#### <u>Chapter 3</u> Work

<u>Work.</u> The term work refers to an inter change of energy between a system and its surroundings. When the hot gases in the cylinders of an automobile engine push against the moving pistons, work is done by the gases. When air is forced into a bicycle tire by a pump, work is done on the air. The work may be mechanical, as above, or it may be electrical, magnetic, or any other types.  $W = \int F \cos \theta ds$  ------- (1)

in most cases of practical interest the work is associated with a change in volume.

Suppose that we have a system of arbitrary shape as in Fig. 1, acted upon by an external hydrostatic pressure  $P_e$ , and that the original boundary of the system, shown by full lines, is displaced out ward against the external pressure to a new position show by dotted lines.



Fig. - 1-

The external force df exerted against a portion of the surface of (dA) is  $dF = P_e dA$  (2)

And if this portion moves out a distance (ds) the work done against the external force is:

$$dW = dFds = P_e dAds \qquad (3)$$

$$dW = P_e Ads \qquad (4) \qquad A = \text{total area of the surface}$$

$$dV = Ads \qquad (5) \qquad \text{the increase in volume of the system}$$

$$dW = P_e dV \qquad (6) \qquad \text{external work}$$

The work dW is ( + tive ) when work is done by a system and the volume of the system increases, and dV is positive. When work is done on a system, the volume decrease, and dV and dW are (- ive ), negative.

 $\left(\frac{dW}{n} = \frac{PdV}{n}\right)$  when the work is divided through by the mass (m) or the number of moles (n) of a system

number of moles ( n ) of a system

The work done per unit mol.

Any reversible process can be represented by a line in the P-v plane. The (dw) done in a small (specific) volume change (dv) is represented graphically by the area of a narrow vertical strip (Fig. 2). The total work (w) done in the finite increase in volume from state <u>a</u> to state <u>b</u>.



(w +ive) if the process from <u>a</u> to <u>b</u>, (w -ive ) if the process in the opposite direction (from <u>b</u> to <u>a</u> ) and the work is done is done on the system, Fig. (3- a, b, c)



The net work done by the system

We next evaluate (  $\int p dv$  ) for a number of processes.

1/ <u>The work done in any isometric process</u> is obviously zero, since in such a process

v = constant, dv = 0, w = 0, fig. 4



2/ In an isobaric process the pressure is constant and the work is  $w = P \int_{v_a}^{v_b} dv = P(v_b - v_a)$  ----- (10)

Which evidently is the area of the shaded rectangle in Fig. 5



3/ <u>Consider next an isothermal</u> process, carried out at the constant temperature T. If the system is an ideal gas

$$P = \frac{RT}{\upsilon} \qquad (11)$$
$$w_T = \int_{\upsilon_a}^{\upsilon_b} \frac{RT}{\upsilon} d\upsilon = RT \ln \frac{\upsilon_b}{\upsilon_a} \qquad (12)$$

 $(w_T)$  is represent by the shaded area in Fig.6, and This equation can be put in a number of different forms



Obviously, there are an infinite number of different processes by which a system can be taken from a given initial state to a final state.

Three possible processes connecting states <u>a</u> and <u>b</u> are show in Fig. 7 The work done by the system is greatest along the path <u>acb</u>, least along path <u>adb</u>, and has some intermediate value along the third path.



Fig. 7

$$w_{path(a\to c\to b)} = \int P d\upsilon + \int_{\upsilon_1}^{\upsilon_2} P_2 d\upsilon = 0 + 2P_1(2\upsilon_1 - \upsilon_1) = 2p_1\upsilon_1 \qquad (14)$$

$$w_{path(a\to d\to b)} = \int_{\nu_1}^{\nu_2} P_1 d\nu + \int P d\nu = P_1 (2\nu_1 - \nu_1) = p_1 \nu_1$$
 (15)

$$w_{path(a\to b)} = \frac{2P_1\nu_1 + P_1\nu_1}{2} = \frac{3}{2}P_1\nu_1$$
 (16)

### Partial derivatives

In a system consisting of a fluid under pressure in a cylinder provided with a movable piston, one can change the V by any arbitrary amount dv and the same time change the T by any arbitrary amount dT. When this has been done, the P will be found to have changed by just such an amount dp that the new values of P, V and T also satisfy the equation of state.

