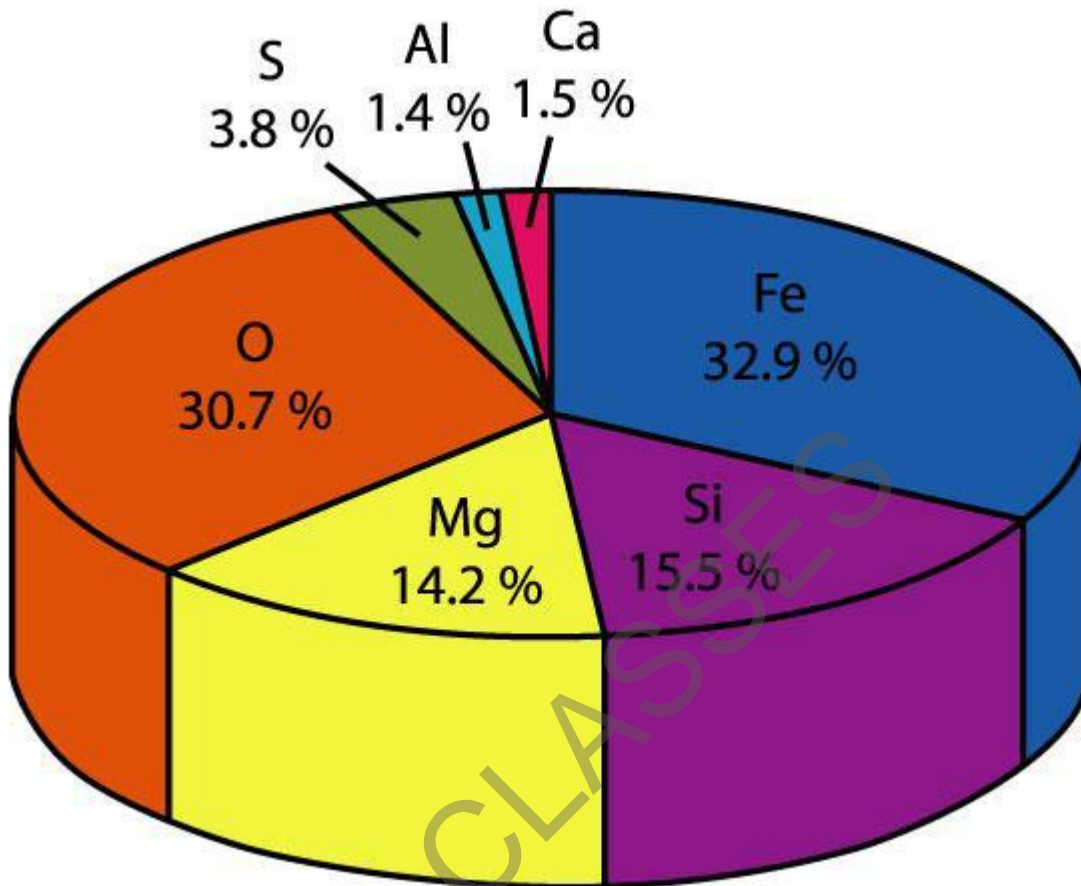
Os Siderophile   
 Cu Chalcophile   
 Rb Lithophile   
 N Atmophile

Mendeleev’s periodic table of the elements and their geochemical classification after Goldschmidt.

