CHEMISTRY

Unit 6

CHEMICAL ENERGETICS

Short Questions • Numericals • Long Questions

Complete Study Booklet with Answer Keys

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Section 1 | Short Questions

Q1. Difference between Exothermic and Endothermic Reactions.

Exothermic reaction: heat is released, Delta H is negative, products have less energy than reactants (e.g. combustion of methane).

Endothermic reaction: heat is absorbed, Delta H is positive, products have more energy than reactants (e.g. decomposition of calcium carbonate).

Q2. What do you understand by enthalpy of a system?

Enthalpy (H) is the total heat content of a system at constant pressure - the sum of internal energy and the product of pressure and volume: H = U + PV.

Q3. Difference between Entropy (S) and Gibbs Free Energy (G).

Entropy (S): a measure of randomness or disorder in a system; determines the direction of spontaneous change; higher S means more disorder.

Gibbs Free Energy (G): the energy available to do useful work; determines the spontaneity of a reaction; G = H - TS.

Q4. Distinguish between standard enthalpy of reaction and standard enthalpy of formation.

Standard Enthalpy of Reaction (Delta Hr): the enthalpy change when a chemical reaction occurs under standard conditions - can apply to any reaction (e.g. CH4 + 2O2 -> CO2 + 2H2O).

Standard Enthalpy of Formation (Delta Hf): the enthalpy change when 1 mole of a compound is formed from its elements in standard states - specific to compound formation (e.g. C(s) + 2H2(g) -> CH4(g)).

Q5. Define standard enthalpy of Solution, Hydration, Atomization and Combustion, with an example each.

(i) Standard Enthalpy of Solution: Delta H when 1 mole of a substance dissolves in a solvent. Example: NaCl(s) -> Na+(aq) + Cl-(aq)

(ii) Standard Enthalpy of Hydration: Delta H when 1 mole of gaseous ions are hydrated. Example: Na+(g) -> Na+(aq)

(iii) Standard Enthalpy of Atomization: Delta H when 1 mole of gaseous atoms is formed from an element in its standard state. Example: 1/2 H2(g) -> H(g)

(iv) Standard Enthalpy of Combustion: Delta H when 1 mole of a substance completely burns in oxygen. Example: CH4(g) + 2O2(g) -> CO2(g) + 2H2O(g)

Q6. Explain why the lattice enthalpy of an ionic compound is typically a large negative value.

Lattice enthalpy is the energy released when gaseous ions form an ionic solid.

The strong electrostatic attraction between oppositely charged ions releases a large amount of energy, giving a large negative value.

Q7. What factors influence the magnitude of the lattice enthalpy?

Ionic Charges: higher charge gives stronger attraction and a more negative lattice enthalpy.

Ionic Radii: smaller ion size gives stronger attraction and a more negative lattice enthalpy.

Q8. Explain why the enthalpy of hydration is always an exothermic process for gaseous ions.

Energy is released when water molecules attract and surround gaseous ions, mainly through ion-dipole interactions between the ions and water molecules.

Q9. For CH4(g) + 2O2(g) -> CO2(g) + 2H2O(g), identify the bonds broken and formed.

Bonds broken (reactants): 4 C-H bonds in CH4, and 2 O=O double bonds.

Bonds formed (products): 2 C=O bonds in CO2, and 4 O-H bonds in H2O.

Q10. For a reaction to be spontaneous, what is the required sign of Delta G? When is a reaction always spontaneous?

For a reaction to be spontaneous, Delta G must be negative.

A reaction is always spontaneous when Delta H is negative (exothermic) AND Delta S is positive (increase in disorder).

Q11. The enthalpy of solution can be either positive or negative. Explain.

A positive Delta H(sol) means energy is absorbed and the process is endothermic (e.g. NH4Cl dissolving in water).

A negative Delta H(sol) means energy is released and the process is exothermic (e.g. NaOH dissolving in water).

The sign depends on the balance between lattice energy (energy needed to break the lattice) and hydration energy (energy released as ions are hydrated).

Q12. How can charge density predict which of two similarly charged but differently sized ions has a more exothermic hydration enthalpy?

Charge density = Charge / Volume (or radius squared).

Higher charge density (smaller size or higher charge) means stronger ion-dipole interaction and a more exothermic hydration enthalpy.

Q13. What is chemical energetics?

Chemical energetics studies the energy changes during chemical reactions, telling us whether a reaction is exothermic (releases heat) or endothermic (absorbs heat).

Example: Combustion of methane is exothermic: CH4 + 2O2 -> CO2 + 2H2O + heat.

Q14. Define system and surroundings.

System: the part of the universe under study (e.g. reactants and products).

Surroundings: everything outside the system.

Example: in a beaker where a reaction occurs, the contents are the system; the beaker and air are the surroundings.

Q15. What is an open, closed, and isolated system?

Open system: exchanges both matter and energy with surroundings (e.g. boiling water in an open pan).

Closed system: exchanges energy but not matter (e.g. a sealed bottle of hot water).

Isolated system: exchanges neither matter nor energy (e.g. a thermos flask).

Q17. What is enthalpy (Delta H)?

Enthalpy is the heat content of a system at constant pressure - a state function, measured in kJ/mol.

Delta H = H(products) - H(reactants).

Q18. State the First Law of Thermodynamics.

Energy cannot be created or destroyed, only transformed.

