which is useful for calculating the variation of the specific heat r with variation of density at constant temperature. A similar expression for the variation of the specific heat 5 at constant pressure is obtained from the second expression in (8), by taking *ρ* and *θ* as independent variables; but it follows more directly from a consideration of the variation of the function *(E-∖-pv).*

7. *Total Heat.*—The function *F=(E+pv),* like *E* itself, has a value depending only on the state of the body. It may con­veniently lie called the *Total Heat,* by a slight extension of the meaning of a term which has been for a long time in use as applied to vapours (see Vaporization). Since *dE=dII-ρdv,* we have evidently for the variation of the total heat from the second ex­pression (8),

*dF≈d(E + pv)=dll+ vdp = Sdθ-(,θdv[dθ-v)dp .* (n) This expression shows that the rate of variation of the total heat with temperature at constant pressure is equal to the specific heat at constant pressure. To find the total heat of a substance in any given state defined by the values of *p* and *0,* starting from any convenient zero of temperature, it is sufficient to measure the total heat required to raise the substance to the final temperature under *a* constant pressure equal to *p.* For instance, in the boiler of a steam engine the feed water is pumped into the boiler against the final pressure of the steam, and is heated under this constant pressure up to the temperature of the steam. The total heat with which we are actually concerned in the working of a steam engine is the total heat as here defined, and not the total heat as defined by Régnault, which, however, differs from *(E+pv)* only by a quantity which is l inappreciable in ordinary practice.

Observing that F is a function of the co-ordinates expressing the state of the substance, we obtain for the variation of 5 with pressure at constant temperature,

*dS∣dp (θ* const) *=d1F∣dβdp = -θ<Pv∣dθi (p* const) . (12)

If the heat supplied to a substance which is expanding rever­sibly and doing external work, *pdυ,* is equal to the external work done, the intrinsic energy, *E,* remains constant. The lines of constant energy on the diagram are called *Isenerξ,ics.* The equation to these lines in terms of *v* and *θ* is obtained by integrating

*dE = sdθ-sr{θdp∣dO-p}dv = o* . . . (13)

If, on the other hand, the heat supplied is equal to *-vdp,* we see from (11) that *F* remains constant. The equation to the lines of constant total heat is found in terms of *p* and *θ* by putting *dF—o* and integrating (11).

8. *Ideal Gases.—*An ideal gas is a . substance possessing very simple thermodynamic properties to which actual gases and vapours appear to approximate indefinitely at low pressures and high temperatures. It has the characteristic equation *pv = Rβ,* and obeys Boyle’s law at all temperatures. The coefficient of expansion at constant pressure is equal to the coefficient of increase of pressure at constant volume. The difference of the specific heats by equation (6) is constant and equal to *R.* The isothermal elasticity *-v(dp[dυ)* is equal to the pressure *p.* The adiabatic elasticity is equal to *yp,* where *y* is the ratio *S/s* of the specific heats. The heat absorbed in isothermal expansion from to to *υ* at a temperature *θ* is equal to the wτork done by equation (8) (since *dθ=o, a.ndθ(dp∣dθ)dυ = ρdv'),* and both are given by the expression *Rå* loge(t√⅛). The energy *E* and the total heat *F* are functions of the temperature only, by equations (9) and (11), and their variations take the form *dE≈sdβ, dF=Sdβ.* The specific heats are independent of the pressure or density by equations (10) and (12). If we also assume that they are constant with respect to temperature (which does not necessarily follow from the characteristic equation, but is generally assumed, and appears from Regnault’s experiments to be approximately the case for simple gases), the expressions for the change of energy or total heat from *θ∏* to *θ* may be written *E-E0 = s(θ-θt,'), F-F<i = S(θ-θo').* In this case the ratio of the specific heats is constant as well as the difference, and the adia­batic equation takes the simple form, *pυy=* constant, which is at once obtained by integrating the equation for the adiabatic elas­ticity, *-v(dpjdυ) =yp.*

The specific heats may be any function of the temperature con­sistently with the characteristic equation provided that their difference is constant. If we assume that r is a linear function of *θ,* r = ∙So(ι 4^α0), the adiabatic equation takes the form,

Sologi(0∕0o)+αso(0-0o)+∙Klog,(v∕ι⅛)=o . . . (14)

where (Θo,t'), (So, no) are any two points on the adiabatic. The corresponding expressions for the change of energy or total heat are obtained by adding the term Jαso(02~0o2) to those already given, thus:

*E—Eq = Sq(Θ—Θq)* -∣-1*aS(1(θ~—θot), F — Fq≈Sq(Θ—*%) -j- ⅛αso(02 — 0o2), where 5o = ro+F.