The general from of the equation of state is  

$$F(P,\upsilon,T) = 0 \qquad (17)$$
Or, if it is solved in turn for each of the state variables,  

$$P = f_1(\upsilon,T), \qquad \upsilon = f_2(T,P), \qquad T = f_3(P,\upsilon) \qquad (18)$$

$$P = f(\upsilon,T), \qquad dP = \left(\frac{\partial P}{\partial \upsilon}\right) d\upsilon + \left(\frac{\partial P}{\partial T}\right) dT \qquad (19) \text{ in mathematics}$$

$$dP = \left(\frac{\partial P}{\partial \upsilon}\right)_T d\upsilon + \left(\frac{\partial P}{\partial T}\right)_{\upsilon} dT \qquad (20) \text{ in thermodynamics}$$

$$\upsilon = f(T,P), \qquad d\upsilon = \left(\frac{\partial \nu}{\partial T}\right)_P dT + \left(\frac{\partial \upsilon}{\partial P}\right)_T dP \qquad (21)$$
Let us now eliminate dv between the latter two equations (20 and 21) and collect coefficients of dp and dT.  

$$dP = \left(\frac{\partial P}{\partial \upsilon}\right)_T \left[\left(\frac{\partial \omega}{\partial T}\right)_P dT + \left(\frac{\partial \upsilon}{\partial P}\right)_T dP\right] + \left(\frac{\partial P}{\partial T}\right)_{\upsilon} dT \qquad (22)$$

$$dP = \left(\frac{\partial P}{\partial \upsilon}\right)_T \left(\frac{\partial \upsilon}{\partial P}\right)_T dP = \left(\frac{\partial P}{\partial \upsilon}\right)_T \left(\frac{\partial \upsilon}{\partial T}\right)_P dT + \left(\frac{\partial P}{\partial T}\right)_{\upsilon} dT$$

But the changes dp and dT are independent, that is, we can assign any value to dT and any other value to dp. Suppose we let dT = 0,  $dp \neq 0$ Then to satisfy the equation above we must have

$$\begin{bmatrix} 1 - \left(\frac{\partial P}{\partial \upsilon}\right)_T \left(\frac{\partial \upsilon}{\partial P}\right)_T \end{bmatrix} = 0,$$

$$\left(\frac{\partial P}{\partial \upsilon}\right)_T = \frac{1}{\left(\frac{\partial \upsilon}{\partial P}\right)_T} \quad ------ \quad (23)$$

Similarly since we can set dP = 0,  $dT \neq 0$ , it must be true that

By combining Eqs.23 and 24, the latter nay be put in the more symmetrical cyclical form (cyclic relation).

### **Coefficient of expansion and compressibility**

Even if the equation of state of a substance is not known or cannot be expressed in any simple analytic form, the partial derivatives  $\left(\frac{\partial \upsilon}{\partial T}\right)_{z}$  and

 $\left(\frac{\partial \upsilon}{\partial P}\right)_T$  can be found from tabulated properties of materials, namely, the coefficient of cubical expansion  $\beta$  and the compressibility K.

$$\hat{\beta} = \frac{V_2 - V_1}{V_1 (T_2 - T_1)} = \frac{\Delta V}{V_1 \Delta T}$$
 (26)

Where  $V_2$  and  $V_1$  are the volume of a specimen of the material at temperatures  $T_2$  and  $T_1$ .

 $\beta$  is the mean fractioned increase in volume, per degree rise in temperature. The true coefficient of volume expansion  $\beta$ .

$$\beta = \lim_{\Delta T \to 0} \left( \frac{\Delta V}{V_1 \Delta T} \right) = \frac{1}{V} X \frac{dV}{dT}$$
 (27)

The <u>mks</u> units of  $\beta$  are (deg.<sup>-1</sup>). However, the volume of an object depends upon pressure as well as upon temperature and it is implied in the definition above that the pressure is to be kept constant.

(28)

$$\beta = \frac{1}{V} X \frac{(dV)_P}{(dT)_P}$$

The ratio of a small change in V to a small change in T, both at constant P, is the same thing as the partial derivative of V with respect to T at constant P. Hence

$$\frac{(dV)_{P}}{(dT)_{P}} = \left(\frac{\partial V}{\partial T}\right)_{P} \quad \text{and} \qquad \beta = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_{P} \qquad (29)$$

Or in terms of specific volumes,

$$\beta = \frac{1}{\upsilon} \left( \frac{\partial \upsilon}{\partial T} \right)_{P} \qquad (30) \qquad \beta \upsilon = \left( \frac{\partial \upsilon}{\partial T} \right)_{P} \qquad (30)$$

It follows from eq. (30) that the  $\beta$  of ideal gases

The van der Waals equation is a cubic in v but can be solved explicitly for **P.** Hence in computing  $\beta$  it is simplest to use eqs. 23 and 25 and write



Where  $V_2$  and  $V_1$  are the volume at pressures  $P_2$  and  $P_1$ .