Mathematically: Delta U = q + w, where Delta U = change in internal energy, q = heat, w = work done.

Q19. What is internal energy (Delta U)?

Internal energy is the total energy stored in a system (kinetic + potential): Delta U = q + w.

Q20. Define heat of reaction.

The amount of heat absorbed or released during a chemical reaction at constant pressure.

Example: H2 + 1/2 O2 -> H2O, Delta H = -285.8 kJ/mol (exothermic).

Q21. Define standard enthalpy of formation (Delta Hf).

The enthalpy change when 1 mole of a compound is formed from its elements in their standard states.

Example: C(graphite) + O2 -> CO2, Delta Hf = -393.5 kJ/mol.

Q22. Define heat of combustion.

The heat change when 1 mole of a substance burns completely in oxygen.

Example: CH4 + 2O2 -> CO2 + 2H2O, Delta H = -890 kJ/mol.

Q23. What is enthalpy of neutralization?

The heat released when 1 mole of acid reacts with a base to form water.

Example: HCl + NaOH -> NaCl + H2O, Delta H = -57.1 kJ/mol.

Q24. Why is enthalpy of neutralization constant for strong acid-base pairs?

Because complete ionization occurs and the same net reaction, H+ + OH- -> H2O, takes place regardless of the specific strong acid or base used.

Q25. Define endothermic reaction with example.

A reaction that absorbs heat. Example: photosynthesis - 6CO2 + 6H2O + sunlight -> C6H12O6 + O2.

Q26. Why is evaporation an endothermic process?

Because molecules must absorb heat to overcome intermolecular forces and escape into the vapour phase.

Q27. State an example where Delta H is positive.

N2 + O2 -> 2NO, Delta H = +180.5 kJ/mol.

Q28. What is calorimetry?

The science of measuring heat changes during chemical reactions using a device called a calorimeter.

Q29. Define specific heat capacity.

The amount of heat required to raise the temperature of 1 gram of a substance by 1 deg C. Unit: J/g/deg C. Water's value = 4.18 J/g/deg C.

Q30. Give the formula for heat (q) calculation.

q = m c Delta T, where m = mass (g), c = specific heat, Delta T = change in temperature.

Q31. How can calorimetry be used to measure enthalpy?

By measuring the temperature change (Delta T) of a known mass of water: q = m c Delta T, then converting q into Delta H per mole.

Q32. Why does dissolving NaOH increase temperature?

It is an exothermic process due to the strong hydration energy released as Na+ and OH- ions become surrounded by water molecules.

Q33. What is a thermochemical equation?

A balanced chemical equation that includes the heat change (Delta H).

Example: H2 + 1/2 O2 -> H2O(l), Delta H = -285.8 kJ/mol.

Q34. What is the standard state of an element?

Its most stable physical form at 298 K and 1 atm pressure. Example: the standard state of oxygen is O2(g).

Q35. What is Hess's Law?

The total enthalpy change of a reaction is the same regardless of the path taken.

Example: C + O2 -> CO2 is equivalent to (C + 1/2 O2 -> CO) followed by (CO + 1/2 O2 -> CO2).

Q36. Why is Hess's Law useful?

It allows calculation of enthalpy changes that are difficult to measure directly, using known enthalpies of related reactions.

Q37. What are state functions?

Properties that depend only on the initial and final states of a system, not on the path taken.

Examples: enthalpy, internal energy, entropy, Gibbs free energy.

Q38. What is bond enthalpy?

The energy required to break one mole of a specific bond in gaseous molecules. Example: bond enthalpy of H-H = 436 kJ/mol.

Q39. What is the relationship between bond energy and enthalpy of reaction?

Delta H = Sum(Bonds broken) - Sum(Bonds formed).

If more energy is released in bond formation than absorbed in bond breaking, the reaction is exothermic.

Q40. What is lattice energy?

The energy released when one mole of an ionic compound forms from its gaseous ions.

Example: Na+(g) + Cl-(g) -> NaCl(s), Delta H(latt) = -787 kJ/mol.

Q41. What factors affect lattice energy?

Ionic charge - higher charge gives more (negative) lattice energy.

Ionic radius - smaller radius gives more (negative) lattice energy.

Q42. Define hydration enthalpy.

The energy released when 1 mole of gaseous ions dissolve in water. Example: Na+(g) -> Na+(aq).

Q43. Define enthalpy of solution.

The heat change when 1 mole of a substance dissolves in a solvent.

Q44. Why is dissolution of NH4NO3 endothermic?

Because the lattice energy absorbed (to break the ionic lattice) is greater than the hydration energy released (as ions are surrounded by water).

Q45. What is the Born-Haber cycle?

A thermochemical energy cycle, based on Hess's Law, used to calculate the lattice energy of ionic compounds indirectly.

Q46. Why is formation of NaCl exothermic?

Due to the large amount of lattice energy released during crystal formation, which outweighs the energy input needed for atomization and ionization.

Q47. Define spontaneous reaction.

A reaction that occurs on its own without a continuous external energy input. Example: rusting of iron.

Q48. What is entropy (Delta S)?

A measure of randomness or disorder in a system; higher Delta S means more disorder.

Order of increasing entropy: Solid < Liquid < Gas.

Q49. Define free energy (Delta G).

Gibbs free energy tells us whether a reaction is spontaneous: Delta G = Delta H - T Delta S.

