The constant a can always be chosen so that k is positive. When thus defined, θ is called the absolute temperature and η the entropy (per gram) of the substance.

Returning to Eq. (10), we may write it

$$m(D\eta/Dt)+\nabla\cdot(\mathbf{q}/\theta) \\ =-[\mathbf{q}\cdot\nabla\theta]/\theta^2+[(\mathfrak{p}\cdot\nabla)\cdot\mathbf{V}]/\theta$$

or, using Eq. (3) and the divergence theorem

$$(d/dt)\int\int\int_S m\eta d\tau+\int\int_S(1/\theta)\mathbf{q}\cdot d\sigma \\ =\int\int\int_S\{[k(\nabla\theta)^2]/\theta^2+[(\mathfrak{p}\cdot\nabla)\cdot\mathbf{V}]/\theta\}d\tau. \quad (15)$$

The first term on the left is the rate of increase of the entropy of the matter inside S; the surface integral is the familiar ratio of heat loss to temperature. Thus, if $\nabla\mathbf{V}=0$ and $\nabla\theta=0$, this equation expresses the ordinary relation between entropy, temperature and heat in reversible processes.

Furthermore, if $\mathfrak{p}=0$ (nonviscous fluid), the right side is never negative—as is asserted by the second law of thermodynamics. It remains to consider the case of a viscous fluid; the commonly accepted expressions for the components of $\mathfrak{p}$ are[2]

$$\mathfrak{p}_{xx}=(2\lambda/3)[2(\partial V_x/\partial x)-(\partial V_y/\partial y)-(\partial V_z/\partial z)], \\ \mathfrak{p}_{xy}=\mathfrak{p}_{yx}=\lambda[(\partial V_x/\partial y)+(\partial V_y/\partial x)], \text{ etc.,}$$

where $\lambda(\geqslant 0)$ is the coefficient of viscosity. Hence

$$(\mathfrak{p}\cdot\nabla)\cdot\mathbf{V}=(2\lambda/3)\{[(\partial V_x/\partial x)-(\partial V_y/\partial y)]^2+\cdots\} \\ +\lambda\{[(\partial V_x/\partial y)+(\partial V_y/\partial x)]^2+\cdots\}\geqslant 0.$$

If, now $\theta>0$, it follows that the right side of Eq. (15) is never negative even for a viscous fluid. If this be accepted as an empirical fact, or included in Kelvin's hypothesis, the latter and Eq. (15) have the inequality

$$(d/dt)\int\int\int_S m\eta d\tau+\int\int_S(1/\theta)\mathbf{q}\cdot d\boldsymbol{\sigma}\geqslant 0 \quad (16)$$

as consequence. As has been remarked, this inequality is a partial expression of the second law of thermodynamics.

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[2] H. Lamb, *Hydrodynamics* (Cambridge, 1924), fifth edition, p. 544.

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The Thermodynamics of Irreversible Processes

II. Fluid Mixtures

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The possibility of constructing a systematic theory of irreversible processes is surveyed in general terms, by utilizing some of the results established in later parts of the paper. Three assumptions underlying Gibbs' application of the second law to equilibrium problems are formulated in explicit but general mathematical form. It is shown that they restrict the equations governing irreversible changes. The theory of a general fluid mixture is developed in some detail, and is then applied to mixtures of ideal gases. It is shown that the usual equations for the velocity of chemical reactions are consistent with the second law provided that the departure from equilibrium is not too great. Mathematical complexities make it difficult to decide whether this is the case for larger deviations also. A somewhat general theory of diffusion and heat flow is considered and the requirements of the second law are formulated as the positive definiteness of a certain matrix whose elements depend on the diffusion coefficients, thermal conductivity, etc.

SURVEY

IN the preceding paper, the rate of increase of the entropy of a simple fluid was calculated and found to be in accord with the second law of thermodynamics. Before proceeding to more complicated cases, it is well to consider what may be accomplished.