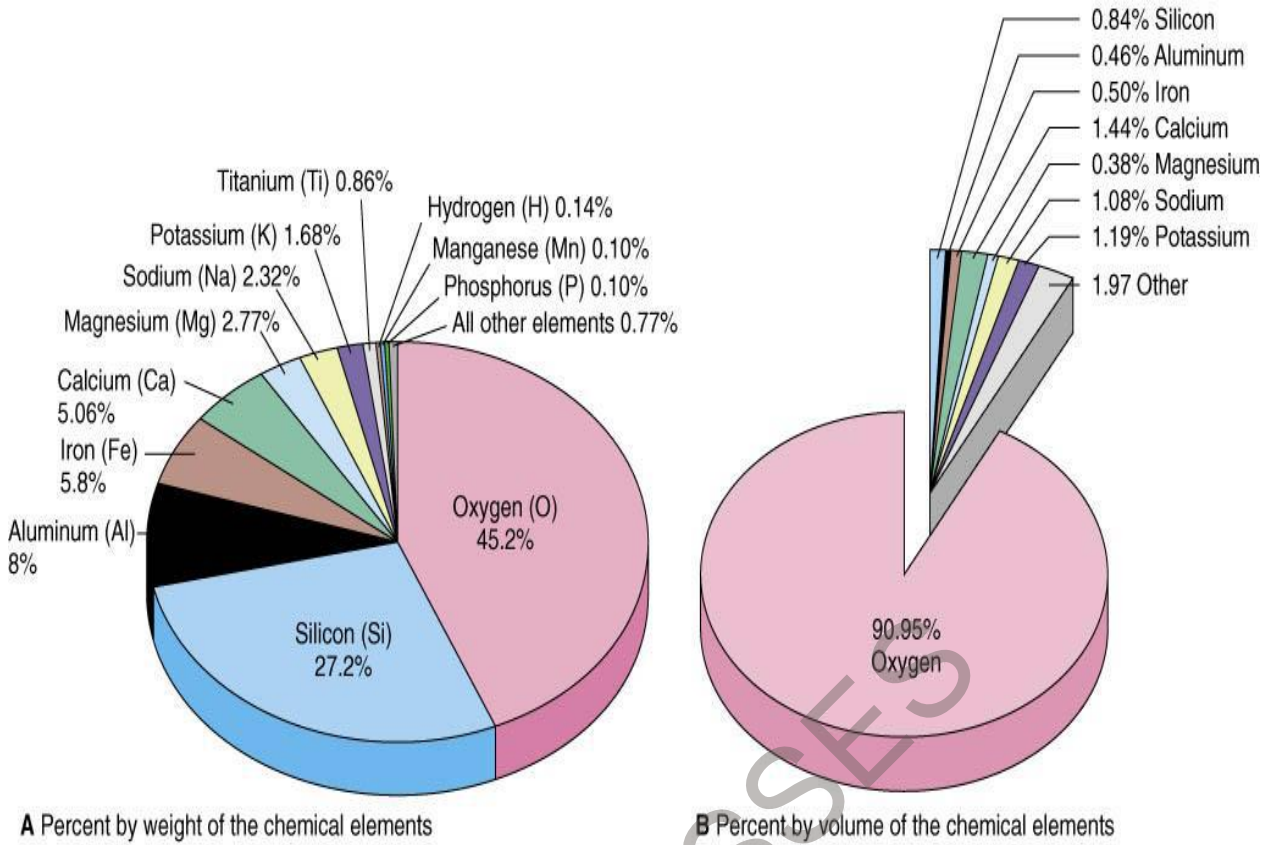
- In the periodic table, groups I (alkali metals) and II (alkaline-earth metals) correspond to the filling of s orbitals, and groups III to VIII to that of the p orbitals. The intermediate groups (transition elements such as iron and platinum) differ in the occupation of their d orbitals.
- When occupied, these d orbitals are normally closer to the nucleus than the s orbitals of the next shell out. Occupation of the orbitals is noted  $nxi$ , where x represents the type of orbital (s, p, d, f), n its principal quantum number and i the number of electrons it contains.

