Thermodynamics

Case Study Based Questions

Read the following passages and answer the questions that follow:

1. As a matter of definition, a system in physics or chemistry is nothing more than a collection of objects (or smaller systems) whose identities can be determined. In many cases, the word "system" refers to a collection that makes solving a problem more manageable. What surrounds the system is everything else. There are three types of systems: (1) Open system (2) closed system and (3) Isolated system. An open system is one that freely allows both energy and matter to be transferred in and out of a system. For example, boiling water without a lid, Heat escaping into the air. A closed system, on the other hand, does not allow the exchange of matter but allows energy to transfer. Example of a closed system - a pressure cooker. Isolated System: This system is completely sealed. Neither matter nor heat can transfer to or from the surroundings. Example - A thermos flask. The purpose of a thermos flask is to keep your food warm. A thermos flask can be considered as an isolated
system but only for a short period of time. It prevents both heat and matter from being transferred to the surrounding. It is often more convenient to use an isolated system, where external influences (either cancel each other out or are negligible) can be ignored. Similarly, two balls rolling across a smooth surface to strike each other can be considered an isolated system, while two balls rolling across a gravel path or thick carpet will be affected by friction that originates outside the system and will not be considered an isolated system.
(A) The humans are which type of system and why? Explain.
(B) The following systems belong to which type of system: Pond and Tea brewed in a kettle.
(C) A person does 10 kJ work on 3 kg of water by stirring using a paddle wheel. While stirring, around 10 kcal of heat is released from water through its container to the surface and surroundings by thermal conduction and radiation. What is the change in internal energy of the system?

Ans. (A) Humans are an example of an open system because we are constantly exchanging matter and energy with our surroundings. If we lift a weight W, simply breathe out and release carbon dioxide into the atmosphere. We take food in and also excrete it out. So, humans are an example of an open system.

(B) Pond-Open system and Tea brewed in a kettle-Closed system.

(C) Work done on the system (By the person
while stirring), w = -10 kJ = -10000 J
Heat flows out of the system
q=10 kcal 10 x 4184 J
q=-41840 J
Using the first law of Thermodynamics,
ΔU = q-w
=-41840 J-(-10000 J)
=-41840 J + 10000 J
= 31840
Here, the heat lost is more than the work done on the system, so the change in internal energy is negative.

2. The work performed by a system is transferred by the system to its surroundings, by a mechanism through which the system can spontaneously exert microscopic forces on its surroundings. There are two types of work done:

(1) Work done by the system: In thermo- dynamics, work performed by a system is energy transferred by the system to its
surroundings, by a mechanism through which the system can spontaneously exert macroscopic forces on its surroundings. In the surroundings, through suitable passive linkages, the work can lift a weight, for example. Energy can also transfer from the surroundings to the system; in a sign convention used in physics, such work has a negative magnitude. Work done by a system is positive.

(2) Work done on the system: "Work done on a system" is a way of saying that energy has been added to a group of objects which are otherwise treated as being isolated from their surroundings. For example, your system may be a tennis ball. If you pick up the ball and place it on a shelf, you have done work on the system. Your work (requiring energy expended by you) of lifting the ball, adds gravitational potential energy to the ball. Work done on a system is negative. It can be found by considering whether system volume expands against a force or system volume contracts under a force.

(A) The work done by the system is considered as:

(a) negative value
(b) positive value
(c) zero
(d) infinite

(B) If the external pressure is greater than the pressure inside means what will happen to the piston:

(a) Move upward
(b) Move inward
(c) No changes
(d) Move towards the side

(C) Which one is the correct expression for the compression of gases?

(a) Pex = (P_{in} + dp)
(b) Pex = (P_{in} + dp)
(c) Pex = (P_{in} $\pm$ dp)
(b) Pex = (P_{in} $\pm$ dp)

(D) The value of work done is negative when:

(a) Volume remains constant
(b) Volume decreases
(c) Volume becomes infinite
(d) Volume increases

(E) Calculate the pressure-volume work done by the system when the gas expands from 2 litres to 3 litres against a constant external pressure of 30 atm.

(a) 30 litres atm
(b) - 20 litres atm
(c) - 30 litres atm
(d) 20 litres atm

Ans. (A) (a) negative value

Explanation: The work done by the system means the system will lose some of its energy to the surroundings. So, the internal energy of the system decreases and the value of work done will be negative.