In the case of the simple fluid, it was possible to establish the existence of entropy and temperature functions. This depended on mathematical properties that are peculiar to Pfaffian forms in two variables (p, v), and it is not to be expected that the discussion can be extended to the case of more variables.[1] It will therefore be advisable to follow Gibbs and suppose that the concepts of temperature and entropy are not in need of definition or existence proof.

It was also possible to deduce the usual incomplete form of the second law from Kelvin's hypothesis, the positiveness of the absolute temperature, and the usual expression for the viscous stresses. This may seem of doubtful interest, since these hypotheses are all less general than the second law itself. Thus the object of the considerations will not be the derivation of the entropy law from other laws.

It will rather be to derive equations of the form[2]

$$(d/dt)\iiint_S m\eta d\tau+\iint_S(1/\theta)\mathbf{q}\cdot d\boldsymbol{\sigma}=\iiint_S Gd\tau, \quad (1)$$

which, when combined with the second law, yields the inequality

$$G\geqslant 0. \quad (2)$$

At this stage of the considerations, it will be shown that G is always the sum of a number of terms, each of which is the product of two factors:

$$G=\Sigma_a X_a Y_a. \quad (3)$$

This decomposition of G, and more particularly, the classification of the factors into X's and Y's, is to a great extent arbitrary. However, it will then be shown that it can be done so that

A. the definition of thermostatic equilibrium is

$$X_a=0$$

together with the vector equation

$$\partial\mathbf{V}/\partial t=0.$$

For example, the X's are the components of the heat flow $\mathbf{q}$, of the velocity gradients, of the diffusion velocity, the rates of production of chemical compounds, etc., etc.

The Y's are determined by this choice of the X's, and it will then be shown that

B. the Gibbsian criteria of thermostatic equilibrium are equivalent to the equations

$$Y_a=0$$

together with the vector equation

$$\nabla p=0.$$

The Y's corresponding to the X's enumerated above are proportional to the components of the temperature gradient, of a stress tensor, of the gradients of chemical potential, and the differences of chemical potential, in the same order as above.

It is desirable to have an inclusive terminology for the X's and Y's; because of the diverse natures of the quantities thus combined into classes, it is difficult to find a terminology that is free from serious objections. The most satisfactory that has occurred to the author is *D-factor* for the X's, (D for *definition*) and *C-factor* for the Y's (C for *criterion*). The components of the acceleration and pressure gradient should be considered D- and C-factors, respectively.

It remains to give an explanation of these observations. This is to be found in tacit assumptions that enter into all discussions of thermodynamics and thermostatics, but are rarely or never formulated clearly:

a. The irreversible changes of thermodynamic state are governed by equations expressing the D-factors as functions of the C-factors and certain other variables (say ξ):

$$X_a=F_a(Y, \xi). \quad (4)$$

These may be called the thermodynamic equations of motion; it should be noted that the C- and D-factors have been defined without reference to the equations of motion. The definition

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[1] In this connection, the work of C. Carathéodory should be mentioned: Math. Ann. **67**, 355 (1909), Berl. Ber. p. 39 (1925); also T. Ehrenfest Afanassjewa, Zeits. f. Physik **33**, 933 (1925), and S. Chandrasekhar, *Introduction to the Study of Stellar Structure* (Chicago, 1939), Chap. I.

There is reason to believe that Carathéodory's theory affords a better basis for a theory of irreversible processes than does that of Gibbs. The author has chosen the latter because of its greater familiarity.

[2] The notation is the same as that of the previous paper; m, η, θ, q are the mass density, entropy per gram, temperature and heat flow, respectively. S is any closed surface moving with the matter.

of thermostatic equilibrium then leads immediately to the equations

$$F_a(Y, \xi) = 0, \tag{5}$$

but it must be assumed that

b. The Eq. (5) are equivalent to the equations under B, i.e., to the vanishing of the C-factors.

c. The inequality

$$\Sigma_a X_a Y_a \geqslant 0 \tag{6}$$

is a consequence of the thermodynamic equations of motion.