Delta G < 0: spontaneous; Delta G > 0: non-spontaneous; Delta G = 0: equilibrium.

Section 2 | Descriptive & Numerical Problems

Descriptive Questions

Q3 (Descriptive). State and explain Hess's Law. Give its two applications.

Hess's Law: the total enthalpy change in a reaction is independent of the route taken, as long as the initial and final states are the same (see Long Questions, Q7, for full treatment).

Applications: (1) calculating enthalpy of formation from enthalpies of combustion; (2) calculating enthalpy of reaction from enthalpies of formation.

Q4 (Descriptive). What is lattice energy? How does the Born-Haber cycle help calculate the lattice energy of NaCl?

Lattice energy is the enthalpy change when one mole of an ionic solid forms from its gaseous ions (see Long Questions, Q13, for the full Born-Haber cycle of NaCl).

Since lattice energy cannot be measured directly, the Born-Haber cycle combines known enthalpies (atomization, ionization, bond energy, electron affinity, and formation) via Hess's Law to calculate it indirectly.

Numerical Problems

Q5. 0.400 g of NaOH is added to 100.0 g of water; temperature rises from 25.00 deg C to 26.03 deg C. Calculate (i) q(water) and (ii) Delta H for the solution process.

Delta T = 26.03 - 25.00 = 1.03 deg C; specific heat of water = 4.18 J/g/deg C

(i) q = m c Delta T = 100.0 x 4.18 x 1.03 = 430.54 J

(ii) Molar mass NaOH = 40 g/mol; moles = 0.400/40 = 0.010 mol

Delta H = q/n = 430.54/0.010 = 43054 J/mol = 43.05 kJ/mol

Answer: Delta H(solution) = -43.05 kJ/mol

Q6. Using Hess's Law, calculate the enthalpy change for formation of aqueous NH4Cl from NH3 gas and HCl gas, given: (i) NH3(g)+aq -> NH3(aq), Delta H=-35.16 kJ/mol; (ii) HCl(g)+aq -> HCl(aq), Delta H=-72.41 kJ/mol; (iii) NH3(aq)+HCl(aq) -> NH4Cl(aq), Delta H=-51.48 kJ/mol.

Target: NH3(g) + HCl(g) -> NH4Cl(aq)

Adding all three steps: Delta H = (-35.16) + (-72.41) + (-51.48) = -159.05 kJ/mol

Answer: Delta H = -159.05 kJ/mol

Q7. Calculate the heat of formation of ethyl alcohol. Heat of combustion of C2H5OH = -1367 kJ/mol; Delta Hf(CO2) = -393.7 kJ/mol; Delta Hf(H2O) = -285.8 kJ/mol. Combustion: C2H5OH(l) + 3O2(g) -> 2CO2(g) + 3H2O(l)

Total Delta Hf of products = 2(-393.7) + 3(-285.8) = -787.4 + (-857.4) = -1644.8 kJ

Delta Hf(C2H5OH) = Sum Delta Hf(products) - Delta H(combustion) = -1644.8 - (-1367) = -277.8 kJ/mol

Answer: Delta Hf(C2H5OH) = -277.8 kJ/mol

Q8. Calculate the lattice energy of potassium bromide using: Delta Hf = -392 kJ/mol; sublimation = +90; ionization = +420; dissociation (1/2 Br2) = +112; electron affinity = -324 (all kJ/mol).

Delta Hf = Sublimation + Ionization + Dissociation + Electron affinity + Lattice energy

-392 = (90 + 420 + 112 - 324) + Delta H(latt) = 298 + Delta H(latt)

Delta H(latt) = -392 - 298 = -690 kJ/mol

Answer: Lattice energy of KBr = -690 kJ/mol

Q9. Calculate the entropy of the surroundings, Delta S(surrounding), at 298 K for: 2Ca(s) + O2(g) -> 2CaO(s), Delta H(reaction) = -1270.2 kJ/mol

Delta H(reaction) = -1270.2 kJ/mol = -1,270,200 J/mol

Delta S(surrounding) = -Delta H(reaction)/T = -(-1,270,200)/298 = +4262.75 J/K/mol

Answer: Delta S(surrounding) = +4262.75 J/K/mol

Q10. For CaSO4(s) -> Ca2+(aq) + SO4(2-)(aq), calculate Delta H, Delta S and Delta G at 25 deg C, and discuss spontaneity. Data: Delta Hf[CaSO4]=-1432.7, Delta Hf[Ca2+]=-543.0, Delta Hf[SO4 2-]=-907.5 (kJ/mol); S[CaSO4]=106.7, S[Ca2+]=-55.2, S[SO4 2-]=+17.2 (J/K).

Delta H = [(-543.0) + (-907.5)] - (-1432.7) = -1450.5 + 1432.7 = -17.8 kJ/mol

Delta S = [(-55.2) + 17.2] - 106.7 = -38.0 - 106.7 = -144.7 J/K = -0.1447 kJ/K

Delta G = Delta H - T Delta S = -17.8 - (298 x -0.1447) = -17.8 + 43.1 = +25.3 kJ/mol

Conclusion: Delta G is positive, so the reaction is non-spontaneous under standard conditions.

Section 3 | Long Questions

Q1. What is thermochemistry? Explain the enthalpy change in a reaction.

Thermochemistry

Definition: Thermochemistry (also called energetics) is the area of thermodynamics concerned with the quantity of heat energy absorbed or evolved during physical or chemical changes.