The true compressibility K is the limiting value of the expression above when the changes in pressure and volume become infinitesimal.

$$K = \lim_{\Delta P \to 0} \left( -\frac{\Delta V}{V_1 \Delta P} \right) = -\frac{1}{V} X \frac{dV}{dP}$$

The (-ive) sign is included in the definition of *K* because an increase in **P** always results in a decrease in volume.

Thus if dp is (+ive), dv is (-ive) and K is a (+ive) quantity.

The mks unite of K are  $(n/m^2)$ .

If the T is constant, the corresponding value of K is called the isothermal compressibility and the derivative becomes the partial of V with respect to P at constant T.

$$\mathbf{K} = -\frac{1}{V} X \frac{(dV)_T}{(dP)_T} = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T \qquad \mathbf{K} = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T \qquad (\mathbf{4})$$

Or in terms of specific volumes.



**The** *K* **of solids and liquids must be determined experimentally.** 

# <u>The work done in terms of $\beta$ and $\kappa$ </u>

Let v = f(T, P), so  $dv = \left(\frac{\partial v}{\partial T}\right)_P dT + \left(\frac{\partial v}{\partial P}\right)_T dP$ 

$$dw = pd\upsilon = P\left[\left(\frac{\partial \upsilon}{\partial T}\right)_{P} dT + \left(\frac{\partial \upsilon}{\partial P}\right)_{T} dP\right] = P\left[\beta \upsilon dT - K\upsilon dP\right]$$

For an ideal gas, this reduces to

$$dw = pd\upsilon = \frac{P\upsilon}{T}dT - \frac{P\upsilon}{P}dP$$
,  $pd\upsilon = RdT - \upsilon dP$ 

A relation which could have been written down at once from the equation of state, since

$$pd\upsilon + \upsilon dP = RdT \qquad ----- \qquad (39)$$

## The work depends on the path

As an example, suppose that a solid or liquid is taken from state 1 to state 2 in Fig.8 first along path  $1\rightarrow 3\rightarrow 2$  and then along path  $1\rightarrow 2$ , where for the latter path,



Fig. 8

$$P = P_o + aT$$

Along path  $1 \rightarrow 3$ ,  $P = P_1 = cons \tan t$ , dp = 0 and

 $w \approx \int P \upsilon [\beta dT - K dP], \qquad \mathbf{dp} = \mathbf{0}$ 

 $w_{1\to3} \approx P_1 \upsilon \beta \int_{T_1}^{T_2} dT \approx P_1 \upsilon \beta (T_2 - T_1)$  (40)

This is the general expression for the work done in any isobaric process by a system having the properties assumed above.

Along path  $3\rightarrow 2$ , T = const., dT = 0 and

 $w = \int P \upsilon [\beta dT - K dP], \quad \mathbf{dT} = \mathbf{0}$   $w_{3 \to 2} = -K \upsilon \int_{P_1}^{P_2} P dP \approx \frac{K \upsilon}{2} (P_1^2 - P_2^2), \quad (41)$ 

This is the general expression for the work done in any isothermal process by a system having the properties assumed.

The total work along the path  $w_{1\rightarrow 3\rightarrow 2}$  is

$$w_{1\to3\to2} = w_{1\to3} + w_{3\to2} \approx \beta \upsilon P_1 (T_2 - T_1) - \frac{K\upsilon}{2} (P_1^2 - P_2^2) \qquad (42)$$

Along the direct path  $1 \rightarrow 2$ ,

$$w_{1\to 2} \approx \upsilon \beta \int_{T_1}^{T_2} (P_o + aT) dT - \upsilon K \int_{P_1}^{P_2} P dP$$
  
$$w_{1\to 2} \approx \upsilon \beta P_o (T_2 - T_1) + \frac{a \upsilon \beta}{2} (T_2^2 - T_1^2) - \frac{\upsilon K}{2} (P_2^2 - P_1^2)$$

