the equation of the border curve giving the relation between *p* and *θ,* but is more easily obtained by considering the equilibrium at constant pressure instead of constant volume.

(δ) The second case, which is of greater practical utility, is that in which the external pressure, *p,* is kept constant. In this case *dW≈pdv=d(pυ),* a perfect differential, so that the external work done is known from the initial and final states. In any possible transformation *d(θφ-E)* cannot be less than *d(pv),* or the function *(E-θφ+pv)=G* cannot increase. The condition of stable equili­brium is that *G* should be a minimum, for which reason it has been called the “thermodynamic potential.at constant pressure.” The product *pι,* for any state such as D in fig. I is represented by the rectangle MDdO, bounded by the isopiestic and the isometric through D. The function *G* is represented by the negative area 9\*D.∖1 under the isothermal, bounded by the isopiestic DM and the axis of pressure. The increment of i⅛> is always greater than that of the total heat *F=E+pv,* except in the special case of an equilibrium change at constant temperature and pressure, in which case both are equal to the heat absorbed in the change, and the function *G* remains constant. This is geometrically obvious from the form of the area representing the function on the indicator diagram, and also follows directly from the first law. The simplest application of the thermodynamic potential is to questions of change of state. If *φ', E', ν';* and <∕>', *E', v',* refer to unit mass of the substance in the first and second states respectively in equilibrium at a temperature *0* and pressure *p,* the heat absorbed, *L,* per unit mass in a change from tne first to the second state is, by definition of the entropy, equal to *θ(φ"-φ'),* and this by the first law is equal to the change of intrinsic energy, *E,-E,,* plus the external work done, *p{v"-v'), i.e.* to the change of total heat, *F’ — F.* If *G,* and *G’* are the values of the function *G* for the two states in equilibrium at the same pressure and temperature, we must have *G,=G".* Assuming the function G to be expressed in terms of *p* and 0, this condition represents the relation between *ρ* and *θ* corresponding to equilibrium between the two states, which is the solution of the relation *(v,-υ,}dp∣dθ = L∣θ,* (5). The direct integration of this equation requires that *L* and *vv-v,* should be known as functions of *p* and 0, and cannot generally be performed. As an example of one of the few cases where a complete solution is possible, we may take the comparatively simple case equation (17), already considered, which is approximately true for the majority of vapours at moderate pressures.

Writing formulae (31) and (33) for the energy and entropy with indeterminate constants *A* and *B,* instead of taking them between limits, we obtain the following expressions for the thermodynamic functions in the case of the vapour:—

*Φ,* =50log^-*R* log,/»—*ncp∣θ+A,* .... (34) *E" = s<0-ncp+B" .......* (35) *F' = S<0-(n+ι)cp+bp+B"* (36)

*G’—* Sc0(ι-log^)+R01oge∕>-(c — *b)p~ A'θ-∖-B, .* (37)

*J,* =so0-*Stβ* logtfl+-R0 log<∕>-*A'β-t-B' · · ·* (38)

The function *J’* may be expressed in terms of *θ* and v by writing for *p* its value, namely, *R0∕(υ+c-b).* We have also in any case the relations

*dG''∣dβ (,p* const) *==Φ" = dJ"'dθ (v* const) . . (39)

<∕G"∕d∕> (fl const) =w, (0 const) =∕> . . (40)

And all the properties of the substance may be expressed in terms of *G* or *J* and their partial differential coefficients. The values of the corresponding functions for the liquid or solid cannot be accurately expressed, as the theoretical variation of the specific heat is unknown, but if we take the specific heat at constant’pres- sure *s'* to be approximately constant, and observe the small residual variation *dh* of the total heat, we may write

>, = √0+d⅛+B, (41)

*Φ' = s'logA+dφ+A'* (42)

*G'≈s'θ(ι-log<ff)+(dh-edφ)-A'β+B' . .* (43)

where *dφ* is the corresponding residual variation of ≠', and is easily calculated from a table of values of *h.*

To find the border curve of equilibrium between the two states, giving the saturation pressure as a function of the temperature, we have merely to equate the values of *G'* and *G,.* Rearranging the terms, and dividing throughout by 0, we obtain an equation of the form

*R ∖ogep=A-B∣6-{s'-S^∖ogβ-∖∙{c-b')p∣θ+{dh∣θ-dφ')* . (44)

in which *B=B,-B,,* and *A =Ar—A’+s'—So.* The value of *A* is determined by observing the value of *θt>* at some known pressure *po, e.g.* at the boiling-point. The value of *B* is determined by observing the latent heat, *L<>≈F’o— F'o,* which gives

*B = B -B'*=Lo+(i, — 5o)flori-(π-}-ι)io∕,o-δ∕>o+d⅛o . (45)

This constant may be called the absolute latent heat,asitexpresses the thermal value of the change of state in a manner independent of temperature.