Basis: largely based on the First Law of Thermodynamics - 'Energy can neither be created nor destroyed, but it can be changed from one form to another.' A special case of this law is Hess's Law.

Applications of Thermochemistry

Calculating enthalpy changes of reactions that cannot be measured directly; used extensively in analytical chemistry; predicting the feasibility/spontaneity of a reaction; broad applications in engineering and physics.

Enthalpy Change (Delta H)

Definition: enthalpy (H) is the sum of all possible potential and kinetic energies of a system - its heat content.

Every substance has a characteristic enthalpy; the total enthalpy of products (Hp) is never equal to that of reactants (HR): Delta H = Hp - HR.

Exothermic Process

Definition: a reaction/change in which heat is evolved from the system to the surroundings.

Example: C(s) + O2(g) -> CO2(g), Delta H = -393.7 kJ/mol. Conditions: Hp < HR, heat is evolved, Delta H is negative.

Endothermic Process

Definition: a reaction/change in which heat is absorbed by the system from the surroundings.

Example: NH4Cl(s) -> NH4+(aq) + Cl-(aq), Delta H = +16.2 kJ/mol. Conditions: Hp > HR, heat is absorbed, Delta H is positive.

Application: the endothermic dissolution of NH4Cl in water is used in cold packs to treat injuries - kneading the pack mixes water and NH4Cl crystals, absorbing energy from the surroundings and producing a cooling sensation.

Q2. Discuss the energy profile diagrams of exothermic and endothermic reactions.

Bond Breaking and Making

All chemical reactions involve breaking bonds in the reactants followed by forming new bonds in the products.

Activation Energy (Ea)

Definition: the minimum energy that reactant molecules must possess for effective collisions to overcome the energy barrier and start a reaction.

Without enough activation energy, molecular collisions will not lead to a reaction.

Exothermic Reactions (Energy Profile)

Reactant energy is more than product energy; Delta H is negative; heat is released; activation energy is comparatively low; products are more stable.

Endothermic Reactions (Energy Profile)

Product energy is more than reactant energy; Delta H is positive; heat is absorbed; activation energy is comparatively high; products are less stable.

Q3. Discuss standard enthalpy changes and their types.

Standard Enthalpy Change (Delta H deg)

Definition: the enthalpy change measured under standard conditions - 25 deg C (298 K) and 1 atm (101 kPa).

The standard state of an element is its most stable form at these conditions (e.g. graphite, not diamond, for carbon); the standard enthalpy of formation of any element in its standard state is zero.

(i) Enthalpy Change of Reaction (Delta Hr)

The enthalpy change when stoichiometric amounts of reactants in their standard states react completely to form products under standard conditions.

Example: H2(g) + 1/2 O2(g) -> H2O(l), Delta Hr = -286 kJ/mol.

(ii) Enthalpy Change of Combustion (Delta Hc)

The enthalpy change when one mole of a substance is completely burnt in excess oxygen under standard conditions - always exothermic.

Example: C2H5OH(l) + 3O2(g) -> 2CO2(g) + 3H2O(l), Delta Hc = -1368 kJ/mol. Used to calculate calorie content of foods and fuels.

(iii) Enthalpy Change of Formation (Delta Hf)

The enthalpy change when one mole of a compound is formed from its elements under standard conditions - can be exothermic or endothermic.

Example: C(s) + 2H2(g) -> CH4(g), Delta Hf = -74.8 kJ/mol.

(iv) Enthalpy Change of Atomization (Delta Ha)

The enthalpy change when one mole of gaseous atoms is formed from an element under standard conditions.

Example: 1/2 H2(g) -> H(g), Delta Ha = +218 kJ/mol (half the H-H bond energy of 436 kJ/mol).

(v) Enthalpy Change of Neutralization (Delta Hn)

The enthalpy change when one mole of water is formed by the reaction of an acid with an alkali under standard conditions - always exothermic.

Example: H+(aq) + OH-(aq) -> H2O(l), Delta Hn = -57.1 kJ/mol. For all strong acid-base reactions, Delta Hn is close to -57.1 kJ/mol.

(vi) Electron Affinity (Delta Hea)

The first electron affinity is the enthalpy change when 1 mole of electrons is added to 1 mole of gaseous atoms to form 1 mole of gaseous uni-negative ions.

Example: Cl(g) + e- -> Cl-(g), Delta H = -348.8 kJ/mol.

Quick Check 6.2

(a) Atomization equations: (i) 1/2 O2(g) -> O(g); (ii) Ba(s) -> Ba(g); (iii) 1/2 Br2(l) -> Br(g).

(b)(i) C(graphite)+O2(g)->CO2(g): standard enthalpy of combustion. (ii) HCl(g)+NH3(g)->NH4Cl(s): enthalpy of formation of an ionic solid from gaseous molecules. (iii) H2(g)+1/2O2(g)->H2O(l): standard enthalpy of formation.

Q4. How can bond energies be used to estimate the enthalpy change of a reaction?

Bond Energy (Bond Dissociation Energy)

Definition: the average energy required to break one mole of a particular bond in a substance, in kJ/mol.

Breaking a bond requires energy (endothermic); forming a bond releases energy (exothermic). Exact bond energy refers to a specific molecule; average bond energy is the mean over different compounds with that bond type.