### 1.4 Abundance of Elements

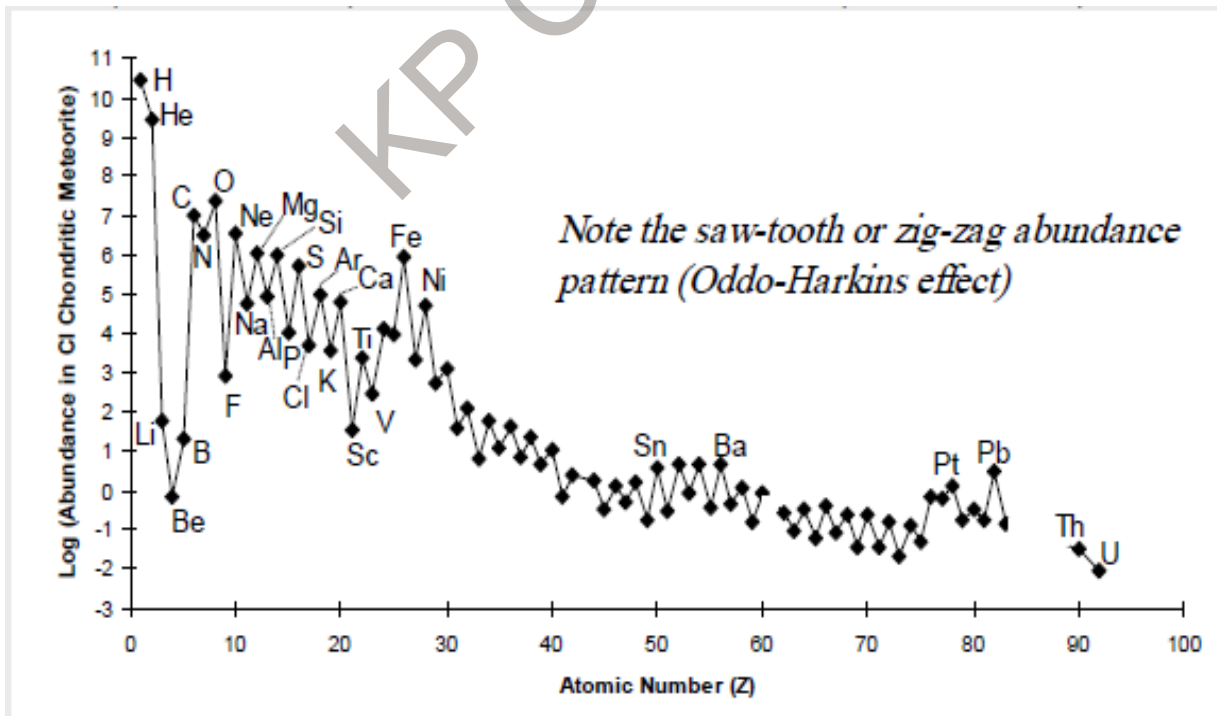
- Seven elements that make up ~97% of the Earth by mass, and which make up various minerals and rocks are-



- Oxygen is the dominant element in the crust (about 47 per cent by weight and 94 per cent by volume). The other major element is silicon, which is about 28 per cent by weight (but less than 1 per cent by volume because of the small size of the silicon atom). The processes involved in the formation of the crust separated certain elements from the main body of the earth and concentrated them in the crust. Even though many of these elements are not abundant in the crust, they have a higher concentration there than in the rest of the earth. The main elements that make up the Earth's crust (by mass and by volume) are-



When the relative abundances of the elements are plotted against atomic number, certain regularities and differences are observed.



