The expression for the change of entropy between any two states is found.by dividing either of the expressions for *dH* in (8) by *θ* and integrating between the given limits, since *dHfi* is a perfect dif­ferential. In the .case of a solid or a liquid, the latent heat of isothermal expansion may often be neglected, and if the specific heat, *s,* be also taken as constant, we have simply √>-√>0 = s logf0∕0o, If the substance at the temperature *θ* undergoes a change of state, absorbing latent heat, *L, we* have merely to add the term *Lfi* to the above expression. In the case of an ideal gas, *dp]dθ* at constant volume*≈R∣v,* and *dv∣dθ* at constant pressure*≈R∣p∖* thus we obtain the expressions for the change of entropy φ-φ0 from the state *pd⅛VQ* to the state *pθvt*

*Φ~Φq = s ∖o%ftfio+R* logβv∕z>o

*≈S∖ogt0∕θo-R∖oξ,p∕po . . .* (32)

In the case of an imperfect gas or vapour, the above expressions are frequently employed, buta more accurate result may be obtained by employing equation (17) with the value of the specific heat, 5, from (29), which gives the expression

*Φ-φo≈Sfiioξt0∣Θo-R ∖ogl,p∕p0~-n(cpfi-Cop0fi0) . .* (33)

The state of a substance may be defined by means of the tempera­ture and entropy as co-ordinates, instead of employing the pressure and volume as in the indicator diagram. This method of repre­sentation is applicable to certain kinds of problems, and has been developed by Macfarlane Gray and other writers in its application to the steam engine. (See Steam Engine.) Areas on the tempera­ture-entropy or 0, *φ* diagram represent quantities of heat in the same way as areas on the indicator diagram represent quantities of work. The.0, ≠ diagram is useful in the study of heat waste and condensation, but from other points of view the utility of the conception of entropy as a “ factor of heat,, is limited by the fact that it does not correspond to any directly measurable physical property, but is.merely a mathematical function arising from the form of the definition, of absolute temperature. Changes of entropy must be calculated, in terms of quantities of heat, and must be interpreted in a similar manner. The majority of thermodynamical problems may be.treated without any reference to entropy, but it affords a convenient method of expression in abstract thermo­dynamics, especially in the consideration of irreversible processes and in reference to the conditions of equilibrium of heterogeneous systems.

14. *Irreversible Processes.—*In order that a process may be strictly reversible, it is necessary that the state of the working substance should be one of equilibrium at uniform pressure, and temperature throughout. If heat passes “ of itself" from a higher to a lower temperature by conduction, convection or radiation, the transfer cannot be reversed without an expenditure of work. If mechanical work or kinetic energy is directly converted into heat by friction, reversal of the motion docs not restore the energy so.converted. In all such cases there is necessarily, by Carnot's principle, a loss of efficiency or available energy, accompanied by an increase of entropy, which serves as a convenient measure or criterion of the loss. A common illustration of an irreversible process is the expansion of a gas into a vacuum or against a pres­sure less than its own. In this case the work of. expansion, *pdυ,* is expended in the first instance in producing kinetic energy of motion of parts of the gas. If this could be co-ordinated and utilized without dissipation, tne gas might conceivably be restored to its initial state; but in practice violent local differences of pressure and temperature are produced, the kinetic energy is rapidly con­verted into heat by viscous eddy friction, and residual differences of temperature are equalized by diffusion throughout the mass. Even if the expansion is adiabatic, in the sense that it takes place inside a non-conducting enclosure and no heat is supplied from external sources, it will not be isentropic, since the heat supplied by internal friction must be included in reckoning the change of entropy. Assuming that no heat is supplied from external sources and no external work is done, the intrinsic energy remains constant by the first law. The final state of the substance, when equilibrium has been restored, may be deduced from this condition, if the energy can be expressed in terms of the co-ordinates. But the line of constant energy on the diagram docs not represent the path of the transformation, unless it be supposed to. be effected in a series of infinitesimal steps between each of which the substance is restored to an equilibrium state. An irreversible process which permits a more complete experimental investigation is the steady flow of a fluid in a tube already referred to in section 10. If the tube, is a perfect non-conductor, and if there are no eddies or frictional dissipation, the state of the substance at any point of the tube as to *E, p,* and *υt* is represented by the adiabatic or isen­tropic path, *dE≈ ~pdv.* As the section of the tube varies, the change of. kinetic energy of flow, *dUi* is represented by *~vdp.* The flow in this case is reversible, and the state of the fluid is the same, at points where the section of the tube is the same. In practice, however, there is always some frictional dissipation, accompanied by an increase of entropy and by a fall of . pressure. In the limiting case of a long fine tube, the bore of which varies in such a. manner that *U* is constant, the state of the substance along a line of flow may be represented by the line of constant total heat, *d{E+pv)* =0; but in the case of a porous plug or small throttling aperture, the steps of the process cannot be followed, though the final state is the same.

