

# حراره وثرموداينمك

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## 5. THE LAWS OF THERMODYNAMICS I

### 5.1 THE ZEROTH LAW—TEMPERATURE

Zeroth Law states that if two bodies are in thermal equilibrium with a third, they are in thermal equilibrium with each other. This statement leads directly to an operational definition of temperature.

### 5.2 THE FIRST LAW—TRADITIONAL APPROACH

The traditional approach to the First Law is based on the assumption that the concepts of work and heat have already been established.

The concept of heat, as alluded to before, is best described in terms of temperature changes.

If a system A, initially at temperature  $t_A$ , is brought in thermal contact with system B at temperature  $t_B$  at constant pressure and volume and the final temperature at equilibrium is  $t$ , then the ratio of the temperature changes, for infinitesimally small differences,

$\delta t_A = t - t_A$  and  $\delta t_B = t - t_B$  defines the ratio of the heat capacities of the two systems

$$(\delta t_A) / (\delta t_B) = -C_B/C_A \quad \dots\dots\dots(5.1)$$

Thus, if a particular value is assigned to one of the heat capacities, the other is then determined. The heat transfer for A is defined as

$$dq_A = C_A dt \quad \text{or} \quad q_A = \int C_A dt \dots\dots\dots(5.2)$$

and for B

$$dq_B = C_B dt \quad \text{or} \quad q_B = \int C_B dt \dots\dots\dots(5.3)$$

The First Law of Thermodynamics then reads

$$\Delta E = q + w \quad \text{for macroscopic changes} \dots\dots\dots(5.4)$$

and

$$dE = dq + dw \quad \text{for infinitesimal changes} \dots\dots\dots(5.5)$$

where  $E$  is the internal energy.

The symbol  $\Delta E$  stands for the energy difference between final and initial states of the system; that is,

$$\Delta E = E_B - E_A.$$

Thus, the first statement does not only imply that the internal energy is the sum of the heat and work energies, but also that  $E$  is a state function; that is, it is independent of the manner in which the state was obtained. The second statement implies that  $dE$  is an exact differential, despite the fact that  $dq$  and  $dw$  are generally not. (Thus,  $dq$  and  $dw$  are inexact differentials and path dependent;  $dE$  is exact and path independent.)

The First Law can also be interpreted as a statement of conservation of energy. Whatever the surrounding loses in the form of heat or work, the system gains in the form of internal energy and vice versa. There is no way to measure  $E$  itself, so this relation cannot be directly verified. What can be verified is that when a system, initially in a state  $A$ , changes to a state  $B$ , the quantity  $q + w$  is path independent, that is, is independent of the manner in which the change is brought about. Also, when the system undergoes a cyclic change,  $A \rightarrow B \rightarrow A$ , then  $q = -w$ .

### 5.3 MATHEMATICAL INTERLUDE I: EXACT AND INEXACT DIFFERENTIALS

Suppose we are given a differential expression of this form:

$M(x,y)_y dx + N(x, y)_x dy$ . Can it be obtained from a function  $f(x, y)$ , which is a function of the same variables? If such a function exists, then

$$df = (\partial f / \partial x)_y dx + (\partial f / \partial y)_x dy \dots \dots \dots (5.6 a)$$

and

$$M(x, y) = (\partial f / \partial x)_y \dots \dots \dots (5.6 b)$$

$$N(x, y) = (\partial f / \partial y)_x \dots \dots \dots (5.6 c)$$

In other words,  $M$  and  $N$  are partial derivatives of  $f(x, y)$ .

A differential  $df = (\partial f / \partial x)_y dx + (\partial f / \partial y)_x dy$  is exact, if any of the following statements are satisfied:

- 1) Its integral is path independent, i.e.  $\int_A^B df = f_B - f_A$ ;

2) The integral along a closed contour is zero, i.e.  $\oint df = 0$ ;

3)  $(\partial M(x, y)/\partial y)_x = (\partial N(x, y)/\partial x)_y$ .

Proof of statement 3 is as follows:

$df = Mdx + Ndy$  then.....(5.7a)

$\partial^2 f(x, y)/\partial y \partial x = [\partial/\partial y(\partial f/\partial x)]_x = (\partial M/\partial y)_x$ .....(5.7b)

$\partial^2 f(x, y)/\partial y \partial x = [\partial/\partial x(\partial f/\partial y)]_y = (\partial N/\partial x)_y$ .....(5.7c)

The left-hand sides of Equations 5.7b and 5.7c are the same, since they only differ by the order of differentiation. Therefore, the right-hand sides of the equations must be equal.