Calculating Enthalpy Change Using Bond Energies

Formula: Delta Hr = Sum ER - Sum EP, where Sum ER = total bond energy of reactants (bonds broken) and Sum EP = total bond energy of products (bonds formed).

Example - Formation of water: 2H2(g) + O2(g) -> 2H2O(g): breaking 2 H-H (872 kJ) + 1 O=O (496 kJ) = 1368 kJ absorbed; forming 4 O-H bonds = 4x463 = 1852 kJ released; Delta Hr = 1368 - 1852 = -484 kJ/mol (exothermic).

Sample Problem 6.1

H2(g) + 1/2 O2(g) -> H2O(g), given E(H-H)=436, E(O=O)=495, E(H-O)=463 kJ/mol.

Delta Hr = [E(H-H) + 1/2 E(O=O)] - [2 E(H-O)] = [436 + 247.5] - [2x463] = 683.5 - 926 = -242.5 kJ/mol

Q5. How is enthalpy change of reaction measured? Explain the construction and working of a glass calorimeter.

Calorimetry

Definition: the measurement of heat evolved or absorbed during a physical or chemical process, using a device called a calorimeter.

Heat/specific heat capacity: the heat required to raise the temperature of 1 kg (or 1 g) of a substance by 1 K. Example: water = 4.18 J/g/K (rounded to 4.2).

Glass Calorimeter - Construction

A beaker reaction vessel, thermometer, stirrer, a loose-fitting lid, and insulating material (cotton wool).

Limitations: not suited to reactions involving gases (may escape) or reactions producing very high temperatures (can damage the glass or lose heat).

Working

The reaction occurs inside the beaker; the temperature change (Delta T) is measured; at constant pressure, the heat energy change equals the enthalpy change (Delta H).

q = m(water) x C(water) x Delta T, where C(water) = 4.18 J/g/deg C and Delta T = Tf - Ti. Convert q to kJ, then Delta H = -q/n (kJ/mol).

Sample Problem 6.2

100 cm3 of 0.5 mol/dm3 NaOH at 25 deg C neutralized with 100 cm3 of 0.5 mol/dm3 HCl raised temperature to 28.5 deg C. Specific heat of water = 4.2 J/g/K.

Total volume approx 200 g; Delta T = 3.5 deg C; q = 200 x 4.2 x 3.5 = 2940 J = 2.94 kJ.

Moles of water formed = moles HCl = moles NaOH = 0.05 mol.

Delta Hn = -q/n = -2.94/0.05 = -58.8 kJ/mol

Quick Check 6.3

50 cm3 of 1.5 mol/dm3 HNO3 with 50 cm3 of 1.5 mol/dm3 NaOH; Delta T = 4 deg C.

q = 100 x 4.18 x 4 = 1672 J = 1.672 kJ; moles water = 0.075 mol.

Delta Hn = -1.672/0.075 = -22.3 kJ/mol

Q6. What is enthalpy change and how can we measure the calorie content of food?

Calorie Content of Food

The calorie content of food measures the energy released when the food is completely consumed in the body, expressed in kilocalories (kcal) or joules. 1 kcal = 4.184 kJ.

Digestion releases the chemical energy stored in food as heat, similar to combustion. The enthalpy of combustion (Delta Hc) of food equals its caloric content and is measured using a bomb calorimeter.

Calorie content = Delta H (kJ/g) / 4.184

Example: Combustion of Glucose

C6H12O6(s) + 6O2(g) -> 6CO2(g) + 6H2O(l), Delta H = -2803 kJ/mol.

Molar mass of glucose = 180 g/mol; Delta H per gram = -2803/180 = -15.57 kJ/g.

Calorie content = 15.57/4.184 = 3.72 kcal/g.

Q7. State Hess's Law of constant heat summation. Show how to calculate enthalpy of formation and reaction using it.

Hess's Law of Constant Heat Summation

Statement: 'The total enthalpy change in a chemical reaction is independent of the route by which the reaction takes place, as long as the initial and final conditions are the same.'

Hess's Law is based on the First Law of Thermodynamics (conservation of energy).

(i) Enthalpy of Formation from Enthalpy of Combustion - Sample Problem 6.3

Given: C(graphite)+O2(g)->CO2(g), Delta H=-393.5 kJ/mol; CO(g)+1/2O2(g)->CO2(g), Delta H=-283 kJ/mol.

Find Delta H1 for C(graphite)+1/2O2(g)->CO(g): Delta H1 = Delta H - Delta H2 = -393.5 - (-283) = -110.5 kJ/mol

(ii) Enthalpy of Reaction from Enthalpies of Formation - Sample Problem 6.4

C2H4 + HCl -> C2H5Cl; Delta Hf(C2H4)=+52.2, Delta Hf(HCl)=-92.3, Delta Hf(C2H5Cl)=-109 kJ/mol.

Delta Hr = Delta Hf(products) - Delta Hf(reactants) = -109 - [52.2+(-92.3)] = -109-(-40.1) = -68.9 kJ/mol

Quick Check 6.4

Standard enthalpy of formation of benzene, 6C(s)+3H2(g)->C6H6(l), using Delta Hc[C]=-394, Delta Hc[H2]=-286, Delta Hc[C6H6]=-3267 (all kJ/mol).