9. *Deviations of Actual Gases from the Ideal State.—*Since no gas is ideally perfect, it is most important for practical purposes to discuss the deviations of actual gases from the ideal state, and to consider how their properties may be thermodynamically explained and defined. The most natural method of procedure is to observe the deviations from Boyle’s law by measuring the changes of pι> at various constant temperatures. It is found by experiment that the change of pt, with pressure at moderate pressures is nearly proportional to the change of *p,* in other words that the coefficient *d(pv)∣dp* is to a first approximation a function of the temperature only. This coefficient is sometimes called the " angular coeffi­cient,” and may be regarded as a measure of the deviations from Boyle's law, which may be most simply expressed at moderate pressures by formulating the variation of the angular coefficient with temperature. But this procedure in itself is not sufficient, because, although it would be highly probable that a gas obeying Boyle’s law at all temperatures was practically an ideal gas, it is evident that Boyle's law would be satisfied by any substance having the characteristic equation *pv∙~f(6),* where *f(θ)* is any arbitrary function of *θ,* and that the scale of temperatures given by such a substance would not necessarily coincide with the absolute scale. A sufficient test, in addition to Boyle’s law, is the condition *dE∣dv≈o* at constant temperature. This gives by equation (9) the condition *θdp∣dθ = p,* which is satisfied by any suυstance possessing the characteristic equation *p∣θ=f(v),* where ∕(t>) is any arbitrary function of *y.* This test was applied by Joule in the well-known experiment in which he allowed a gas to expand from one vessel to. another in a calorimeter without doing external work. Under this condition the increase of intrinsic energy would be equal to the heat absorbed, and would be indicated by fall of temperature of the calorimeter. Joule failed to observe any change of tempera­ture in his apparatus, and was therefore justified in assuming that the increase of intrinsic energy of a gas in isothermal expansion was. very small, and that the absorption of heat observed in a similar experiment in which the gas was allowed to do external work by expanding against the atmospheric pressure was equivalent to the external work done. But owing to the large thermal capacity of his calorimeter, the test, though sufficient for his immediate purpose, was not delicate enough to detect and measure the small deviations which actually exist.

\_ 10. *Method of Joule and Thomson.—*William Thomson (Lord Kelvin), who was the first to realize the importance of the absolute scale in thermodynamics, and the inadequacy of the test afforded by Boyle’s law or by experiments on the constancy of the specific heat of gases, devised a more delicate and practical test, which he carried out successfully in conjunction with Joule. A continuous stream of gas, supplied at a constant pressure and temperature, is forced through a porous plug, from which it issues at a lower pressure through an orifice carefully surrounded with non-con­ducting material, where its temperature is measured. If we con­sider any. short length of the stream bounded by two imaginary cross-sections A ana B on either side of the plug, unit mass of the fluid in passing A has work, *p'υ',* done on it by the fluid behind and. carries, its.energy, R' + (7,, with it into the space AB, where *U'* is the kinetic energy of flow. In passing B it does work, *p"v',* on the fluid in front, and carries its energy, *E,+ U,,* with it out of the space AB. If there is no external loss or gain of heat through the walls of the pipe, and if the flow is steady, so that energy is not accumulating in the space AB, we must evidently have the condition *E'-(-Ul+f,'v' = El,+ U,+p,v'* at any two cross-sections of the stream. It is easy to arrange the experiment so that *U* is small and nearly constant. In this case the condition of flow is simply that of constant total heat, or in symbols, *d(E+pv)≈o.* We have therefore, by equation, (11),

*Sdθ = (θdv∣dθ-v)dp* (15)

where *do* is the fall of temperature of the fluid corresponding to a diminution of pressure *dp.* If there is no fall of temperature in passing the. plug, dβ = o, and we have the condition *Θav∣d9=v.* The characteristic equation of the fluid must then be of the form *v∣θ≈f(p~),* where *f(p)* is any arbitrary function of *p.* If the fluid is a gas also obeying Boyle’s law, *pv=f(θ),* then it must be an ideal gas. As the result of their experiments on actual gases (air, hydrogen, and CO2), Joule and Thomson *(Phil. Trans.,* 1854, 1862) found that the cooling effect, *dβ,* was of the same order of magnitude as the deviations from Boyle's law in each case, and that it was proportional to the difference of pressure, *dp,* so that *dθ!dp* was nearly constant for each, gas over a range of pressure of five or six atmospheres. By experiments at different temperatures between 00 and 100° C.., they found that the cooling effect per atmosphere of pressure varied inversely as the square of the absolute tempera­ture for.air and CO2. Putting *dθ∣dρ≈A∣01* in equation (15), and integrating on the assumption that the. small variations of 5 could be neglected over the range of the experiment, they found a solution of the type, *v∕θ=f(p)-SA∣^θt,* in which *f(p)* is an arbitrary function of *p.* Assuming that the gas should approximate indefinitely to the ideal state *pv = Rβ* at high temperatures, they put *f(p) = R'lp,* which gives a characteristic equation of the form

*v = RΘ∣ρ-SΛ∣r,(P* (16)

An equation of a similar form had previously been employed by Rankmc *(Trans. Roy. Soc. Ed.,* 1854) to represent Regnault's experiments on the deviations of CO2 from Boyle’s law. This equation is practically identical for moderate pressures with that