(B) (b) Move inward

Explanation: If the external pressure is greater than the pressure inside the gas then, the piston will move inward which is it undergoes compression. Due to the high pressure outside the internal pressure of the gas cannot hold this. So, the external pressure will push the piston inward that is towards the low-pressure region.

(C) (a) Pex = (Pin + dp)

Explanation: If the pressure of the gas is not constant but changes in the process are always infinitesimally greater than the pressure of a gas at each stage of compression, then the volume will be decreased by an infinitesimal amount of dV. The work done on the gas can be calculated by:

$$w_{rev} = -\int_{V_1}^{V_2} p_{ex}\,dV$$

During each stage of the compression process, Pex = (Pin + dp)

(D) (d) Volume increases

Explanation: When the system's volume increases, w is -ve. This is because the work done is negative and the energy is lost by the system. The increase in volume is associated with the expansion of the system which corresponds to work done by the system.

(E) (c)-30 litre atm

Explanation:

$$\begin{aligned} w &= -p_{\text{external}} \times \Delta V \\ &= -p_{\text{external}} (V_{\text{final}} - V_{\text{initial}}) \\ &= -(30)\,(3\ 0\ 2) \\ &= -30 \text{ litre-atm} \end{aligned}$$

3. We can measure the movement of heat from one system to another that results in a temperature change. The magnitude of the temperature shift is determined by the substance's heat capacity. Hess's law states that the enthalpy change of reaction remains constant regardless of the number of steps. It aids in the calculation of the enthalpy of production, combustion, and other enthalpy changes. Bond enthalpies can also be used to calculate enthalpy change. Enthalpy is the measurement of energy in a thermodynamic system. The quantity of enthalpy equals to the total content of heat of a system, equivalent to the system's internal energy plus the product of volume and pressure. A mole of acetone takes less heat to vaporise than one mol of water.

(A) Which of the two liquids i.e., acetone and water has the greater vaporisation enthalpy?

(a) Acetone

(b) Water

(c) Equal

(d) Cannot be determined

(B) Calculate Δ,H° for the following reaction at 25°C:

$Fe_3O_{4(s)} + CO_{(g)} \rightarrow 3FeO_{(s)} + CO_{2(g)}$

$\Delta_f H°$ (kJ/mol)

–1118 –110.5 –272 –393.5

(a) –263 kJ (b) 54 kJ

(c) 19 kJ (d) –50 kJ

(C) Consider the following reaction between zinc and oxygen

$2Zn_{(s)} + O_{2(g)} \rightarrow 2ZnO_{(s)}; \Delta H = -693.8 \text{kJ mol}^{-1}$

(a) The enthalpy of two moles of ZnO is equal to the total enthalpy of two moles of Zn and one mole of oxygen by 693.8 kJ.

(b) The enthalpy of two moles of ZnO is more than the total enthalpy of two moles of Zn and one mole of oxygen by 693.8 kJ.

(c) 693.8 kJ mol^1 energy is evolved in the reaction.

(d) 693.8 kJ mol^1 energy is absorbed in the reaction.

(D) Increase in the enthalpy of the surrounding environment is equal to a decrease in the system's enthalpy. When the system and its surroundings are in thermal equilibrium, will their temperatures be the same?

(a) Yes

(b) No

(c) Depends on the pressure

(d) Always the same

Ans. (A) (b) Water

Explanation: Acetone requires less heat to vaporise due to the weak force of attraction between molecules. As a result, water has a higher enthalpy of vaporisation. It can be represented as:

ΔH_{vap} (water) > ΔH_{vap} (*acetone*)

(B) (c) 19 kJ

Explanation: $\Delta_r H° = \Delta_f H°$ (products) – $\Delta_f H°$ (reactants)

$= [(3 \times (-272)] + (-393.5) - (-1118 - 110.5)$

$= 19$ kJ

(C) (c) 693.8 kJ mol^{-1} energy is evolved in the reaction.
Explanation: As the value of heat is negative, that means heat is evolved during the reaction and heat is released when reactants have energy higher than that of products.
(D) (a) Yes
Explanation: Yes, when the system and its surroundings are thermally balanced, their temperatures are the same.