- The extreme abundance of hydrogen and helium (more than 99 percent by weight of all atoms).
  - The general decrease in abundance with increasing atomic number.
  - The relatively low abundance of some elements (such as lithium, beryllium, boron, and scandium) and the relatively high abundance of other elements (such as iron, nickel, and lead).
  - The greater abundance of even atomic number elements as compared to odd atomic number elements (Oddo Harkins effect).
- The relative proportions of the major elements (Cl, Na, Mg, S, Ca, and K) in seawater are constant. This is true even though the total amount of dissolved salts (salinity) is very low and shows some variation from place to place. Those elements that are involved in biological activity (such as C, O, N, and P) vary in concentration with depth, mainly because photosynthesis can occur near the surface but not in deeper water.
- The major dissolved gases in seawater (N<sub>2</sub>, O<sub>2</sub>, and CO<sub>2</sub>) all show large variations in concentration.
- There are some critical features in the solar abundance of elements which can be linked to their origin and origin of elements. 1) Hydrogen and helium are the two primordial elements that formed during Big Bang and dominated the early universe. Expectedly they are the two most abundant elements in the solar system. 2) Beyond helium, the abundance of the first 50 elements decreases rapidly perhaps reflecting of increasing difficulty in synthesizing these elements. 3) The abundances of elements having atomic number more than 50 are very low and does not change appreciably with atomic number. Most of these elements are produced only in large-mass stars during supernova explosion in very restricted astrophysical environments, which explains their low abundances. 4) The abundances of Li, Be and B are anomalously low compared to that of their neighbours and can be explained by the fact that these elements are not synthesized either during Big Bang or stellar nucleosynthesis (except traces of <sup>7</sup>Li during Big Bang) and are created only during galactic nucleosynthesis. 5) Iron is far the most abundant compared to those having atomic numbers close to it. Iron has the highest binding energy per nucleon and therefore formation of iron leads to a dead end of nuclear fusion reactions during stellar evolution resulting in higher abundance.

Composition of the Earth's upper mantle(depleted MORB):

COMPOUND	MASS PERCENT
SiO <sub>2</sub>	44.71
Al <sub>2</sub> O <sub>3</sub>	3.98
FeO	8.18
MnO	0.13
MgO	38.73
CaO	3.17
Na <sub>2</sub> O	0.13
Cr <sub>2</sub> O <sub>3</sub>	0.57
TiO <sub>2</sub>	0.13
NiO	0.24
K <sub>2</sub> O	0.006
P <sub>2</sub> O <sub>5</sub>	0.019

Mass per volume fraction, in kg/L. (The average density of sea water in the surface is 1.025 kg/L)

Element	W1	W2	Element	W1	W2
Hydrogen	$1.08 \times 10^{-1}$	$1.1 \times 10^{-1}$	Potassium	$3.99 \times 10^{-4}$	$3.9 \times 10^{-4}$
Helium	$7 \times 10^{-12}$	$7.2 \times 10^{-12}$	Calcium	$4.12 \times 10^{-4}$	$4.1 \times 10^{-4}$
Carbon	$2.8 \times 10^{-5}$	$2.8 \times 10^{-5}$	Scandium	$6 \times 10^{-13}$	$< 4 \times 10^{-12}$
Nitrogen	$5 \times 10^{-7}$	$1.6 \times 10^{-5}$	Manganese	$2 \times 10^{-10}$	$1.9 \times 10^{-9}$
Oxygen	$8.57 \times 10^{-1}$	$8.8 \times 10^{-1}$	Iron	$2 \times 10^{-9}$	$3.4 \times 10^{-9}$
Fluorine	$1.3 \times 10^{-6}$	$1.3 \times 10^{-6}$	Zinc	$4.9 \times 10^{-9}$	$1.1 \times 10^{-8}$
Sodium	$1.08 \times 10^{-2}$	$1.1 \times 10^{-2}$	Arsenic	$3.7 \times 10^{-9}$	$2.6 \times 10^{-9}$
Magnesium	$1.29 \times 10^{-3}$	$1.3 \times 10^{-3}$	Bromine	$6.73 \times 10^{-5}$	$6.7 \times 10^{-5}$
Aluminium	$2 \times 10^{-9}$	$1 \times 10^{-9}$	Rubidium	$1.2 \times 10^{-7}$	$1.2 \times 10^{-7}$
Silicon	$2.2 \times 10^{-6}$	$2.9 \times 10^{-6}$	Strontium	$7.9 \times 10^{-6}$	$8.1 \times 10^{-6}$
Phosphorus	$6 \times 10^{-8}$	$8.8 \times 10^{-8}$	Zirconium	$3 \times 10^{-11}$	$2.6 \times 10^{-11}$
Chlorine	$1.94 \times 10^{-2}$	$1.9 \times 10^{-2}$	Silver	$4 \times 10^{-11}$	$2.8 \times 10^{-10}$

