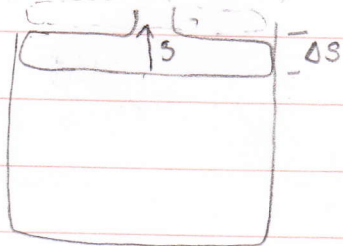


gas expands from 1 L to 3 L at 1 atm (initial)



$$W = F \Delta s = p A \Delta s = p \Delta V$$

$$dW = p dV$$

$$W = \int p dV$$

Thus, a positive change in volume does positive work, corresponding to an expanding gas doing work on its surroundings

$$\Delta V = 2 \text{ L} \quad \Delta P = ?$$

$$P_i = 1 \text{ atm} = P_f - \Delta P$$

$$\text{if } p \propto V \rightarrow P_f = 3 \text{ atm}$$

$$\rightarrow \Delta P = 2 \text{ atm}$$

$$y = ax + b \quad ; \quad a = 1 \quad b = 0$$

$$p = V$$

$$W = \int V dV = \frac{1}{2} V^2 \Big|_1^3 = \frac{9}{2} - \frac{1}{2} = 4 \text{ atm} \cdot \text{L} \approx 400 \text{ J}$$

ΔE ?

$$\left. \begin{array}{l} \text{Equipartition: } \langle E \rangle_{\text{thermal}} = \frac{3}{2} N k T \\ \text{Ideal gas: } P V = N k T \end{array} \right\} \langle E \rangle = \frac{3}{2} P V$$

$$\begin{aligned} \Delta E = \Delta \langle E \rangle_{\text{thermal}} &= \frac{3}{2} (P_f V_f - P_i V_i) \\ &= \frac{3}{2} (3 \text{ atm} \cdot 3 \text{ L} - 1 \text{ atm} \cdot 1 \text{ L}) \\ &\approx 1200 \text{ J} \end{aligned}$$

Q? Heat added to cause expansion? (not adiabatic)

$$\begin{aligned} 1^{\text{st}} \text{ Law: } q &= \Delta E + W \leftarrow \\ &= 1200 \text{ J} + 400 \text{ J} \\ &= 1600 \text{ J} \quad \checkmark \end{aligned}$$

theorem concerning the impossibility of constructing a *perpetuum mobile* of the first kind.

We must obtain a mathematical expression of the First Law. To this end we introduce the total energy U as a function of the thermodynamic variables. Evidently this quantity must be a single-valued function of the independent variables, say of T and v , for otherwise it would be possible to construct a mechanism which creates energy. For example, if the energy content were greater when 1 litre of air is first warmed from 0° to 100°C . and then compressed to 10 cm^3 than when the same amount of air is first compressed to 10 cm^3 and then heated to 100°C ., it would be possible to gain energy by bringing the substance back to its initial state by the second process, which requires the smaller amount of energy. We must therefore have

$$U = U(T, V) \quad \text{or} \quad U(T, p) \quad \text{or} \quad U(p, V). \quad (1)$$

Hence the differential

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \quad (2)$$

is the total differential of a function of the thermodynamic variables. In contrast with this, the total quantity of heat supplied to a system is not a unique function of the variables, for it is not necessary that the part of the energy of the system which exists in the form of heat be supplied as heat; it may be supplied in part, for example, as mechanical energy in compression. As a result, a small quantity of heat supplied to a system is not the total differential of a function of the thermodynamic variables; it is therefore denoted by δQ instead of by dQ .

The internal energy of a system may be increased by supplying energy from the outside, part as heat and part by doing mechanical or electrical work. If we take every quantity of energy supplied to be positive, regardless of what form it is in, the First Law is

$$\delta Q + \delta W = dU. \quad (3)$$

The commonest instance in which work is done is the change of volume accompanying an external pressure p . If every element dS of the surface experiences a displacement δs , an amount of work

$$\delta W = - \oint p dS \delta s = -p \oint dS \delta s \quad (4)$$

is done. The negative sign is to be used, since energy is supplied to

the system if δs forms an obtuse angle with dS (cf. fig. 1). Now the integral $\oint dS \delta s$ is merely the change in volume dV resulting from the displacement. Hence in this special case the First Law may be written

$$\delta Q - p dV = dU, \quad (5)$$

$$\text{or} \quad \delta Q = dU + p dV. \quad (5')$$

This last form may also be interpreted thus: the energy supplied to the system in the form of heat goes in part toward increasing the internal energy U and in part to performing external work.

With regard to the pressure, the following may be added: If the outside pressure p on the freely movable piston of a gas-filled cylinder is equal to the gas pressure, the piston will remain at rest. If the external pressure is much diminished to a value p' , a sudden expansion will follow and the gas will acquire energy of flow which, however, is soon converted into heat because of turbulence. In this instance, then, the useful work obtained is smaller than if there had been only an infinitely small difference between inside and outside pressure, and hence an infinitely slow expansion. The latter condition would obviously yield the maximum external work, and we term the process a *reversible* one. Unless otherwise remarked, we shall assume reversibility for all processes discussed.

2. Specific Heat at Constant Volume and at Constant Pressure. The Energy Function of a Gas.

According to p. 487, the specific heat per gramme or per mol represents that quantity of heat necessary to impart to one gramme or to one mol a temperature increase of one degree. One must differentiate, however, between the case where heat is supplied at constant volume and that where the pressure is held constant while the heat is supplied. In the first instance no external work is done, while in the second, expansion against the outside pressure does mechanical work. This distinction is important chiefly for gases, on account of their large coefficients of thermal expansion. If we apply the First Law to the energy supplied, the definition of specific heat per mol yields the equation

$$c = \frac{\delta q}{dT} = \frac{du + p dv}{dT}. \quad (6)$$

Now the energy u is a function of the thermodynamic variables, of which we take T and v to be the independent ones. We then have for constant volume

$$du = \left(\frac{\partial u}{\partial T}\right)_v dT, \quad (7)$$

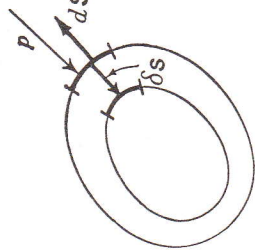


Fig. 1