Expressing the constants  $P_o$  and a in terms of  $P_1$ ,  $P_2$ ,  $T_1$  and  $T_2$ 

$$w_{1\to2} \approx \upsilon \beta \left[ P_o (T_2 - T_1) + \frac{a}{2} (T_2 - T_1) (T_2 + T_1) \right] - \frac{\upsilon K}{2} (P_2^2 - P_1^2)$$

$$w_{1\to2} \approx \upsilon \beta (T_2 - T_1) \left[ P_o + \frac{a}{2} (T_2 + T_1) \right] - \frac{\upsilon K}{2} (P_2^2 - P_1^2) \quad \dots \quad (a)$$

$$P = P_o + aT , \quad P_1 = P_o + aT_1 , \quad P_2 = P_o + aT_2 ,$$

$$P_1 + P_2 = 2P_o + a (T_2 + T_1), \quad \frac{P_1 + P_2}{2} = P_o + \frac{a}{2} (T_2 + T_1) \quad \dots \quad (b)$$
from eqs. a & b  

$$w_{1\to2} \approx \upsilon \beta \frac{P_1 + P_2}{2} (T_2 - T_1) - \frac{\upsilon K}{2} (P_2^2 - P_1^2) \quad \dots \quad (43)$$

From eqs. 42 and 43,  $d_W$  is not an exact differential and that the work depends on the path and not merely on the end points.

From eqs. 24 and 25

$$\left(\frac{\partial P}{\partial \upsilon}\right)_{T}\left(\frac{\partial \upsilon}{\partial T}\right)_{P}\left(\frac{\partial T}{\partial P}\right)_{\upsilon} = -1, \qquad \left(\frac{\partial P}{\partial T}\right)_{\upsilon} = -\frac{\left(\frac{\partial \upsilon}{\partial T}\right)_{P}}{\left(\frac{\partial \upsilon}{\partial P}\right)_{T}}$$

From the definition of  $\beta$  and K

$$\left(\frac{\partial P}{\partial T}\right)_{\nu} = -\frac{\nu\beta}{\nu K} = \frac{\beta}{K} \qquad (44)$$

Then for a solid or a liquid, and to the degree of approximation to which the ratio  $\frac{\beta}{K}$  can be considered constant, the increase in pressure (P<sub>2</sub>-P<sub>1</sub>), when the temperature is increased from T<sub>1</sub> to T<sub>2</sub> and the volume is kept constant, is

$$P_{2} - P_{1} \approx \frac{\beta}{K} (T_{2} - T_{1})$$
 (45)

## Questions

 $\underline{O.(1)}$  Steam at a constant ( absolute ) pressure of (20atm.) is admitted to the cylinder of a steam engine. The length of the stroke is (60 Cm) and the diameter of the cylinder ( 20 Cm ). How much in joules is done by the steam per stroke?

<u>Q.(2)</u> 1 kgm of water, when converted to steam at atmospheric pressure, occupies a volume of (1.67 m<sup>3</sup>). Compute the work done against atmospheric pressure.

<u>Q.(3)</u> 5 kgm. of oxygen occupy a volume of (10 m<sup>3</sup>) at a temperature of (300 K). Find the work necessary to decrease the volume to (5 m<sup>3</sup>), <u>a//</u> at constant pressure, <u>b//</u> at constant temperature. <u>c//</u> what is the temperature at the end of process <u>a</u>?. <u>d//</u> what is the pressure at the end of process <u>b</u>?. <u>e//</u> show both process in a p-v diagram.

<u>Q.(4)</u> An ideal gas originally at a temperature  $T_1$  and pressure  $P_1$  expands reversibly against a piston to a volume equal to twice its original volume. The temperature of the gas is varied during the expansion as that at each instant the relation P = KV is satisfied, where K is a constant. <u>a//</u> Draw a diagram of the process in the P-V plane. <u>b//</u> Find the work done by the gas, in terms of n, R,  $T_1$  and  $P_1$ .

<u>Q.(5)</u> An ideal gas at an initial pressure  $P_1$  and volume  $V_1$  is heated at constant volume until the pressure is doubled, allowed to expand isothermally until the pressure drops to its original value, and then compressed at constant pressure until the volume returns to its initial value. <u>a//</u> Sketch the process in the P-V plane. <u>b//</u> Compute the net work done in the process, if ( n = 2 kgm.-moles,  $P_1 = 2$  atm. and  $V_1 = 4m^3$ ).