The term *(dh]θ-dφ)* depending on the variation of the specific heat of the liquid may be made very small in the case of water by a proper choice of the constant *s'.* It is of the same order as the probable errors of observation, and may be neglected in practice. (See Vaporization, § 16.) The expression for *R* log/» for an im­perfect gas of this type differs from that for a perfect gas only by the addition of the term (c—δ)∕>∕0. This simple result is generally true, and the corresponding expressions for G, and *J’* are valid, provided that *c — b* in formula (17) is a function of the temperature only. It is not necessary to suppose that *c* varies inversely as the nth power of the temperature, and that *b* is constant, as assumed in deducing the expressions for *Φ, E,* and *F.*

Although the value of *G* in any case cannot be found without that of *Φt* and although the consideration of the properties of the thermodynamic potential cannot in any case lead to results which are not directly deducible from the two fundamental laws, it affords a convenient method of formal expression in abstract thermo­dynamics for the condition of equilibrium between different phases, or the criterion of the possibility of a transformation. For such purely abstract purposes, the possibility of numerical evaluation of the function is. of secondary importance, and it is often possible to make qualitative deductions with regard to the general nature of a transformation without any knowledge of the actual form of the function. A more common method of procedure, however, is to infer the general relations of the thermodynamic potential from a consideration of the phenomena of equilibrium.

As it would be impossible within the limits of this article to illustrate or explain adequately the applications which have been made of the principles of thermodynamics, it has been necessary to select such illustrations only as are required for other reasons, or could not be found elsewhere. For fuller details and explana­tions of the elements of the subject, the reader must be referred to general treatises such as Baynes’s *Thermodynamics* (Oxford), Tait’s *Thermodynamics* (Edinburgh), Maxwell’s *Theory of Heat* (London), Parker’s *Thermodynamics* (Cambridge), Clausius's *Mechanical Theory of Ileal* (translated by Browne, London), and Preston’s *Theory of Heat* (London}. One or two chapters on the subject are also generally included in treatises on the steam engine, or other heat engines, such as those of Rankine, Perry or Ewing. Of greater, interest, particularly from a historical point of view, are the original papers of Joule, Thomson and Rankine, some of which have been reprinted in a collected form. A more complete and more elaborate treatment of the subject will be found in foreign treatises, such as those of Clausius, Zcuner, Duhem, Bertrand, Planck and others.

*Alphabetical Index of Symbols Employed.*

0, Thermodynamic or absolute temperature.

*Φ,* Entropy. Section 13.

*b,* Covolume of molecules of gas. Equation (17).

c, c0, Co-aggregation volume per unit mass. Equation (17).

*e,* Base of Napierian logarithms.

*E,* Intrinsic energy per unit mass. Section 2.

*F=E+pv,* Total heat. Section 7.

G, *J,* Thermodynamic potential functions. Section 15.

*H,* Quantity of heat (in mechanical units). Section 2.

*K, k,* Adiabatic and isothermal elasticities. Equation (7).

*L,* Latent heat of fusion or vaporization. Equation (5).

*M,* Molecular weight. Section 8.

*m,* Mass of substance or molecule.

*n,* Index in expression for c. Equation (17).

∕>, Pressure of fluid, *po,* Initial pressure.

*R = So-so,* Constant in gas-equation (17).

5, Specific heat of gas at constant pressure.

So, Limiting value of S when ∕>=o. Section 12.

*s,* Specific heat of gas at constant volume.

So, Limiting value of s when ∕>=o. Section 12.

*s', s’,* Specific heat under other conditions. Equation (5).

*U,* Kinetic energy of flow of fluid. Section 10.

*u,* Mean velocity of gaseous molecules. Section 8.

*V=RΘ∣ρ,* Ideal volume of gas per unit mass. Equation (17).

*v.* Specific volume of fluid, reciprocal of density.

*W,* External work done by fluid. (H. L. C.)

**THERMOELECTRICITY.** 1. *Fundamental Phenomena.—* Alessandro Volta (1801) showed that although a separation of the two electricities was produced by the contact of two different metals *(Volta Effect),* which could be detected by a sensitive electrometer, a continuous current of corresponding magnitude could not be produced in a purely metallic circuit -without the interposition of a liquid, because the electromotive force at one junction was exactly balanced by an equal and opposite force at the other. T. J. Scebeck (1822), employing a galvanometer then recently invented, which was more suited for the detection of small electromotive forces, found that a current was produced if the junctions of the two metals were at different temperatures. He explained this effect by supposing that the Volta contact electromotive force varied with the temperature, so that the exact balance was destroyed by unequal heating. The intensity