## PRACTICE QUESTIONS

### Previous year Moderate Questions

#### IIT JAM 2020

1. The most abundant element in the Earth's continental crust is  
 a) silicon      b) aluminium      c) oxygen      d) iron

Ans-C

#### IIT JAM 2018

2. The second-most abundant oxide in the Earth's crust is  
 a)  $Al_2O_3$       b)  $SiO_2$       c)  $CaO$       d)  $Na_2O$

Ans-A

#### IIT JAM 2016

3. The most abundant metal (by weight %) in the Earth's crust is  
 a) Al      b) Fe      c) Na      d) Mg

Ans-B

#### GATE 2015

4. The two most abundant elements in the Earth are  
 a) oxygen and iron      b) iron and magnesium  
 c) oxygen and silicon      d) iron and silicon

Ans- A



**CSIR NET 2016 DEC**

5. The relative abundance of elements, in decreasing order, in the Earth is  
 a) iron, oxygen, silicon, magnesium                      b) oxygen, silicon, aluminium, iron  
 c) iron, magnesium, silicon, oxygen                      d) oxygen, silicon, aluminium, magnesium

Ans-A

**CSIR NET 2017 JUNE**

6. Which of the following represents the correct increasing order of abundance in the earth's crust?  
 a) O-Si-Al                      b) Si-O-Al                      c) Al-Si-O                      d) O-Al-Si

Ans-A

**CSIR NET 2018 JUNE**

7. What is the third most abundant element (after H and He) in the solar system?  
 a) O                      b) Fe                      c) Si                      d) Ni

Ans-A

**Previous year Difficult Questions**

**IIT JAM 2020**

8. Which of the following statements in relation to the solar system is/are correct?  
 a) The most abundant elements are H and He.  
 b) The abundances of elements with atomic numbers 1-50 show an overall decreasing trend.  
 c) The abundances of heavier elements (atomic number >50) are mostly higher than that of lighter elements (atomic number <50).  
 d) Elements having odd atomic numbers are more abundant than their immediate neighbours  
 A,B

9. The wt.% (correct to two decimal places) of Cu in chalcopyrite (CuFeS<sub>2</sub>) (atomic weight of Cu=63.55, Fe=55.85, S=32.07) is \_\_\_\_.

Ans-

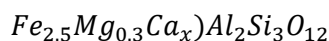
$$\text{At wt of Cu/Total at wt of Chalcopyrite} = \frac{63.55}{(63.55+55.85 + (2*32.07))} * 100 = 34.62\%$$

**IIT JAM 2018**

10. In the garnet formula (Fe<sub>2.5</sub>Mg<sub>0.3</sub>Ca<sub>x</sub>)Al<sub>2</sub>Si<sub>3</sub>O<sub>12</sub>, x represents the number of atoms of Ca. The mole % of grossular in the garnet is \_\_\_\_ (answer in one decimal place).

6.6 to 6.8

Charge on Fe - +2, Mg +2, Ca+2, Al+3, Si+4, O<sup>2-</sup>



$$2*2.5+2*0.3+2x+3*2-2*12=0$$

$$5+0.6+2x+6+12-24=0$$

$$2x=24-23.06$$

$$2x=0.4$$

$$X=0.2$$

$$\text{Mole \% of grossular} = \frac{\text{No. of moles of grossular}}{\text{Total no of moles}} * 100$$

$$= \frac{0.2}{(2.5+0.3+0.2)} * 100 = 6.66\%$$

**GATE 2019**

11. Choose the correct combination of the following two statements.  
 Statement I: Four elements that make up about 90% of the bulk earth are Fe, O, Si and Mg (in decreasing order of wt% abundance).  
 Statement II: The four most abundant elements in the Earth's crust (in decreasing order of wt % abundance are O, Si, Al and Fe.
- Both statements I and II are correct.
  - Both statements I and II are incorrect.
  - Statement I is correct and Statement II is incorrect.
  - Statement I is incorrect and Statement II is correct.

