devised by Clausius *(Phil. Mag.,* 1880) to represent the behaviour of CO2 up to the critical point. Experiments by Natanson on CO2 at 170 C. confirm those of Joule and Thomson, but show a slight increase of the ratio *df)∣dp* at higher pressures, which is otherwise rendered probable by the form of the isothermals as determined by Andrews and Amagat. More recent experiments by J. H. Grindley *(Proc. Roy. Soc.,* 1900, 66, p. 79) and Callendar *(Proc. Roy. Soc.,* 19∞) on steam confirm this type of equation, but give much larger values of the cooling effect than for CO2, and a more rapid rate of variation with temperature.

11. *Modified Joule-Thomson Equation.—*G. A. Hirn *(Théorie Mec. de la Chaleur,* ii. p. 211, Paris, 1869) proposed an equation of the form *(p+pa)(v-*i) *=R0,* in which the effect of the size of the molecules is represented by subtracting a quantity *b,* the “ co­volume,” from the volume occupied by the gas, and the effect of the mutual attractions of the molecules is represented by adding a quantity *pa,* the internal pressure, to the external pressure, *ρ.* This type of equation, was more fully worked out by van der Waals, who identified the internal pressure, ∕>o, with the capillary pressure of Laplace, and assumed that it varied directly as the square of the density, and could he written *a∕vt.* This assumption represents qualitatively the theoretical isothermal of James Thomson (see Vaporization) and the phenomena of the critical state (see Con­densation of Gases) ; but the numerical results to which it leads differ so w,idely from experiment that it is necessary to suppose the constant, *a,* to be a function of the temperature. Many com­plicated expressions have been suggested by subsequent writers in the attempt to represent the continuity of the gaseous and liquid states in a single formula, but these are of a highly empirical nature, and beyond the scope of the present inquiry. The simplest assump­tion which suffices to express the small deviations of gases and vapours from the ideal state *at moderate pressures* is that the coeffi­cient *a* in the expression for the capillary pressure varies inversely as some power of the absolute temperature. Neglecting small terms of the second order, the equation may then be written in the form

*v—b = Rβ∣p-*Co(βo,'β)n = *V —c, . .* . (17) in which *c* is a small quantity (expressing the defect from the ideal volume *V = R6∣p* due to co-aggregation of the molecules) which varies inversely as the nth power of 0, but is independent of *p* to a first approximation at moderate pressures. The constant *c0* is the value of *c* at some standard temperature 0». The value of the index, *n,* appears to be different for different types of mole­cule. For CO2 at ordinary temperatures n=2, as in the Joule- Thomson equation. For steam between 100° and 150o C. it approaches the value 3∙5. It is probably less than 2 for air and the more perfect gases. The introduction of the covolume, *b,* into the equation is required in order to enable it to represent the behaviour of hydrogen and other gases at high temperaturesand pressures according to the experiments of Amagat. It is generally taken as constant, but its value at moderate pressures is difficult to determine. According to van der Waals, assuming spherical molecules, it should be four times; according to O. E. Meyer, on slightly different assumptions, it should be 4√2 times, the actual volume of the molecules. It appears to be a quantity of the same order as the volume of the liquid, or as the limiting volume of the gas at very high pressures. The value of the co-aggregation volume, *c,* at any temperature, assuming equation (17), may be found by observing the deviations from Boyle’s law and by experi­ments on the Joule-Thomson effect. The value of the angular coefficient *d(pυ)∣dp* is evidently *(b—*c), which expresses the defect of the actual volume *v* from the ideal volume *Rθ∣p.* Differentiating equation (17) at constant pressure to find *dv∣dθ,* and observing that *dc∣dθ= -nc∣θ,* we find by substitution in (15) the following simple expression for the cooling effect *dθ∣dp* in terms of *c* and *b,*

*Sdθ∣dρ = (n+ι~)c-b* .... (Ï8)

Experiments at two temperatures suffice to determine both *c* and *n* if we assume that *b* is equal to the volume of the liquid. But it is better to apply the Boyle’s law test in addition, provided that errors due to surface condensation can be avoided. The advantage of this type of equation is that *c* is a function of the temperature only. Other favourite types of equation for approxi­mate work are (1) ∕> = A0∕v+∕(r), which makes *ρ* a linear function of *0* at constant volume, as in van der Waal’s equation; (2) *v =RS∣pfi-f(P'),* which makes *v* a linear function of *β* at constant pressure. These have often been employed as empirical formulae *(e.g.* Zeuner’s formula for steam), but they cannot be made to represent with sufficient approximation the deviations from the ideal state at moderate pressures and generally lead to erroneous results. In the modified Joule-Thomson equation (17), both *c* and *n* have simple theoretical interpretations, and it is possible to express the thermodynamical properties of the substance in terms of them by means of reasonably simple formulae.