<u>Q.(6)</u> <u>a//</u> Derive the general expression for the work done per mole by a van der Waals gas in expanding reversibly and at a constant temperature T from a specific volume  $v_1$  to a specific volume  $v_2$ . <u>b//</u> Using the constants (a =580 n-m<sup>4</sup> /(kgm-mole)<sup>2</sup>, b = 0.0319 m<sup>3</sup>/kgm.-mole). Find the work done when <u>2</u>moles of steam expand from a volume of ( 30 m<sup>3</sup>) to a volume of ( 60 m<sup>3</sup> ) at a temperature of ( 100°C ). <u>C//</u> Find the work done by an ideal gas in the same expansion.

<u>*Q.(7)*</u> The Clausius equation of state is P(v-b) = RT<u>a//</u> Compute the coefficient of cubical expansion, and the compressibility, for a substance obeying this equation. <u>b//</u> Show that if ( **a** = **0** ), the

14

corresponding quantities for a van der Waals gas reduce to the expressions derived in ( a ).

<u>Q.(8)</u> The Dieterici equation of state is  $P(v-b)e^{\frac{a}{vRT}} = RT$ , where (a & b) are constants, different for different gases. <u>a//</u> Making use of the cyclic relation, eq. 25, find the coefficient of cubical expansion of a substance obeying this equation. <u>b//</u> At high temperatures and large specific volumes, all gases approximate ideal gases. verify that for large values of T & v, the Dieterici equation and the expression for  $\beta$  derived in <u>a//</u>, both go over into the corresponding equations for an ideal gase.

<u>Q.(9)</u> Express the coefficient of cubical expansion and the compressibility, in terms of the density ( $\rho$ ) and its partial derivatives.

<u>Q.(10)</u> A cylinder provided with a piston contains  $(1m^3)$  of a fluid at a pressure of (1 atm.) and a temperature of (300 K). The pressure is increased reversibly to (100 atm.) and the temperature is kept constant. Find the work done on the system, <u>a//</u> if the fluid is an ideal gas, <u>b//</u> if it is a liquid of compressibility [ $5x10^{-10}$  ( $n/m^2$ )<sup>-1</sup>], about equal to that of water. <u>C//</u> Find the change in volume of each fluid.

<u>Q.(11)</u> A fluid in a cylinder is at a pressure of ( $700 \times 10^3 \text{ n/m}^2$ ). It is expanded at constant pressure from a volume of ( $0.28 \text{ m}^3$ ) to a volume of ( $1.68 \text{ m}^3$ ). Determine the work done.

<u>Q.(12)</u> One Kmole of a gas at (  $27^{\circ}$ C ) expands isothermally until its volume is doubled. Find the work done.

<u>*Q.(13)*</u> Work done in a thermodynamic cycle. One mole of an ideal gas goes through the thermodynamic cycle shown in fig. if ( $P_A = 2x10^4$  pa,  $P_D = 1x10^4$  pa,  $V_A = 0.25$  m<sup>3</sup>, and  $V_B = 0.5$  m<sup>3</sup>), find the work done along the path, <u>a//</u> AB, <u>b//</u> BC, <u>C//</u> CD, <u>d//</u> DA, and <u>e//</u> ABCDA.



<u>Q.(14)</u> The volume of a glass beaker is (200 Cm<sup>3</sup>) which was filled with mercury at the temperature of (20° C). How much the mercury is spilled, when the temperature of the system is raised to (100° C)?. The coefficient of cubical expansion for glass is 1.2x10<sup>-5</sup>/°C, The coefficient of cubical expansion for Hg is 18.1x10<sup>-5</sup>/°C,

<u>Q.(15)</u> At constant temperature, increase the pressure from Zero to (1000 atm.) on (10 gm) of Cu. Determine the work done if the density of Cu is (8.93 gm/Cm<sup>3</sup>), and coefficient of compressibility is (0.716x10<sup>-6</sup> atm.<sup>-1</sup>).

<u>Q.(16)</u> Determine the work done at vaporization (100gm) of C<sub>6</sub>H<sub>6</sub> at the pressure of (1 atm.), and the boiling point of it is (80.2° C). (molecular weight of C<sub>6</sub>H<sub>6</sub> is 78).

 $\underline{O.(17)}$  Find the work done for one mole of an ideal gas at constant pressure P, where is expanded by rising the temperature of one degree.

<u>*Q.(18)*</u> Find the work done for (75 kgm.) of water when it is compressed from (140 Kpa) to (7.5 Mpa) at constant temperature (40°C). If the specific volume of water at the temperature (40°C), and the initial pressure was (1.0078 Cm<sup>3</sup>/gm) and at the final pressure was (1.0045 Cm<sup>3</sup>/gm)