of temperature *(θ' — θ’)* is small, the figure ABCD may be regarded as a parallelogram, and its area *W* as equal to the rectangle BE×EC. This is accurately true in the limit when *(θ' —θ’)* is infinitesimal, but in practice it is necessary to measure specific heats, &c., over finite ranges of temperature, and the error involved is generally negligible if the range does not exceed a few degrees. BE is the increase of pressure *(p' —p’)* produced by the rise of temperature (β'-β') if the volume is kept constant. EC is the expansion (f'-»') produced by the same rise of temperature if the pressure is kept constant. Substituting these symbols in the expression for the area, the relation becomes

H=0(∕>'-∕>-,)(√→')∕(β'-0') - (3)

This relation may be interpreted in two ways, according as wc require the heat absorbed in terms of the change of pressure or volume, (ι) The heat, *II,* absorbed in isothermal expansion (latent heat of expansion) from *p'* to *p',* is equal to the diminution of pressure *(p’— p')* multiplied by the absolute temperature and by the expansion per degree (t>\*-*v')∣(θ' — θ')* at constant pressure. (2) The heat, *II,* absorbed in isothermal expansion from v' to *v\** is equal to the increase of volume *(y"-v')* multiplied by the abso­lute temperature, and by the increase of pressure per degree *(p' — p )∣(θ' —Θ"),* at constant volume. In the notation of the calculus the relations become

*-dll∣dp (θ* const) *=θdv'ldθ (p* const) ) t »

*dll∣dv (θ* const) *=θdpjdθ* (t> const) ) ’ ' · W

The negative sign is prefixed to *dlljdp* because absorption of heat -f-dZZ corresponds to diminution of pressure *—dp.* The utility of these relations results from the circumstance that the pressure and expansion co­efficients are familiar and easily measured, whereas the latent heat of expansion is difficult to determine.

The most instructive ex­ample of the application of relations (1) and (2) is af­forded by the change of state of a substance at constant temperature and pressure. Starting with unit mass of the substance in the first state (e.g. liquid) pos- , sessing volume *v'* at a tem­perature *θ'* and pressure *p'* represented by the point A in fig. 3, the heat absorbed in raising the temperature to *θ'* and the pressure to *p’* without change of state may be written *s' (θ'-θ'),* where *s'* is the specific heat of the substance in the first state at saturation pressure. If now the substance in the state B is entirely con­verted at constant temperature and pressure into the second state (e.g. saturated vapour), in which it occupies a volume t>\*, the line BC represents the change of volume (»"—»'). The heat absorbed in this change is called the latent heat of change of state, and may be represented by the symbol *L'.* The substance is then cooled to the lower temperature *θ'* along the path CD, keeping it in the saturated state. The heat evolved in this process may be represented by *s"(θ'-θ,),* where *s'* is the specific heat of the substance in the second state at saturation pressure. Finally, the substance is reconverted into the first state at the temperature *θ',* completing the cycle by the abstraction of a quantity of heat *L'.* By the application of the first law, the difference of the quantities of heat absorbed and evolved in the cycle must be equal to the work represented by the area of the cycle, which is equal to (p' — *p')(v'—*t>') in the limit when the difference of pressure is small. By the application of the second law, relations (2), the same work area is equal to *(θ'-θ")L'jθ'.* Dividing by *(θ' —θ’),* and writing *dpjdß* and *dL∣dθ* for the limiting values of 'the ratios *(p’-p')∣(θ' —θ’)* and *(L'-L,)∣(Θ'—θ’),* we obtain the important relations

i'-√-HZ√d9 = (t>'-√)1⅛>∕d9=Z,∕0, . . . (5)

in which *dp∣dθ* is the rate of change of pressure with temperature when the two states are in equilibrium. It is not necessary in this example that AB, CD should be adiabatics, because the change of volume BC is finite. The same equations apply to the case of fusion of a solid, if *L* is the latest heat of fusion, and v', s', *ν’, s’* the specific volumes and specific heats of the solid and liquid respectively.