Delta Hf = [6x(-394) + 3x(-286)] - (-3267) = [-2364-858] - (-3267) = -3222+3267 = +45 kJ/mol

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Q8. Calculate enthalpy of formation using combustion/formation data, and enthalpy change using bond energies.

Sample Problem 6.5 - Enthalpy of Formation of Propane

C3H8(g)+5O2(g)->3CO2(g)+4H2O(g). Burning 14.64 g propane releases 678.6 kJ. Delta Hf(CO2)=-393.51, Delta Hf(H2O)=-241.82 (kJ/mol).

Moles propane = 14.64/44.096 = 0.3320 mol; heat per mole = 678.6/0.3320 = -2044 kJ/mol.

-2044 = [3x(-393.51)+4x(-241.82)] - Delta Hf(C3H8) = -2147.81 - Delta Hf(C3H8)

Delta Hf(C3H8) = -103.81 kJ/mol

(ii) Enthalpy Change Using Bond Energies - Sample Problem 6.6

H2(g)+Cl2(g)->2HCl(g); E(H-H)=436, E(Cl-Cl)=242, E(H-Cl)=431 (kJ/mol).

Bonds broken: Sum ER = 436+242 = 678 kJ; Bonds formed: Sum EP = 2x431 = 862 kJ.

Delta Hr = 678-862 = -184 kJ (for 2 mol HCl); Delta Hf(HCl) = -184/2 = -92 kJ/mol

Quick Check 6.5(a) - Haber Process

N2(g)+3H2(g)->2NH3(g); E(N triple-bond N)=945, E(H-H)=436, E(N-H)=391 (kJ/mol).

Bonds broken: 945+3(436)=2253 kJ/mol; bonds formed: 6(391)=2346 kJ/mol.

Delta H = 2253-2346 = -93 kJ/mol

Quick Check 6.5(b) - Ethanol Combustion

C2H5OH(l)+3O2(g)->2CO2(g)+3H2O(l); E(C-C)=347, E(C-H)=410, E(C-O)=336, E(O=O)=496, E(C=O)=805, E(O-H)=465 (kJ/mol).

Bonds broken: 5(C-H)=2050, 1(C-C)=347, 1(C-O)=336, 1(O-H)=465, 3(O=O)=1488; Sum ER=4686 kJ/mol.

Bonds formed: 4(C=O)=3220, 6(O-H)=2790; Sum EP=6010 kJ/mol.

Delta H = 4686-6010 = -1324 kJ/mol

Q9. What is dissolution? Explain standard enthalpy change of solution and how it is calculated.

Dissolution

Definition: the process of dissolving a solute in a solvent.

Three steps: (1) expanding the solvent - overcoming intermolecular forces to make space; (2) expanding the solute - breaking it into individual ions/molecules; (3) interaction - solute and solvent molecules interact to form a homogeneous solution.

Standard Enthalpy of Solution (Delta Hsol)

Definition: the heat absorbed or evolved when one mole of a substance dissolves in a solvent to give an infinitely dilute solution - may be exothermic (-ve) or endothermic (+ve).

Examples: Na2CO3(s)+aq -> 2Na+(aq)+CO3(2-)(aq), Delta Hsol=-25 kJ/mol (exothermic); NH4Cl(s)+aq -> NH4+(aq)+Cl-(aq), Delta Hsol=+16.2 kJ/mol (endothermic).

Selected heats of solution (kJ/mol): NaCl +4.98, KCl +17.8, KBr +19.9, KI +21.4, NH4Cl +16.2, NH4NO3 +26.0.

Factors Affecting Dissolution of Ionic Compounds

(i) Lattice Energy: the energy required to break the ionic lattice - higher lattice energy means more energy is needed to dissolve.

(ii) Hydration Energy: the energy released as ions become surrounded by water - higher hydration energy favours dissolution.

Q10. What is hydration? Explain the factors affecting hydration energy.

Hydration

Definition: when ionic compounds dissolve in water, they dissociate into ions that are surrounded by water molecules.

Ion-dipole forces form between the solute's ions and the polar water molecules.

Enthalpy of Hydration (Delta Hhyd)

Definition: the enthalpy change when one mole of a solute's gaseous ions dissolve in excess water to make an infinitely dilute solution - always exothermic, since new ion-dipole bonds are formed.

Factors Affecting Hydration Energy

(i) Charge on the ion: higher charge gives stronger attraction to water molecules and greater hydration energy.

(ii) Size of the ion: smaller ions have higher charge density (charge per unit area/volume) and stronger hydration energy.

Order of hydration energies: Al3+ > Mg2+ > Na+. For anions, smaller more negatively charged ions (F-) have higher hydration energy than larger ones (I-).

Q11. What is lattice energy? Explain the two main factors affecting it.

Lattice Energy

Definition: the enthalpy change when one mole of an ionic compound is formed from its gaseous ions under standard conditions.

Example: Na+(g)+Cl-(g) -> NaCl(s), Delta Hlatt = -787 kJ/mol.

(i) Charge on the Ion

Greater ionic charge gives greater lattice energy, as higher-charged ions attract each other more strongly.

Example: Delta Hlatt(MgO) = -3923 kJ/mol (Mg2+, O2-) vs Delta Hlatt(LiF) = -1049 kJ/mol (Li+, F-).

(ii) Size of the Ion

Smaller ions pack closer together, giving stronger attraction and higher lattice energy; lattice energy decreases with increasing ion size.