4. A calorimeter is a device that is in use for measuring the warmth of chemical reactions or physical changes also as heat capacity. Normally a calorimeter consists of a thermometer. This thermometer is then attached to a metal container filled with water suspended above a combustion chamber. It is one of the measurement devices useful in the study of thermodynamics, chemistry, and biochemistry. For finding the enthalpy change per mole of a substance P in a reaction between two substances P and Q. Here, both the substances P and Q, are separately added to a calorimeter and the initial and final temperatures are noted. Multiplying the natural process by the mass and heat capacities of the substances gives worth for the energy given off or absorbed during the reaction. Dividing the energy change by what percentage of moles of A were present gives its enthalpy change of the reaction.
$q=C_v(T_f-T)q=Cv(T_f-T)$
Where q is the amount of warmth consistent with the change in temperature measured in joules and C, is the heat capacity of the calorimeter which is measured in units of energy per temperature (Joules/Kelvin).
(A) Explain the need of using a calorimeter.
(B) What is the AH sign of endothermic reactions, and why is it so? What is the relationship between the standard enthalpy of formation and a compound's enthalpy?
(C) What are the specific heat capacity and molar heat capacity for water? Why is the enthalpy of neutralisation lower when either the acid or the base, or both, is weak?

Ans. (A) Calorimetry is the process of measuring the amount of heat released or absorbed during a chemical reaction. It is a crucial part of thermodynamics. In order to measure the heat of a reaction, the reaction must be isolated so that no heat is lost to the environment. By knowing the change in heat, it can be determined whether or not a reaction is exothermic (releases heat) or endothermic (absorbs heat). Calorimetry also plays a large part in everyday life, controlling the metabolic rates in humans and consequently maintaining such functions like body temperature.

(B) ΔH is postive as $\Delta H = H_p - H_r$ and H, <Hp The relationship between the standard enthalpy of formation and a compound's enthalpy is that they are equal.

(C) Specific heat capacity for H_2O
= 4.1 JK- ^{1}g-1
Molar heat capacity for H_2O
= 4.18 x 18
= 75.24 J mol-^{1} K-1
A part of the heat is used up for dissociation of the weak acid or weak base or both.

5. Lattice energy is the change in the enthalpy which takes place when one mole of an ionic compound is breakdown into the gaseous ion state. Alternately, it can be defined as the energy that must be supplied to one mole of an ionic crystal in order to separate it into gaseous ions in a vacuum via an endothermic process. Therefore, this quantity always holds a positive value. Some sources define lattice energy in the opposite manner, i.e., the amount of energy released when an ionic solid is formed from its gaseous ionic constituents via an exothermic process. According to this definition, lattice energy must always hold a negative value. The two primary factors that affect the lattice energy of an ionic compound are the magnitude of charge associated with the constituent ions and the distance between the ions. Due to the electrostatic forces between them, the individual ions in an ionic lattice are attracted to each other. The strength of the electrostatic force of attraction is directly proportional to the magnitude of the charge held by the constituent ions, i.e., the greater the charge and the stronger the force of attraction, the stronger the lattice. The lattice energy of an ionic compound is inversely proportional to the distance between the ions. The further the distance between the ions in a lattice, the weaker the electrostatic forces holding them together and the lower the lattice energy. Since it is impossible to determine lattice enthalpies directly by experiment, we use an indirect method where we construct an enthalpy diagram called a Born-Haber Cycle.

(A) Name the energy when the decomposition of NaCl transforms into a sodium ion and chloride ion during this reaction 788 kJmol^1 energy release.
(a) Lattice energy
(b) Dilution energy
(c) Neutralization energy
(d) Translation energy

(B) Choose the correct option for analyzing the reaction energies:

(a) Chemical cycle (b) Born-Haber cycle

(c) Nitrogen cycle (d) Carbon cycle

(C) The enthalpy of dilution of a solution will be............. on the original concentration of the solution and the amount of solvent added.

(a) Independent

(b) May be dependent

(c) May be independent

(d) Dependent

(D) The enthalpy of the solution will be positive or:

(a) does not exist

(b) negative

(c) zero

(d) infinity

(E) For the given reaction

$NaCl_{(s)} \rightarrow Na^{+}_{(g)} + Cl^{-}_{(g)}$

What is the type of enthalpy involved in the reaction?