Unless *a*, *b*, and *c* are true, it is not true that "For the equilibrium of any isolated system it is necessary and sufficient that in all possible variations of the state of the system which do not alter its energy, the variation of its entropy shall either vanish or be negative"[3] which is the principle on which Gibbs based his theory of thermostatics. In order that this principle follow from *a*, *b*, *c*, it is further necessary that *B* be true.

In the next section, the results that have been anticipated in this survey will be established for the case of a fluid mixture.

FLUID MIXTURES

For the sake of formal simplicity, it is essential to consider the possibility that the mixture may contain all of its chemical elements in the free monatomic form; let c_α, $\alpha = 1, 2, \cdots n$ be the concentrations of the free elements in moles/gram of mixture. Let the other possible components of the mixture be molecular compounds, the ith containing $\nu_{i\alpha}$ atoms of element α in each of its molecules. For simplicity, the numbering may be such that i runs from $n+1$ to N, and let c_i be the concentration of compound i. The word *substance* will be used to designate either free elements or compounds.

Let $\mathbf{V}_k$ be the velocity of the substance k and m the density of the mixture in g/cm^3; then

$$\partial(mc_k)/\partial t + \nabla \cdot (mc_k \mathbf{V}_k) = m\Gamma_k \tag{7}$$

defines Γ_k, the rate of production of substance k in moles/g/sec. Since the atoms of the elements are not created or destroyed by the chemical reactions, the Γ_k are not independent, but related by

$$\Gamma_\alpha + \Sigma_{i=n+1}{}^N \nu_{i\alpha}\Gamma_i = 0, \quad \alpha = 1 \cdots n. \tag{8}$$

If M_k is the molecular (atomic) weight of substance k, the concentrations are related by

$$\Sigma_{k=1}{}^N M_k c_k = 1, \tag{9}$$

and the M_k by

$$M_i = \Sigma_{\alpha=1}{}^n \nu_{i\alpha} M_\alpha, \quad i = n+1, \cdots N. \tag{10}$$

Equations (8) and (10) combine to give the equation of conservation of mass

$$\Sigma_{k=1}{}^N M_k \Gamma_k = 0. \tag{11}$$

The momentum density of the mixture is $m\mathbf{V}$, where

$$\mathbf{V} = \Sigma_{k=1}{}^N M_k c_k \mathbf{V}_k, \tag{12}$$

and the Eqs. (7), (9), (11), (12) combine to give the equation of continuity:

$$\begin{aligned} &\partial m/\partial t + \nabla \cdot (m\mathbf{V}) = 0 \\ \text{or} \\ &mDv/Dt = \nabla \cdot \mathbf{V}. \end{aligned} \tag{13}$$

The diffusion velocities of the various substances are

$$\mathbf{U}_k = \mathbf{V}_k - \mathbf{V}, \tag{14}$$

and Eqs. (7), (13), (14) combine to give

$$mDc_k/Dt = m\Gamma_k - \nabla \cdot (mc_k \mathbf{U}_k). \tag{15}$$

The hydrodynamic equation will be assumed in the form

$$mD\mathbf{V}/Dt = \nabla \cdot \mathfrak{p}, \tag{16}$$

the stress tensor $\mathfrak{p}$ now including the hydrostatic pressure as well as the viscous stresses. There is now the possibility that $\mathfrak{p}$ may also depend on the $\mathbf{U}_k$, but this complication may be ignored. In any case, the kinetic energy equation in the form

$$(d/dt)\int\int\int_S \tfrac{1}{2}mV^2 d\tau = \int\int\int_S \mathbf{V} \cdot (\nabla \cdot \mathfrak{p}) d\tau \tag{17}$$

will still be valid. Following Gibbs, it will be assumed that the internal energy (per gram of mixture), ϵ, is a function only of v, of the c_k, and of the entropy η. The possibility that ϵ may depend on the $\mathbf{U}_k$ will be ignored, but this constitutes an approximation.