In any small reversible change in which the substance absorbs heat, *dll,* from external sources, the increase of entropy, <⅜>, must be equal to *dHfi.* If the change is not reversible, but the final state is the same, the change of entropy, *dφi* is the same, but it is no longer equal to *d∏fi.* By Carnot’s principle, in all irreversible processes, *d∏fi* must be algebraically less than *dφ,* otherwise it would be possible to devise a cycle more efficient than a reversible cycle. This affords a useful criterion (see Energetics) between transformations which are impossible and those which are possible but irreversible. In the special case of a substance isolat(⅛ from external heat supply, *dH ≈ot* the change of entropy is zero in a reversible process, but must be positive if the process is not rever­sible. The entropy, cannot diminish. Any cnange involving de­crease of entropy is impossible. The. entropy tends to a maximum, and the state is one of stable equilibrium when the value of the entropy is the maximum value consistent with the conditions of the problem.

15. *Heterogeneous Equilibrium.—*In a *system,* as distinguished from a homogeneous substance, consisting of two or more states or phases, a.similar condition of equilibrium applies. In any spontaneous irreversible change, if the system is heat-isolated, there must be an increase of entropy. The total entropy of the system is found by multiplying the entropy per unit mass of the substance in each state by the mass existing in that state, and adding the products so obtained. The simplest case to consider is that of equilibrium between solid and liquid, or liquid and vapour. The more general case is discussed in the article Energetics, and in the. original memoirs of. Willard Gibbs and others. Since the condition of heat-isolation is impracticable, the condition of maxi­mum entropy cannot, as a rule, be directly applied, and it is neces­sary to find a more convenient method of expression. · If *dW* is the external work done, *dH* the heat absorbed from external sources, and *dE* the increase of intrinsic energy, we have in all cases by the first law’, *dII-dE=dW.* Since *θdφ* cannot be less than *dll,* the difference *(θdφ-dE)* cannot be less than *dW..* This inequality holds in all cases, but cannot in general be applied to an irrever­sible change, because *θdφ* is not a perfect differential, and cannot be evaluated without a.knowledge of the path or process of trans­formation. In the special case, however, in which the transforma­tion is conducted in an isothermal enclosure, a common condition easily realized in practice, the. temperature at the end of the trans­formation is reduced to its initial value throughout the substance. The value of *θdφ* is then the same as *d(βφ),* which is a perfect differential,, so that the condition may be written *d(φ^-E)≈dW.* The condition in this form can be readily applied provided that the external work *dW* can be measured. There are two special cases of importance:—(a) If the volume is constant, or *dW*=0, the value of the function (0φ-E). cannot diminish, or (E-0φ) cannot increase, if the temperature is kept constant. This function may be represented, for each state or phase, of the system con­sidered, by an area on the indicator diagram similar to that repre­senting the intrinsic energy, *E.* The product *θφ* may be represented at any point such as D in Fig. 1 by the whole area 0\*DZ'VO under the isothermal 0rD and the adiabatic DZ', bounded by. the axes of pressure and volume. The intrinsic energy, *E,* is similarly repre­sented by the area DZ'Vd under the adiabatic to the right of the isometric *Dd.* The difference *Θφ-E* is represented by the area 0\*DdO to the left of the isometric DJ under the isothermal 0\*D. The increment of this area (or the decrement of the negative area *E~0φ)* at constant temperature, represents the external, work obtainable from the substance in isothermal expansion, in the same way that the decrement of the intrinsic energy represents the work done in adiabatic expansion. The function *J≈E~θφ,* has been called the “ free energy ” of the substance by Helmholtz, and *θφ* the “bound energy.” These functions do not,.how,ever. represent energy existing in the substance, like the intrinsic energy; but the increment of *θφ* represents heat, supplied to, and the decre­ment of (E-0≠) represents work obtainaole from, the substance when the temperature is kept constant. The condition of stable equilibrium of a system at constant temperature and. volume is that the total *J* should be a minimum. This function is also called the “ thermodynamic potential, at constant volume ” from the analogy w,ith the condition, of minimum potential energy as the criterion of stable equilibrium in statics.

As an example, we may apply this condition to the case of change of state. If J', J\* represent the values of the function for unit mass of the substance of specific volumes *v,* and *v”* in. the two states at temperature 0 and pressure *p,* and if a mass *m* is in the state v', and 1 — *m* in the state »\*, the value of *J* for unit mass of the mixture is wJ'+(ι-m)Jr. This must be a minimum in the state of equilibrium at constant temperature. Since the volume is constant, w,e have the condition mt,'⅛(ι-wι)v\*≡con­stant. Since *dj--φd∂-pd,v,* we have also the relations *dJ,!dv, =-p=dJΙdυ",* at constant temperature. PuttingdJ∕<frn = o at constant volume, we obtain as the condition of equilibrium of the two states Jz+∕>V = J\*+ρ\*v\*. This may be interpreted as