Example - alkali metal halides: Li+ > Na+ > K+ > Rb+ > Cs+ (decreasing lattice energy).

Q12. What is the solubility trend of Group 2 hydroxides and sulfates? How is enthalpy change of solution calculated?

Solubility Trends

Delta Hsol depends on both lattice energy and hydration enthalpy: Delta Hsol = Hydration enthalpy - Lattice energy.

(i) Group 2 hydroxides: solubility increases down the group (Mg(OH)2 lowest to Ba(OH)2 highest), because lattice energy decreases faster than hydration enthalpy, making Delta Hsol more exothermic.

(ii) Group 2 sulfates: solubility decreases down the group (MgSO4 highest to BaSO4 lowest), because SO4(2-) is large so lattice energy barely changes, while hydration energy falls significantly, making Delta Hsol more endothermic.

Calculating Enthalpy Change of Solution

Energy cycle: Delta Hlatt + Delta Hsol = Delta Hhyd

Sample Problem 6.7 - NaF

Lattice energy of NaF = -902 kJ/mol; hydration of Na+ = -406 kJ/mol; hydration of F- = -506 kJ/mol.

Delta Hsol = (-406)+(-506)-(-902) = -912+902 = +10 kJ/mol

Q13. How is the Born-Haber cycle used to calculate the lattice energy of NaCl?

Born-Haber Cycle

Definition: an application of Hess's Law used to determine the lattice energy of binary ionic compounds (M+X-), since lattice energy cannot be measured directly in a single experiment.

For NaCl: Delta Hf = Delta Ha(Na) + 1/2 B.E.(Cl2) + I.E.(Na) + E.A.(Cl) + Delta Hlatt(NaCl).

Steps in the Born-Haber Cycle for NaCl

1. Atomization of Na(s): +107 kJ/mol
2. Bond energy of Cl2 (half): +121 kJ/mol
3. Ionization energy of Na: +496 kJ/mol
4. Electron affinity of Cl: -349 kJ/mol
5. Lattice energy of NaCl: -787 kJ/mol

Quick Check 6.6 - Heat of Formation of LiF

Given: atomization of Li = +161, half bond energy F2 = +79, ionization energy Li = +520, electron affinity F = -328, lattice energy LiF = -1107 (all kJ/mol).

Delta Hf = 161+79+520-328-1107 = -675 kJ/mol

Answer: standard enthalpy of formation of LiF(s) = -675 kJ/mol

Q14. What is entropy? Give a comparison of entropy values.

Entropy (S)

Definition: a measure of the number of ways energy can be distributed within a system at a given temperature - or, more simply, a measure of randomness/disorder. Higher disorder means greater entropy.

Diffusion is driven by random particle motion; as particles spread out, the number of possible microstates (and hence entropy) increases. Number of arrangements = x^y (x = number of places, y = number of particles); e.g. 3 molecules in 2 jars gives 2^3 = 8 arrangements.

(i) Number of Particles

A smaller number of particles gives lower entropy, and vice versa.

Example: CaCO3(s) has higher entropy (92.9 J/K/mol) than CaO(s) (39.7 J/K/mol).

(ii) Physical Properties (Hardness)

Harder substances have lower entropy than softer ones. Example: Diamond has lower entropy than Graphite.

(iii) Physical States

Entropy order: Solids < Liquids < Gases.

Example - water: Ice (48.0 J/K/mol) < Water (69.9 J/K/mol) < Water Vapour (188.7 J/K/mol).

Quick Check 6.8

(i) Br2(l) S=151.6 J/K/mol vs I2(s) S=116.8 J/K/mol: Br2 is a liquid with more freedom of movement and disorder; I2(s) is a solid with a more ordered, restricted structure.

(ii) Diamond vs Graphite: diamond's rigid 3D bonding gives limited vibration and lower entropy; graphite's softer, layered structure allows more freedom of movement and higher entropy.

Q15. How are entropy changes used to predict spontaneity?

(i) Gas Formation from Solid or Liquid

Entropy increases significantly when a gas is produced.

Example: CaCO3(s) -> CaO(s) + CO2(g): solid to solid+gas means entropy increases (Delta S positive), favouring spontaneity.

(ii) Increase in Number of Gas Molecules

Example: 2N2O5(g) -> 4NO2(g) + O2(g): reactants have 2 gas molecules, products have 5 - Delta S is positive (more disorder), favouring spontaneity.

Calculating Entropy Change of the System

Delta S(system) = S(products) - S(reactants).

Worked Example

2Ca(s)+O2(g) -> 2CaO(s); S[Ca]=41.40, S[O2]=205.0, S[CaO]=39.70 (J/K/mol).

Delta S(system) = 2x39.70 - (2x41.40+205.0) = 79.40-287.8 = -208.4 J/K/mol.

Interpretation: even though entropy decreases, the reaction is spontaneous - so Gibbs Free Energy must also be considered to fully judge spontaneity.

Q16. What is total entropy change and how is it calculated?

Total Entropy Change (Delta Stotal)

Definition: the sum of the standard entropy change of the system and of the surroundings.

Delta Stotal = Delta Ssystem + Delta Ssurrounding

Delta Ssystem = Sum S(products) - Sum S(reactants); Delta Ssurrounding = -Delta Hr/T (Delta Hr in kJ/mol must be converted to J/mol; the negative sign is part of the formula, not the sign of Delta Hr).