Because of the arbitrary zero of energy, and of Eq. (9), all equations must be invariant when

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[3] J. W. Gibbs, *Scientific Papers* (Longmans Green & Co., New York), Vol. I, p. 56.

ϵ is replaced by $\epsilon+f(\Sigma_k M_k c_k)$, where f is arbitrary. This will be called an ϵ-substitution.[4]

An application of the energy law to the volume whose boundary S moves with the mass of the fluid yields

$$(d/dt)\iiint_S \{\tfrac{1}{2}mV^2+m\epsilon\}d\tau$$

$$=-\iint_S \mathbf{q}\cdot d\boldsymbol{\sigma}+\iint_S (\mathfrak{p}\cdot\mathbf{V})\cdot d\boldsymbol{\sigma}$$

$$-\Sigma_{k=1}{}^N\iint_S (\partial\epsilon/\partial c_k)mc_k\mathbf{U}_k\cdot d\boldsymbol{\sigma}. \quad (18)$$

The first integral on the right is the rate at which heat enters the volume; the second is the rate at which the fluid outside S does work on the fluid inside S; the remainder is the rate at which energy enters the volume due to the diffusion processes. It is readily verified that this equation is invariant under an ϵ-substitution.

Subtracting Eq. (17) from (18), transforming the surface integrals into volume integrals, and recalling that S is arbitrary, one obtains:

$$mD\epsilon/Dt-(\mathfrak{p}\cdot\nabla)\cdot\mathbf{V}+\nabla\cdot\mathbf{q}$$

$$+\Sigma_{k=1}{}^N\nabla\cdot[m(\partial\epsilon/\partial c_k)c_k\mathbf{U}_k]=0. \quad (19)$$

Following Gibbs, the temperature is defined by

$$\theta=\partial\epsilon/\partial\eta, \quad (20)$$

the chemical potentials[5] by

$$\mu_k=\partial\epsilon/\partial c_k, \quad (21)$$

and the hydrostatic pressure by

$$p=-\partial\epsilon/\partial v. \quad (22)$$

(Under an ϵ-substitution, μ_k is replaced by $\mu_k+M_kf'(1)$, so that $\nabla\mu_k$ is invariant.) Then

$$D\epsilon/Dt=\theta D\eta/Dt-pDv/Dt+\Sigma_{k=1}{}^N\mu_k Dc_k/Dt,$$

which combines with Eqs. (13), (15), and (19) into

$$m\theta D\eta/Dt-p\nabla\cdot\mathbf{V}-(\mathfrak{p}\cdot\nabla)\cdot\mathbf{V}+\nabla\cdot\mathbf{q}$$

$$+\Sigma_{k=1}{}^N m\{\mu_k\Gamma_k+c_k\mathbf{U}_k\cdot\nabla\mu_k\}=0. \quad (23)$$

From Eq. (8), it follows that

$$\Sigma_{k=1}{}^N\mu_k\Gamma_k=\Sigma_{i=n+1}{}^N\Delta_i\Gamma_i, \quad (24)$$

where

$$\Delta_i=\mu_i-\Sigma_{\alpha=1}{}^n\nu_{i\alpha}\mu_\alpha \quad (25)$$

is the difference in chemical potential between the compound i and its equivalent in free elements. Because of Eq. (10) the Δ_i and therefore also the Eq. (23) are invariant under an ϵ-substitution.

Dividing Eq. (23) through by θ, integrating the result over the volume bounded by S, and comparing with Eq. (1), show clearly that

$$G=\mathbf{q}\cdot\nabla(1/\theta)+(1/\theta)\{p\nabla\cdot\mathbf{V}+(\mathfrak{p}\cdot\nabla)\cdot\mathbf{V}$$

$$-\Sigma_{i=n+1}{}^N m\Delta_i\Gamma_i-\Sigma_{k=1}{}^N mc_k\mathbf{U}_k\cdot\nabla\mu_k\}. \quad (26)$$

The derivation of Eq. (26) completes the first stage of the program outlined in the survey (cf. Eq. (3)). It remains to verify the propositions A and B.