12. *Application of the Modified Equation.*—We may take equation (17) as a practical example of the thermodynamical principles already given. The values of the partial differential coefficients in terms of *n* and *c* are as follows :—

*dυ∣dθ(p* const) *≈(R∣p)(∖+nc∣V)* (19)

*diυ∣d(P „ = — n(n+ι)c∕θ2* (20)

*dp∣dθ(v* const) *= (R∣V)(t+∏c∣V) . . . .* (21)

*CPp/dtP „ =Rnc(l-n+2nc∕V)∣0Vt . . '.* (22)

*d(pv)∣dp(θ* const) *=b—c* (23)

Substituting these values in equations already given, we find,

from (6) *S-s = R(ι+nc∣vy* (24)

„ (9) *dE∣dv (β* const) *=ncp∣V* (25)

*„ (ιι)dFjdp „ =(n+ι)c-b* (26)

*„ ho)ds∣dv „ =(ι-n+2nc∣V')Rnc∕Vi . . .* (27)

*„ (12) dS∣dp „ =n(n-f-ι)c∕θ (28).*

In order to deduce the complete variation of the specific heats

from these equations, it is necessary to make some assumption

with regard to the variation of the specific heats with temperature. The assumption usually made is that the total kinetic energy of the molecules, including possible energy of rotation or vibration if the molecules consist of more than one atom, is proportional to the energy of translation in the case of an ideal gas. In the case of imperfect gases, all the available experimental evidence shows that the specific volume tends towards its ideal value, *V=RΘ∣p,* in the limit, when the pressure is indefinitely reduced and the molecules are widely separated so as to eliminate the effects of their mutual actions. We may therefore reasonably assume that the *limiting* values of the specific heats at zero pressure do not vary with the temperature, provided that the molecule is stable and there is no dissociation. Denoting by *St>, s0,* these constant limiting values at ∕> = o, we may obtain the values at any pressure by integrating the expressions (27) and (28) from x to r and from o to *p* respectively. We thus obtain

5=50+n(n + ι)∕>c∕9 (29)

5 = 5o+(n-ι *-nc∣V)ncp∣e . . . .* (30)

In working to a first approximation, the small term *nc∣V* may be omitted in the expression for s.

The expression for the change of intrinsic energy *E* between any given limits *pj)a* to *pθ* is readily found by substituting these values of the specific heats in equations (11) or (13), and integrat­ing between the given limits. We thus obtain

*E-Ea=s'o(e-Od)-n(pc-pifa) . . .* (31)

We have similarly for the total heat *F=E-∖-pυ,*

*F— Fa-So(θ-θ0) — (n-∖-l)(cp-Capò)fi-b(p—pti).*

The energy is less than that of an ideal gas by the term *npc.* If we imagine that the defect of volume *c* is due to the formation of molecular aggregates consisting of two or more single molecules, and if the kinetic energy of translation of any one of these aggre­gates is equal to that of one of the single molecules, it is clear that some energy must be lost in co-aggregating, but that the proportion lost will be different for different types of molecules and also for different types of co-aggregation. If two monatomic molecules, having energy of translation only, equivalent to 3 degrees of freedom, combined to form a diatomic molecule with 5 degrees of freedom, the energy lost would be *pc∣2* for co-aggregation, *c,* per unit mass. In this case n = l∕2. If two diatomic molecules, having each 5 degrees of freedom, combine to form a molecule with 6 degrees of freedom, we should have *n=2,* or the energy lost would be *2 pc* per unit mass. If the molecules and molecular aggregates were more complicated, and the number of degrees of freedom of the aggregates were limited to 6, or were the same as for single mole­cules, we should have *n = s<fR.* The loss of energy could not be greater than this on the simple kinetic theory, unless there were some evolution of latent heat of co-aggregation, due to the work done by the mutual attractions of the co-aggregating molecules.

It is not necessary to suppose that the co-aggregated molecules are permanently associated. They are continuallychanging partners, the ratio *c∣V* representing approximately the ratio of the time during which any one molecule is paired to the time during which it is free. At higher densities it is probable that more complex aggregates would be formed, so that as the effect of the collisions became more important *c* would cease to be a function of the temperature only; experiment, indeed, shows this to be the case.

13. *Entropy.—*It follows from the definition of the absolute scale of temperature, as given in relations (2), that in passing at constant temperature 0 from one adiabatic *Φ'* (Fig. 1) to any other adia­batic *Φ,,* the quotient *H∣θ* of the heat absorbed by the temperature at which it is absorbed is the same for the same two adiabatics whatever the temperature of the isothermal path. This quotient is called the change of entropy, and may be denoted by (≠\*-φ'). In passing along an adiabatic there is no change of entropy, since no heat is absorbed. The adiabatics are lines of constant entropy, and are also called *Isentropics.* In virtue of relations (2), the change of entropy of a substance between any two states depends only on the initial and final states, and may be reckoned along any reversible path, not necessarily isothermal, by dividing each small increment of heat, *dH,* by the temperature, *θ,* at which it is acquired, and taking the sum or integral of the quotients, *dH∣θ,* so obtained.