6. *Ratio and Difference of Specific Heats.—*If we take unit mass of the substance at B, fig. 2, and cool it at constant volume to E, through an interval of temperature *(θ'—θ’),* the amount of heat abstracted may be written *h==s(θ' —Θ"),* where s is the specific heat α∕ *constant volume.* If, starting from E, *the same* amount of heat *h* is restored«/ *constant pressure,* we should arrive at the point F on the adiabatic through B, since the substance has been trans­formed from B to F by a reversible path without loss or gain of heat on the whole. In order to restore the substance to its original temperature *θ' at constant pressure,* it would be necessary to supply a further quantity of heat, *II,* represented by the area between the two adiabatics from FC down to the absolute zero. This quantity of heat is the same as that already found in equation (3), but for the small area ■ BFC, which is negligibly small in the limit compared with *II.* The whole quantity of heat required to raise the temperature from 0" to *θ'* at constant pressure along the path EC is *II∙rh,* which is equal to *S(θ'--θ"),* where 5 is the specific heat at constant pressure. Since *h=s(θ' —O’),* the difference *S—s* between the specific heats at constant pressure and volume is evidently

*H∕(θ'-θ").* Substituting for *II* its value from (3), and employing the notation of the calculus, we obtain the relation

*S-s=θ(dp∣dθ)(dv∣dθ)* (6)

in which the partial differential coefficients have the same meaning as in (4).

Since the amounts of heat supplied at constant pressure from E to F and from E to C are in the limit proportional to the expan­sions EF and EC which they produce, the ratio *S∣s* is equal to the ratio EC∕EF. EF is the change of volume corresponding to a change of pressure BE when no heat is allowed to escape and the path is the adiabatic BF. EC is the change of volume for *the same* change of pressure BE when the path is the isothermal BC. These changes of volume are directly as the compressibilities, or inversely as the elasticities. If we write *K* for the adiabatic elas­ticity, and *k* for the isothermal elasticity, we obtain

S∕s=EC∕EF=K∕\* . . . . (7)

The value of the specific heat 5 at constant pressure can always be determined by experiment, and in practice is one of the most important thermodynamical properties of a substance. The value of the specific heat s at constant volume can also be measured in a few cases, but it is generally necessary to deduce it from that at constant pressure by means of relation (6). It is often impossible to observe the pressure-coefficient *dp∣dθ* directly, but it may be deduced from the isothermal compressibility by means of the geometrically obvious relation, BE = (BE∕EC)×EC. The ratio BE/EC of the diminution of pressure to the increase of volume at constant temperature, or *—dptdv,* is readily observed.

The amount of heat absorbed in any small change of state, as from E to G in fig. 2, may be found by adding to the heat required for the change of temperature at constant volume, *sdθ,* or at con­stant pressure, *Sdθ,* the heat absorbed in isothermal expansion as given by relations (4). We thus obtain the expressions

*dll = sdθ +θ(dp∣dθ)dv = Sdθ-θ(dv∕dθ)dp . .* . (8) The first is equivalent to measuring the heat along the path EBG, the second along the path ECG. The two differ by the area BEC, which can be neglected if the change is small. For a finite change it is necessary to represent the path by a series of small steps, which is the graphic equivalent of integration along the path repre­sented by the given relation between *v* and *θ,* or *p* and *θ.* If we put *dli≈o* in equations (8), wc obtain the relations between *dυ* and *dθ,* or *dp* and *dθ,* under the condition of no heat-supply, *i.e.* along the adiabatic, which can lie integrated, giving the equations to the adiabatics, provided that the values of the specific heats and expansion-coefficients are known.

6. *Intrinsic F.nergy.—*The change of intrinsic energy *E* along any path is found by subtracting the work *pdv* from cither of the expressions for *dH.* Since the change of energy is independent of the path, the finite change between any two given states may be found by integration along *any* convenient path. It is generally convenient to divide the path into two steps, isothermal and isometric, or isothermal and isopiestic, and to integrate along each separately. The change of energy at constant volume is simply *sdθ,* the change at constant temperature is *(θdp∣dθ-p)dv,* which may be wτitten

*dE∣dθ (v* const) =5, *dE∣dv (θ c.cmιt)=θdp)dθ-p ,* (9)

These must be expressed as functions of t> and *θ,* which is theo­retically possible if the values of *s, p,* and *dp∣dθ* are known. Since the two expressions (9) are the partial differential-coefficients of a single function *E of* the independent variables *v* and *θ,* we shall obtain the same result, namely *tPE!dθdv,* if we differentiate the first with respect to *v* and the second with respect to *θ.* We thus obtain the relation

*ds∣dυ(θ* const) *≈θdiip∣d(P (v* const), . . . (10)