(a) Enthalpy of atomization

(b) Enthalpy of dilution

(c) Lattice enthalpy

(d) Enthalpy of ionisation

Ans. (A) (a) Lattice energy

Explanation: Lattice enthalpy is the change in enthalpy that takes place when the dissociation of one mole of an ionic compound which is transformed into a gaseous ions state.

(B) (b) Born-Haber cycle

Explanation: It is difficult to find the lattice enthalpy of the ionic compounds through a direct experiment. Therefore, we find the enthalpy through an indirect method that is Born Haber cycle.

(C) (d) Dependent

Explanation: Enthalpy of dilution is dependent on the concentration of the original solution and the amount of solvent. The heat is produced or exhausted by dissolving a mole of the compound in the excess solvent.

(D) (b) negative
Explanation: It can be exothermic and endothermic depending on the reaction.
(E) (c) Lattice enthalpy
Explanation: Lattice energy can be defined as the energy required to convert one mole of an ionic solid into gaseous ionic constituents. Thus, the given reaction represents the lattice enthalpy.

6. The amount of heat energy released or absorbed when one mole of a substance dissolves in a specified amount of solvent is known as enthalpy of solution. Enthalpies of solution may be either positive or negative, in other words, some ionic substances dissolved endothermically (for example, NaCl); others dissolve exothermically (for example, NaOH). An infinitely dilute solution is one where there is a sufficiently large excess of water that adding any more doesn't cause any further heat to be absorbed or evolved. So, when 1 mole of sodium chloride crystals is dissolved in an excess of water, the enthalpy change of solution is found to be +3.9 kJ mol^1. The change is slightly endothermic, and so the temperature of the solution will be slightly lower than that of the original water. The enthalpy of solution in the infinite dilution we can observe the change in the enthalpy by dissolving the substance in the infinite amount of solvent there will be minimal interaction between the ions. The enthalpy change is associated with the addition of a specific amount of solute to the specific amount of solvent at a constant temperature. The values show general dependence of the enthalpy of solution on amount of solvent. As more solvent is used, the enthalpy of solution approaches a limiting value. That is the value in an infinitely dilute solution.
(A) Explain the enthalpy of dilution.
(B) Is the dissolution of hydrated copper sulphate an exothermic or endothermic process? Why is copper sulphate taken in powdered form?
(C) When liquid A is mixed with liquid B, the resulting solution is found to be cooler. What do you conclude about the nature of the solution? What type of deviation is expected of a solution obtained by adding concentration H_2SO, to water?

Ans. (A) The enthalpy change is associated with the addition of a specific amount of solute to the specific amount of solvent at a constant temperature.
(B) When the dissolution of hydrated copper sulphate is an endothermic process. The copper sulphate is taken in powdered form to facilitate its dissolution in minimum time. Hence, preventing heat loss to the surroundings.

(C) The solution shows a positive deviation. Absorption of heat takes place. A-B interaction is weaker than A-A and B-B interaction. By adding a concentrated H_2SO_4 to water the solution shows a negative deviation. The heat is liberated and A-B interactions are stronger than A-A and B-B interactions.

7. Nernst stated that the entropy changes for each chemical or physical transition between condensed phases, at temperatures very close to the absolute zero, is equal to zero:

$$\lim_{T \to 0} \Delta S = 0$$

This statement is also referred to as the Nernst heat theorem. The statement of Nernst was simplified by Planck. He stated that not only the entropy changes for processes but also the actual entropy of each condensed substance equals zero if the temperature approaches absolute zero. This statement explicitly excludes mixtures. The following statement makes the explicit exclusion of mixtures unnecessary: for each system in equilibrium, the entropy equals zero when the temperature approaches the absolute zero. The current "extended form" of the third principle is the one introduced by Planck (1917) which admits, in two stages, that the absolute value of the thermodynamic entropy of any homogeneous solid at 0 Kelvin is: (i) "a universal constant"; (ii) "that one can set to zero without loss of generality". This choice corresponds to the cancellation of the additive constant So in the Planck- Boltzmann statistical formula. An important caution is that this definition only concerns solids, and is therefore not applicable to perfect gases. By a lack of luck, the water which constitutes an important component of the atmosphere possesses the singular property of having a residual entropy still present at OK. The work of Pauling (1935) completed by Nagle (1966) was used to estimate the value at So= 0.82 cal/K/mole, by calculating the impacts due to the transfer of charges via the hydrogen bonds still at work at OK within the molecule H_2O. So, just for water, you need to include that difference S, to have a reference that is "the most stable" at zero Kelvin.