Predicting Spontaneity - Sample Problems 6.9 & 6.11

For 2Ca(s)+O2(g) -> 2CaO(s): Delta Ssystem = -208.4 J/K/mol (from Q15).

Delta Hr = -1270.2 kJ/mol, T = 298 K: Delta Ssurrounding = -(-1270.2x1000)/298 = +4262.4 J/K/mol.

Delta Stotal = -208.4+4262.4 = +4054.0 J/K/mol.

Conclusion: total entropy change is positive, so the reaction is feasible/spontaneous.

Q17. What is free energy change and how is Gibbs free energy for a reaction calculated?

Gibbs Free Energy Change

Delta G = -T Delta Stotal. Multiplying the Delta Stotal expression by -T and simplifying gives the Gibbs equation: Delta G = Delta Hr - T Delta S (where Delta S is Delta Ssystem).

Delta G < 0: process may occur spontaneously; Delta G > 0: cannot occur spontaneously (reverse may occur); Delta G = 0: system at equilibrium.

Sample Problem 6.12 - CaSO4 Dissolution

CaSO4(s) -> Ca2+(aq)+SO4(2-)(aq); Delta Hf[CaSO4]=-1432.7, Delta Hf[Ca2+]=-543.0, Delta Hf[SO4 2-]=-907.5 (kJ); S[CaSO4]=106, S[Ca2+]=-55.2, S[SO4 2-]=+17.2 (J/K).

Delta H = [-543.0+(-907.5)]-(-1432.7) = -17.8 kJ. Delta S = [(-55.2)+17.2]-106 = -144 J/K = -0.1447 kJ/K.

Delta G = -17.8-298(-0.1447) = -17.8+43.1 = +25.3 kJ. Conclusion: non-spontaneous at 25 deg C standard conditions.

Sample Problem 6.13 - Haber's Process

N2(g)+3H2(g) -> 2NH3(g); Delta Hf[NH3]=-45.9 kJ; S[N2]=191.5, S[H2]=130.6, S[NH3]=+193 (J/K).

Delta H = 2x(-45.9) - 0 = -91.8 kJ. Delta S = [2x193]-[191.5+3x130.6] = 386-583.3 = -197 J/K = -0.197 kJ/K.

Delta G = -91.8-298(-0.197) = -91.8+58.7 = -33.1 kJ. Conclusion: Delta G is negative, so Haber's process is spontaneous at 25 deg C standard conditions.

Q18. Explain the relationship between spontaneity and temperature change.

General Equation

Delta G = Delta H - T Delta S. Delta G depends strongly on temperature, so a reaction's spontaneity can change with temperature depending on the signs of Delta H and Delta S:

Delta H(-), Delta S(+): spontaneous at all T. Delta H(+), Delta S(-): non-spontaneous at all T. Delta H(-), Delta S(-): spontaneous at low T, non-spontaneous at high T. Delta H(+), Delta S(+): non-spontaneous at low T, spontaneous at high T.

Sample Problem 6.14

CaCO3(s) -> CaO(s)+CO2(g) at 1000 deg C; Delta H=+178.0 kJ, Delta S=+160.4 J/K = 0.1604 kJ/K.

T = 1000+273 = 1273 K. Delta G = 178.0-1273(0.1604) = 178.0-204.2 = -26.2 kJ.

Conclusion: the reaction is spontaneous at 1000 deg C and 1 atm - limestone will decompose in an open container at this temperature.

Section 4 | Formula, Constants & Bond Energy Summary

Important Formulas

Formula	Description
Delta H = Hp - HR	Enthalpy Change (Exothermic -ve, Endothermic +ve)
q = m x c x Delta T	Heat Change in Calorimetry
Delta Hr = Sum ER - Sum EP	Enthalpy Change Using Bond Energies
Delta Hf = Sum Delta Hf(products) - Sum Delta Hf(reactants)	Hess's Law - Enthalpy of Reaction
Delta S = S(products) - S(reactants)	Entropy Change of System
Delta S surrounding = -Delta H / T	Entropy Change of Surroundings
Delta S total = Delta S system + Delta S surrounding	Total Entropy Change (Spontaneity)
Delta G = Delta H - T Delta S	Gibbs Free Energy Change
Delta H latt + Delta H sol = Delta H hyd	Energy Cycle for Enthalpy of Solution

Key Constants

Constant	Value
Specific Heat Capacity of Water	4.18 J/g deg C (approx 4.2 J/g deg C)
Enthalpy of Neutralization (strong acid + strong base)	-57.1 kJ/mol
Standard Enthalpy of Formation of Elements	0 kJ/mol
Gas Constant (R)	8.314 J/mol/K
Standard Conditions	298 K (25 deg C), 1 atm (101 kPa)
1 kcal	4.184 kJ
Bond Energy H-H	436 kJ/mol
Bond Energy O=O	496 kJ/mol
Bond Energy O-H	463 kJ/mol
Lattice Energy of NaCl	-787 kJ/mol

Average Bond Energies (kJ/mol)

Bond	Energy	Bond	Energy	Bond	Energy
H-H	436	C-H	410	C-C	347
H-F	565	C-O	336	C=O	805

H-Cl	431	C-Cl	328	N-H	391
H-Br	366	C-Br	276	N-N	163
H-I	298	O-H	463	N=N	945
F-F	158	O=O	496	-	-

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