A

**GATE 2017**

12. The Bulk Silicate Earth (BSE) is best approximated by the average
- enriched upper mantle
  - mantle and continental crust composition
  - depleted mantle composition
  - primitive upper mantle composition

B

**GATE 2016**

13. The ionic strength of a solution having 0.5 molal NaCl and 0.25 molal CaCl<sub>2</sub> is \_\_\_\_\_ molal.

Ans- 1.25

NaCl=0.5 molal = Na<sup>+</sup> + Cl<sup>-</sup>

CaCl<sub>2</sub>=0.25 molal= Ca<sup>2+</sup> + 2Cl<sup>-</sup>

$$I = \frac{1}{2} \sum_{i=1}^n C_i Z_i^2$$

C<sub>i</sub>= molal concentration of ion i

Z<sub>i</sub>= charge no of ion i

$$I = \frac{1}{2} \{0.5(+1)^2 + (0.5)(-1)^2 + 0.25(+2)^2 + 0.25 * 2(-2)^2\}$$

$$I = \frac{1}{2} (2.5)$$

$$I = 1.25$$

**GSI 2015**

14. Oddo- Harkins effect in REE normalization.

**Level 6(Multiple Select Questions)**

15. Elements that make up ~97% of the Earth by mass are
- Si
  - O
  - Mn
  - Mg

Ans- A, B, D

16. Which of the following statements in relation to the solar system is/are correct?
- The most abundant elements are H and He.
  - The abundances of elements with atomic numbers 1-50 show an overall decreasing trend.

c) The abundances of heavier elements (atomic number >50) are mostly higher than that of lighter elements (atomic number <50).

d) Elements having odd atomic numbers are more abundant than their immediate neighbours

Ans- A,B

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## CHAPTER 2 FUNDAMENTAL THERMODYNAMICS CONCEPTS

### 2.1 Laws of Thermodynamics

#### First Law of Thermodynamics

- It states that the energy is conserved in any transformation or the internal energy,  $U$ , of an isolated system is constant.
- In a closed system, there cannot be a loss or gain of mass, but there can be a change in energy,  $dU$ .
- The change in energy is the difference between the heat,  $Q$ , gained or lost, and the work,  $W$  done by the system. So,
  - $dU = dQ - dW$  (1)
- Work,  $W$ , is defined as force x distance. Since Pressure,  $P$ , is defined as Force/surface area, Force =  $P$  x surface area, and thus
  - $W = P \times \text{surface area} \times \text{distance} = P \times V$ , where  $V$  is volume.
- If the work is done at constant pressure, then  $W = PdV$ . Substitution of this relationship into (1) yields:
  - $dU = dQ - PdV$  (2)
  - Work done by the system is taken as negative
  - Work done on the system is taken as positive, hence energy flowing into the system is considered as positive.

#### Second Law of Thermodynamics

- It states that the change in heat energy of the system is related to the amount of disorder in the system.
  - Entropy is a measure of disorder, and so at constant Temperature and Pressure:
  - $dQ = TdS$  (3)
  - Thus, substituting into (2) we get:
  - $dU = TdS - PdV$  (4)
  - Entropy Change in Mixing of Two Ideal Gases:
- For an ideal gas, the energy is not a function of volume, and, for each gas, there is no change in temperature.
- The energy of the overall system is unchanged, the two gases were at the same temperature initially, so the final temperature is the same as the initial temperature.
- The entropy change of each gas is thus the same as that for a reversible isothermal expansion from the initial specific volume  $V_i$  to the final specific volume,  $V_f$ .
- For a mass  $m$  of ideal gas, the entropy change is
  - $\Delta S = mR \ln \left( \frac{v_f}{v_i} \right)$
  - Enthalpy:
- Enthalpy is a composite function and is the sum of the internal energy plus the product  $PV$ :
  - $H = U + PV$  (5)
  - $dH = dU + PdV + VdP$
  - $= TdS - PdV + PdV + VdP$
  - $dH = TdS + VdP$  (6)