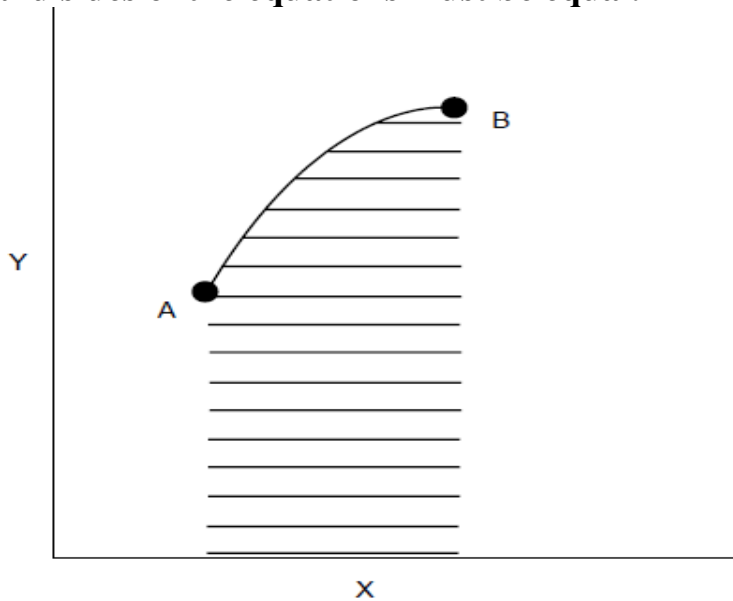


Figure 5.1a Graphical representation of the integral  $I = \int y dx$ . The shaded area represents the value of the integral.

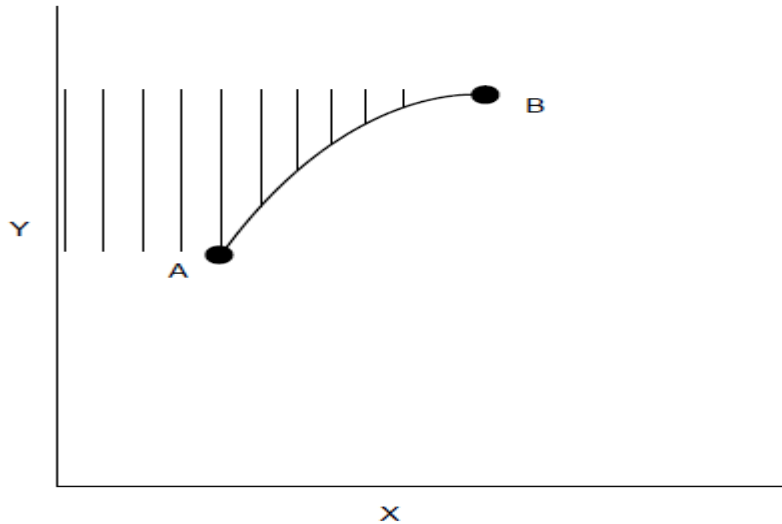


Figure 5.1b Graphical representation of the integral  $I = \int x dy$ . The shaded area represents the value of the integral.

