**First law of thermodynamics**

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**Introduction**

The first law of thermodynamics is sometimes called the law of conservation of energy because it accounts for the input and output energies when a system does work. The law can be stated as follows,

―*The change in internal energy of a system, when heat is absorbed will lead to work done by the system or against the system*‖

From the statement of the law expressed above, three set of parameters are significant. These are heat, internal energy and work. Mathematically, the first law can be expressed as follows,

𝑑𝑈 = ∂𝑞 + ∂W 3

where ∂q is the infinite quantity of heat absorbed. The ∂U is the infinite change in internal energy and ∂ W is the work done. Equation 3 is the differential form of the first law of

thermodynamics. If the equation is integrated, in a closed system, we will have the integrated form of the equation according to equation 4,

𝑈2 ∂𝑈

∫𝑈

1

= ∫ ∂𝑞 + ∫ ∂W = ∆𝑈 = 𝑞 + W 4

The above equation indicates that whenever there is a change in internal energy of a system, heat will be absorbed and work will be done on the system or by the system. The sign of W is positive when the heat absorbed leads to increase in internal energy and negative when the heat absorbed leads to decrease in internal energy. Therefore, positive heat is energy entering the system, and negative heat is energy leaving the system. Positive work is work done against the system, and negative work is work done by the system on the surroundings.

Heat refers to the transfer of energy across the boundary caused by a temperature gradient at the boundary. Work refers to the transfer of energy across the boundary caused by the displacement of a macroscopic portion of the system on which the surroundings exert a force, or because of other kinds of concerted, directed movement of entities (e.g., electrons) on which an external force is exerted.

* 1. **Consequences of the first law of thermodynamics**

# Thermodynamic work

Thermodynamic work is usually considered as the work done by expansion of a gas. In order to gain insight into this concept, let us consider a piston (whose cross sectional area is A), compressing a gas (at pressure, P and volume, V). If the piston moves a distance called dx, then it can be stated that the force acting on the piston is given as,

𝐹 = 𝑃𝐴 5

The volume created as a results of this compression will be given as dV = Adx, indicating that A

= dV/dx or dx = dV/A The work done is equal to the product of the applied force and the distance ,

𝑑W = 𝐹𝑑𝑥 6

Substituting for F and dx in equation 6, we have,

𝑑W = −𝑃𝐴 𝑑𝑉

𝐴

= −𝑃𝑑𝑉 7

Equation 7 can be simplified by integration, hence we have,

W = − ∫𝑉2 𝑃𝑑𝑉 = −( 𝑉 − 𝑉 ) 8

𝑉1 2 1

Returning to the mathematical expression of the first law, i.e, ∆𝑈 = ∂𝑞 + ∂W, we can replace W with PdV and we have,

𝑑𝑈 = ∂𝑞 + 𝑃∂𝑉 9

# Heat change at constant pressure and at constant volume

Equation 9 provides the basis for several transformational applications of the first law. Let us start by considering the two major conditions under which experimental study can be carried out. These are at constant pressure and at constant volume. At constant pressure, the heat absorbed is qp and the pressure will be constant at, P, the volume will change from V2 to V1 while the internal energy will change from U1 to U2 (note that internal energy is a state function). Therefore, the first law is slightly modified to equation 10.

𝑈2 − 𝑈1 = 𝑞𝑃 + + (𝑉2 − 𝑉1) 10

Rearrangement of equation 10 leads to equations 11 and 12

𝑞𝑃 = 𝑈2 − 𝑈1 + (𝑉2 − 𝑉1) 11

𝑞𝑃 = (𝑈2 + 𝑃𝑉2) – (𝑈1 + 𝑃𝑉1) 12

At this juncture, we define a state function call enthalpy, denoted as H. Enthalpy is the heat absorbed at constant pressure. It is a state function and can be represented as, H = U + PV. Therefore, U2 + PV2 = H2, U1 + PV1 = H1, hence (𝑈2 + 𝑃𝑉2) – (𝑈1 + 𝑃𝑉1) = H2 – H1 = H. Consequently, the heat absorbed at constant pressure is equal to change in enthalpy. As a consequence of the first law if the reaction is carried out at constant volume , dV will be equal to zero and we have 𝑈2 − 𝑈1 = 𝑞𝑣, which translates to the statement that the heat absorbed at constant volume is equal to change in internal energy, U = 𝑈2 − 𝑈1

# Solved problem 1

1. From first principle, Show that thermodynamic work can be written in terms of pressure volume work.
2. Show that the heat absorbed by a body at constant pressure and at constant volume is equal to change in enthalpy and change in internal energy respectively.

# Solution

1. Consider a piston (whose cross sectional area is A), compressing a gas (at pressure, P and volume, V). If the piston moves a distance called dx, then it can be stated that the force acting on the piston is given as,

𝐹 = 𝑃𝐴 5

The volume created as a results of this compression will be given as dV = Adx, indicating that A

= dV/dx or dx = dV/A Therefore the work done is equal to the product of the applied force and the distance,

𝑑W = 𝐹𝑑𝑥 6

Substituting for F and dx in equation 6, we have,

∂W = 𝑃𝐴 𝑑𝑉

𝐴

= 𝑃∂𝑉 7

Equation 7 can be simplified by integration, hence we have,

W = 𝑉2 𝑃∂𝑉 = ( − 𝑉 ) 8

∫𝑉1 2 1

Returning to the mathematical expression of the first law, i.e, ∆𝑈 = 𝑑𝑞 + 𝑑W, we can replace W with PdV and we have,

𝑈 = ∂𝑞 + 𝑃∂𝑉

1. From the first law of thermodynamics, 𝑈 = ∂𝑞 + 𝑃∂𝑉, therefore,

𝑈2 − 𝑈1 = 𝑞𝑃 + (𝑉2 − 𝑉1) 1

Rearrangement of equation 1 leads to equations 2 and 3

𝑞𝑃 = 𝑈2 − 𝑈1 + (𝑉2 − 𝑉1) 2

𝑞𝑃 = (𝑈2 + 𝑃𝑉2) – (𝑈1 + 𝑃𝑉1) 3

At this juncture, we define a state function call enthalpy, denoted as H. Enthalpy is the heat absorbed at constant pressure. It is a state function and can be represented as, H = U + PV. Therefore, U2 + PV2 = H1, U1 + PV1 = H1, hence (𝑈2 + 𝑃𝑉2) – (𝑈1 + 𝑃𝑉1) = H2 – H1 = H. Consequently, we state that the heat absorbed at constant pressure is equal to change in enthalpy. Let us consider the consequence of the first law if the reaction is carried out at constant volume. In this case, dV will be equal to zero and we have 𝑈2 − 𝑈1 = , which translates to the statement that the heat absorbed at constant volume is equal to change in internal energy, U =

𝑈2 − 𝑈1