- Helmholtz Free Energy:
- Rearrange equation (5) to  $dU - TdS = -PdV$ .
  - $-PdV$  term is the work term
  - $TdS$  term is the heat function
  - $TdS$  is the energy unavailable for work
  - $dU - TdS$  is the amount of internal energy available for work, or the Free Energy.
  - It is defined as  $A$ , the Helmholtz Free Energy:
    - $A = U - TS$  (7)
    - $dA = dU - d(TS)$
    - $dA = dU - SdT - TdS$

## 2.2 Gibbs Free Energy

- $G$ , is defined as the energy in excess of the internal energy as follows:
  - $G = H - TS$
  - $dG = U + PV - TS$  (8)
  - $dG = TdS + VdP - TdS - SdT$
  - $dG = VdP - SdT$  (9)
- For a system in equilibrium at constant  $P$  and  $T$ ,  $dG = 0$ . If we differentiate equation (9) with respect to  $P$  at constant  $T$ , the result is:
  - $\left(\frac{\partial G}{\partial P}\right)_T = V$  (10)
- If we differentiate equation (9) with respect to  $T$  at constant  $P$  we get:
  - $\left(\frac{\partial G}{\partial T}\right)_P = -S$  (11)
- Equation (10) tells us that phases with small volume are favoured at higher pressure
- Equation (11) tells us that phases with high entropy (high disorder) are favoured at higher temperature.
- Equation (9) tells us that the Gibbs Free Energy is a function of  $P$  and  $T$ .
- If two phases  $A$  and  $B$  are in equilibrium or  $G_A = G_B$  then we can write:
  - $\Delta G = G_B - G_A = 0$
- Taking a similar approach, we can rewrite equation (9), above, as:
  - $\Delta G = \Delta VdP - \Delta SdT$  (12)
- $\Delta G$  = the change in Gibbs Free Energy of the reaction =  $\Delta G$  products -  $\Delta G$  reactants
- $\Delta S$  = the change in entropy of the reaction =  $\Delta S$  products -  $\Delta S$  reactants
- $\Delta V$  = the change in volume of the reaction =  $\Delta V$  products -  $\Delta V$  reactants
- $\Delta G$ ,  $\Delta H$ ,  $\Delta S$ , and  $\Delta V$  are dependent of Pressure and Temperature, but at any given  $T$  &  $P$ :
  - If  $\Delta G < 0$  (negative) the chemical reaction will be spontaneous and run to the right,
  - If  $\Delta G = 0$  the reactants are in equilibrium with products,
  - If  $\Delta G > 0$  (positive) the reaction will run from right to left.

## 2.3 Maxwell's Relation

Consider the given equation

$$dU = TdS - PdV$$

the partial differential of U in terms of S and V we have:

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

Rewrite it as:

$$\left(\frac{\partial U}{\partial S}\right)_V = T \quad \text{or} \quad \left(\frac{\partial U}{\partial V}\right)_S = -P$$

$$\left(\frac{\partial U}{\partial V}\right)_S = \left(\frac{\partial P}{\partial S}\right)_V$$

Other Maxwell Relations are:

$$\text{From } dH \quad \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \quad (13)$$

$$\text{From } dA \quad \left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T \quad (14)$$

$$\text{From } dG \quad \left(\frac{\partial V}{\partial T}\right)_P = \left(\frac{\partial S}{\partial P}\right)_T \quad (15)$$

## 2.4 Gibbs Phase Rule

Gibbs' Phase Rule provides the theoretical foundation, based in thermodynamics, for characterizing the chemical state of a (geologic) system, and predicting the equilibrium relations of the phases (minerals, melts, liquids, vapours) present as a function of physical conditions such as pressure and temperature. Gibbs' Phase Rule also allows us to construct phase diagrams to represent and interpret phase equilibria in heterogeneous geologic systems. In the simplest understanding of phase diagrams, stable phase (mineral) assemblages are represented as "fields" in "P-T space", and the boundaries between stable phase assemblages are defined by lines (or curves) that represent reactions between the phase assemblages. The reaction curves actually represent the condition (or the locus of points in P-T space) where  $\Delta G_{\text{rxn}} = 0$ .