It will be obvious that when the mixture reaches thermodynamic equilibrium, the following quantities will vanish: (1) the heat flow, $\mathbf{q}$; (2) the velocity gradient, $\nabla\mathbf{V}$ (and therefore also $\nabla\cdot\mathbf{V}$); (3) the rates of production of the various substances, $m\Gamma_i$; (4) the diffusion currents, $mc_k\mathbf{U}_k$; (5) the acceleration, $\partial\mathbf{V}/\partial t$. The first four of these quantities appear as factors in the various terms of G, thus verifying A. The corresponding C-factors are

(1) $\nabla(1/\theta)$; (3) $-(1/\theta)\Delta_i$;
(2)[6] $(1/\theta)(p\mathfrak{i}+\mathfrak{p})$; (4) $-(1/\theta)\nabla\mu_k$;

while the Gibbs criteria for thermostatic equilibrium are

(1) $\nabla\theta=0$; (2) $\mathfrak{p}=-p\mathfrak{i}$; (3) $\Delta_i=0$;
(4) $\nabla\mu_k=0$; (5) $\nabla p=0$;

thus verifying B.

However several remarks are called for in this connection: the second criterion is not found explicitly in Gibbs' paper, but is implicitly as-

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[4] It will be noted that the theory of ϵ-substitutions is not used to prove any equation, but only as a check and guide. Because of the equivalence of mass and energy, the status of the ϵ-substitutions in a fundamental theory is not clear, and it has seemed preferable to restrict the use of these methods. Other types of invariance are also associated with Eq. (9) and can presumably be used in a similar manner.

[5] Gibbs calls the μ_i simply "the potential of the substance i." Other writers call them "partial molal thermodynamic potentials."

[6] Here $\mathfrak{i}$ is the unit tensor.

sumed at an early stage of the calculations. The criterion (5) follows from criterion (2), the hydrodynamic equation (Eq. (16)), and $\partial \mathbf{V}/\partial t=0$. The exceptional character of the fifth criterion is thus seen to be related to the exceptional position accorded the hydrodynamic equation as compared to the other equations of motion.

ELIMINATION OF THE ENTROPY FROM THE EQUATIONS

The equations just derived involve functions of v, the c_i, and the entropy, η. This proves to be inconvenient, for it is an empirical fact that these functions are very complicated. The equations are very much simplified by eliminating the entropy and replacing it by the temperature, using Eq. (20) to accomplish this. This is an algebraic process, but can be very laborious, so that it deserves some consideration.

It appears that the process can be much simplified by introducing the function

$$\psi(v,\, c_i,\, \theta)=\epsilon(v,\, c_i,\, \eta)-\theta\eta, \tag{27}$$

the entropy being eliminated from the right side. The function ψ is one of those introduced by Massieu under the name *characteristic function*, and is usually called the *free energy*, or *work function* (per g of the mixture). Once ψ has been determined, the quantities p, μ_i and η can be expressed as functions of v, c_i and θ by means of the equations

$$p=-\partial\psi/\partial v, \tag{28}$$

$$\mu_i=\partial\psi/\partial c_i, \tag{29}$$

$$\eta=-\partial\psi/\partial\theta, \tag{30}$$

which follow from Eqs. (20), (21), (22) and (27).