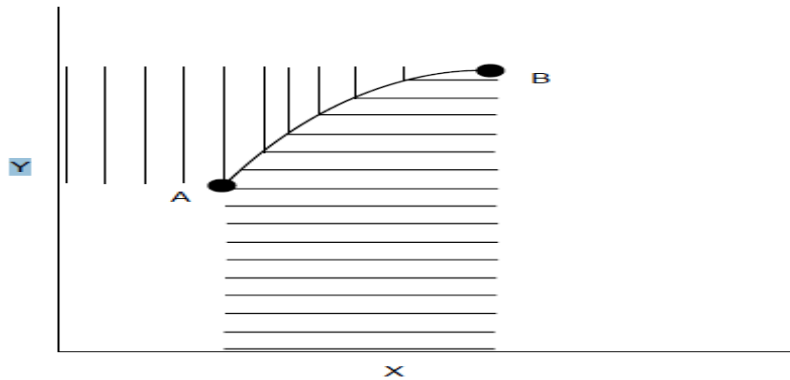


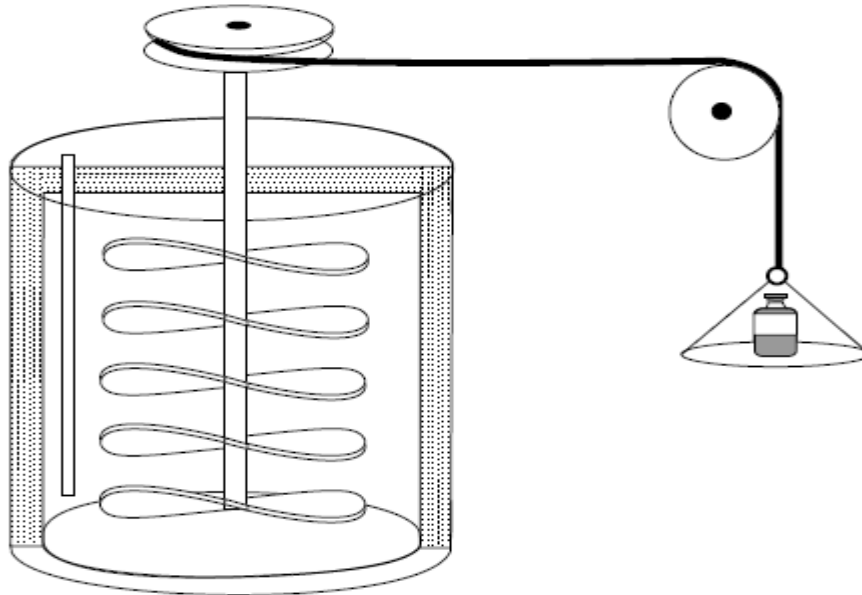
Figure 5.1c Graphical representation of the integral  $I = \int (y dx + x dy)$ . The shaded area represents the value of the integral

Figure 5.2 is a schematic diagram of the Joule Paddle-Wheel experiment. An adiabatically encased fluid is stirred by a paddle wheel, which rotates as a result of placing weight on the tray or by some other mechanical device.

The fluid is the system, and the paddle wheel is considered part of the surrounding. The rotating paddle wheel causes the temperature of the fluid to rise, thereby altering the state of the system. The change in the state is determined by observing the change in the temperature. It is found that the change in temperature, and thus the change in the state of the system, is independent of the manner in which the transition takes place. It is immaterial whether the transition is reversible or irreversible or whether it is produced by mechanical work or some other kind of work, such as electrical work.

Because the work in this adiabatic process is found to be independent of path, the differential  $dw_{ad}$  must be exact. Furthermore, because it

is universally accepted (or believed) that energy—mass energy, since Einstein— cannot be created or destroyed, it is natural to assume that the lost adiabatic work, a form of energy, is transformed into another form of energy, the



**Figure 5.2** Joule’s Paddle–Wheel Experiment. The weight in the pan sets the paddle wheel in motion, producing work on the fluid, which is dissipated as heat causing the temperature to rise.

internal energy,  $E$ . This energy is a property of the system, a state function, and must be independent of the manner in which it was created. These statements can be summarized concisely in the form of the First Law, which reads:

*When a system makes a transition from state A to B by adiabatic means the change in internal energy is*

$$\Delta E = E_B - E_A = w_{ad} \dots \dots \dots (5.8a)$$

or

$$dE = dw_{ad} \dots \dots \dots (5.8b)$$

What happens if the system is transformed from the same initial state A to the same final state B by work,  $w$ , which is nonadiabatic? There is no reason to assume that the Equation 5-8a will hold, and in fact

$$\Delta E = E_B - E_A \neq w \dots \dots \dots (5.9)$$

To replace the inequality sign by an equal sign, a “correction” factor,  $q$ , must be added

$$\Delta E = q + w \dots \dots \dots (5.10)$$

This correction factor defines the heat. Obviously,  $q = w_{ad} - w$ .  
 [Actually, this equation does not really define the concept of heat, but rather the measure of heat.] In summary,

$$\Delta E = E_B - E_A = w_{ad} \dots \dots \dots (5.11a)$$

$$\Delta E = E_B - E_A = q + w \dots \dots \dots (5.12a)$$

or, in differential form

$$dE = dw_{ad} \dots \dots \dots (5.11b)$$

$$dE = dq + dw \dots \dots \dots (5.12b)$$

Note: Both  $E$  and  $q$  are defined operationally and entirely in terms of the mechanical quantity work. Furthermore, the notion that the  $E_B - E_A$  is path independent, and thus that  $E$  is a state function, is not a mere assumption but has an experimental basis.