- Gibbs Phase Rule is expressed by the simple formulation:  $P + F = C + 2$ , where
- P is the number of phases in the system
  - A phase is any physically separable material in the system. Every unique mineral is a phase (including polymorphs); igneous melts, liquids (aqueous solutions), and vapor are also considered unique phases.
- C is the minimum number of chemical components required to constitute all the phases in the system.
- F is the number of degrees of freedom in the system (also referred to as the variance of the system).
  - For geologic applications, this generally refers to the number of variables (e.g. pressure and temperature) that can be independently changed without altering the state of the system (i.e. the number of phases and their compositions are constant).
- The integer in the Gibbs Phase Rule is related to the number of intensive parameters (i.e. those that are independent of mass; such as pressure and temperature) that are being considered. Note that many phase diagrams consider only one intensive parameter.
- It is important to recognize that the simple formulation of Gibbs' Phase Rule is derivative from fundamental thermodynamic principles. The Gibbs- Duhem equation establishes the relationship

between the intensive parameters temperature (T) and pressure (P) and the chemical potential of all components  $(\mu_i)$  in the system:  
 $dG = Vdp - SdT + \sum n_i d\mu_i$

This means that there are

- C + 2 independent variables that describe the system: P, T and one each for the chemical potential for all components, and
- P independent equations (of the Gibbs-Duhem form) that describe the energetics of the system--one equation for each phase.

In mathematical terms, the variance (F) is determined by the difference between (C+2) variables and (P) equations. Thus,

$$F = C + 2 - P \text{ or as originally written, } P + F = C + 2$$

## 2.5 Clausius – Clapeyron Equation

At equilibrium, as we have just seen,  $\Delta G = 0$ , so from equation (12)  $0 = \Delta VdP - \Delta SdT$

Rearranging this equation yields

$$\left(\frac{dP}{dT}\right) = \frac{\Delta S}{\Delta V} \quad (16)$$

This relation is known as the Clausius - Clapeyron Equation. It is important because it tells us the slope of the equilibrium boundary or reaction boundary on a Pressure versus Temperature phase diagram.

Temperature dependence of Enthalpy Entropy and Gibbs Free Energy:

- The isobaric heat capacity defines the relation of enthalpy with temperature as
- $\left(\frac{\partial H}{\partial T}\right)_P = C_p \quad (17)$
- $dH = C_p dT \quad (18)$
- Where  $C_p$  is the heat capacity at constant pressure.
- The heat capacity is the amount of heat necessary to raise the temperature of the substance by  $1^\circ \text{K}$  equation to determine H at the new temperature:
- $H_T = H_{298} + C_p(T-298) \quad (19)$
- $\Delta H_T = \Delta H_{298} + \Delta C_p(T-298) \quad (20)$
- The temperature dependence of entropy, S, is given by:
- $\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_p}{T} \quad (21)$
- At 298 K and 0.1MPa, for a reaction, this can be written as:
- $\Delta S_T = \Delta S_{298} + \Delta C_p \ln\left(\frac{T}{298}\right) \quad (22)$
- Equation (8) can then be combined with equations (20) and (22) to give the dependence of  $\Delta G$  on temperature:
- $\Delta G_{T,P} = \Delta H_{298} + \Delta C_p(T - 298) - T \left[ \Delta S_{298} + \Delta C_p \ln \frac{T}{298} \right]$
- Simplify this even further if we assume that for a reason  $\Delta C_p = 0$
- $\Delta G_{T,P} = \Delta H_{298} - T[\Delta S_{298}] \quad (23)$
- This can be written as by substituting in ideal gas law
- $\left(\frac{\partial G}{\partial P}\right)_T = \frac{RT}{P} dP \quad (24)$
- Integrating this from P1 to P2 results in:
- $G_{P2} - G_{P1} = RT \ln \frac{P2}{P1} \quad (25)$