(A) Is the third law is applicable to perfect gases? What are the exceptions of the third law of thermodynamics?

(B) Why is the third law of thermodynamics important?

(C) What are the limitations of this law and under which conditions the third law of thermodynamics is not being obeyed?

Ans. (A) No, it is only applicable to solids. The third law of thermodynamics states that a system's entropy approaches a constant value as the temperature approaches absolute zero. With the exception of non-crystalline solids (glasses), the entropy of a system at absolute zero is typically close to zero.

(B) The third law of thermodynamics has two important consequences: it defines the sign of the entropy of any substance at temperatures above absolute zero as positive, and it provides a fixed reference point that allows us to measure the absolute entropy of any substance at any temperature.

(C) Limitations:

(1) If any disorder like impurity or imperfection is found in a substance then the entropy of such crystal is non-zero at 0 K. For example: The entropy of pure carbon dioxide and nitric oxide is not zero at 0 K. This shows that there exists disorder in the arrangement of such molecules.

(2) This law is applicable only to pure compounds. Thus, we can say that this law is not applicable to glass which is a supercooled liquid. It is also not applicable to amorphous substance and supercooled solutions.

(3) It is impossible by any procedure, no matter how idealised, to reduce the temperature of any closed system to zero temperature in a finite number of finite operations.

8. Melting of ice into water happens spontaneously as soon as ice is left at room temperature. Ice is a solid with an ordered crystalline structure as compared to water, which is a liquid in which molecules are more disordered and randomly distributed. All natural processes tend to proceed in a direction which leads to a state that has more random distribution of matter and energy. All of these processes take place spontaneously, meaning that once they start, they will proceed to the end if there is no external intervention. You will never witness the reverse of this process, in which water converts back to ice at room temperature. In other words, it would be inconceivable that this process could be

reversed without tampering with the external conditions (you will have to put water in the freezer to force it to form ice).

(A) This is an example of which law of thermodynamics?

(a) Zeroth law

(b) First law

(c) Second law
(d) Third law

(B) What determines the direction in which a process will go under a given set of conditions?
(a) Temperature
(b) Pressure
(c) Entropy
(d) Enthalpy

(C) Effect on entropy during this change:
(a) Increase
(b) Decrease
(c) No change
(d) Cannot be determined

(D) Melting of ice is:
(a) Endothermic process
(b) Exothermic process
(c) Equilibrium process
(d) Adiabatic process

(E) In the melting of ice, which one of the conditions will be more favourable?
(a) High temperature and high pressure
(b) Low temperature and low pressure
(c) Low temperature and high pressure
(d) High temperature and low pressure

Ans. (A) (c) Second law

Explanation: A crystalline solid is composed of an ordered array of molecules, ions, or atoms that occupy fixed positions in a lattice, whereas the molecules in a liquid are free to move and tumble within the volume of the liquid; molecules in a gas have even more freedom to move than those in a liquid. Each degree of motion increases the number of available microstates, resulting in a higher entropy. Thus, the entropy of a system must increase during melting.

(B) (c) Entropy

Explanation: The second law of thermodynamics states that the total entropy of a chemical system and that of its surroundings always increases if the chemical or physical change is spontaneous. The preferred direction in nature is toward maximum entropy.

(C) (a) Increase

Explanation: When ice melts, it means solid is converting into liquid so the entropy of the system increases and the process becomes spontaneous.

(D) (a) Endothermic process

Explanation: Water in a higher energy state, as the liquid can rotate and vibrate while solid ice can only vibrate. This means for ice to turn into a higher energy state(water) it has to absorb energy, hence it is an endothermic process with respect to the system (surrounding temperature decreases).

(E) (a) High temperature and high pressure

Explanation: Since the change of ice into water is an endothermic process, hence with rising of temperature ice melts into water. Since the volume of ice is more than that of water so an increase of pressure favour melting.