## 5.5 SOME APPLICATIONS OF THE FIRST LAW

### 5.5.1 Heat Capacity

The heat capacity is defined as

$$C = \lim_{(\delta T \rightarrow 0)} dq / \delta T = dq / dT \dots \dots (5.13)$$

In general,  $C$  is a function of temperature, mass, pressure, volume, and other variables. Usually, one or more of the variables are held constant, indicated here by a subscript on  $C$ . In particular,

$$C_V = dq_V / dT = (\partial E / \partial T)_V \dots \dots (5.14a)$$

$$C_P = dq_P / dT \dots \dots \dots (5.14b)$$

$$C_{adiabatic} = 0 \dots \dots \dots (5.14c)$$

### 5.5.2 Heat and Enthalpy

The enthalpy is defined as

$$H = E + PV \dots\dots\dots(5.15)$$

**H is a state function (path independent integral) because E and PV are state functions. If the system is taken from state A to state B,**

$$\Delta H = \Delta E + \Delta(PV) = E(T_B, V_B) - E(T_A, V_A) + (P_B V_B - P_A V_A) \dots\dots\dots(5.16)$$

**At constant pressure,  $P_A = P_B = P$ , the right-hand side of the equation is identical to Equation 3-27a; thus**

$$q_P = \Delta H \dots\dots\dots(5.17)$$

**Another way to reach the same conclusion is to observe that at constant pressure**

$$\Delta H = \Delta E + \Delta(PV) = q + w + P\Delta V = q_P - P\Delta V + P\Delta V = q_P \dots\dots(5.17a)$$

**Writing H as a function of T and P shows that**

$$dH = dE + PdV + VdP \dots\dots\dots(5.18)$$

$$= dq - PdV + PdV + VdP = dq + VdP \dots\dots\dots(5.19)$$

**Or**

$$dq = dH - VdP \dots\dots\dots(5.20)$$

**Thus, at constant P**

$$C_P = dq_P/dT = (\partial H/\partial T)_P \dots\dots\dots(5.21)$$

**Similarly, from the expression**

$$dq = dE + PdV \dots\dots\dots(5.22)$$

**we obtain for constant volume**

$$C_V = dq_V/dT = (\partial E/\partial T)_V \dots\dots\dots(5.23)$$

### **5.5.3 Isothermal Change, Ideal Gas (1 mol)**

**At constant temperature,  $\Delta E = 0$ , and**

$$q = -w = \int_1^2 PdV = RT \int_1^2 d\bar{V}/\bar{V}$$

$$= RT \ln \bar{V}_2/\bar{V}_1 = RT \ln P_1/P_2 \quad \dots\dots\dots(5.24)$$

**5.5.4 Adiabatic Change, Ideal Gas (1 mol)**

$$dq = dE - dw = \bar{C}_V dT + Pd\bar{V} = 0 \quad \dots\dots\dots(5.25a)$$

$$\bar{C}_V dT/T + R d\bar{V}/\bar{V} = \bar{C}_V d \ln T + R d \ln \bar{V} = 0 \quad \dots\dots(5.25b)$$

Using Eq.

$$\bar{C}_P - \bar{C}_V = R \quad \dots\dots\dots(5.26)$$

and replacing  $C_P/C_V$  by  $\gamma$ , we get, after integration

$$\ln T_2/T_1 + (\gamma - 1) \ln \bar{V}_2/\bar{V}_1 = 0 \quad \dots\dots(5.27a)$$

Or

$$(T_2/T_1)(\bar{V}_2/\bar{V}_1)^{\gamma-1} = 1 \quad \dots\dots\dots(5.27b)$$

If we replace  $T_2/ T_1$  by  $P_2V_2/P_1V_1$ , we get

$$(P_2/P_1)(V_2/V_1)^\gamma=1 \quad \dots\dots\dots(5.28 a)$$

Equations 5.27 b and 5.28 a are often expressed in the form

$$T\bar{V}^{\gamma-1} = \text{const} \quad \text{and} \quad P\bar{V}^\gamma = \text{const} \quad \dots\dots\dots(5.28b)$$