GENERAL CONSEQUENCES OF *a*, *b*, *c*

The assumptions a, b, c have important consequences for the theory of irreversible processes, inasmuch as b, and c impose marked restrictions on the equations of motion. From b it follows that

$$(\partial F_a/\partial \xi)_0=0, \tag{31}$$

the subscript zero indicating that the $Y_a=0$ while the ξ's have general values.[7] Equation (6) imposes further restrictions on the F_a; it can be given another form if the F_a are linear functions of the Y_a, which is probably the case whenever the departure from equilibrium is not very great. In this case, Eq. (4) becomes

$$X_a=\Sigma_b A_{ab} Y_b, \tag{32}$$

where

$$A_{ab}=(\partial F_a/\partial Y_b)_0, \tag{33}$$

is in general a function of the ξ's. Equation (6) is then

$$\Sigma_a\Sigma_b A_{ab} Y_a Y_b \geqslant 0, \tag{34}$$

which must be true for all values of the Y_a and the ξ's. Therefore the matrix

$$B_{ab}=\tfrac{1}{2}(A_{ab}+A_{ba}) \tag{35}$$

must be positive definite. This implies such inequalities as

$$B_{aa}\geqslant 0, \tag{36}$$

$$B_{aa}B_{bb}-(B_{ab})^2\geqslant 0. \tag{37}$$

MIXTURES OF IDEAL GASES

In order to work out special cases of the general principles, it is convenient to consider a mixture of ideal gases, for which the work function is

$$\psi(v,\, c_i,\, \theta) =\Sigma_{i=1}^{N} c_i\{u_i(\theta)+R\theta[\log\,(c_i/v)-1]\}, \tag{38}$$

the u_i being functions characteristic of the substances and R the gas constant per mole.[8] Equation (29) then yields

$$\mu_i=u_i(\theta)+R\theta\,\log\,(c_i/v), \tag{39}$$

and Dalton's law of partial pressures, etc., can also be derived.

This ideal mixture may be the scene of chemical reactions, proceeding at rates given by the usual formulae. It is to be considered, whether these formulae are consistent with a, b, c. Before doing so, however, it will be shown that Eq. (39) leads to the usual form of the law of mass action.

Let M_k stand for the chemical symbol of substance k, as well as for its molecular weight. Then the general form of a reaction may be

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[7] If the quantities dX_a/dt are among the ξ's, this generality must be restricted, since these derivatives vanish at equilibrium.

[8] See, e.g., K. F. Herzfeld, *Handbuch der Physik*, Vol. 9, p. 101, Eq. (1).

written (the ν's are integers)

$$\Sigma_{k=1}{}^{N}\nu_k{}'M_k \rightleftarrows \Sigma_{k=1}{}^{N}\nu_k{}''M_k. \tag{40}$$

Since the reaction balances,

$$\Sigma_{k=1}{}^{N}\nu_k{}'\nu_{k\alpha}=\Sigma_{k=1}{}^{N}\nu_k{}''\nu_{k\alpha}=n_\alpha, \quad \alpha=1\cdots n, \tag{41}$$

$\nu_{k\alpha}$ being the number of atoms of element α in one molecule of substance k. (If $\alpha \leqslant n$, $\nu_{k\alpha}=\delta_{k\alpha}$.) The criteria for chemical equilibrium ($\Delta_i=0$) yield

$$\Sigma_{i=n+1}{}^{N}(\nu_i{}''-\nu_i{}')\Delta_i=0,$$

which may also be written

$$\Sigma_{i=1}{}^{N}(\nu_i{}''-\nu_i{}')\mu_i=0 \tag{42}$$

because of Eq. (41). Substituting from Eq. (39) gives

$$\Sigma_{i=1}{}^{N}(\nu_i{}''-\nu_i{}')[u_i/R\theta+\log\,(c_i/v)]=0, \tag{43}$$

which is essentially the Arrhenius form of the law of mass action.

The commonly accepted (and empirically verified) formulae for the rate of a chemical reaction in the gaseous phase were first deduced by Guldberg and Waage from rather vague kinetic theory considerations. These have since been made somewhat more specific and brought into agreement with Eq. (42).[9] According to these formulae, the net rate at which the reaction proceeds to the right is the difference $\rho'-\rho''$, where

$$\begin{aligned}\rho' &= \phi \exp\,(\Sigma_{i=1}{}^{N}\nu_i{}'\mu_i/R\theta),\\ \rho'' &= \phi \exp\,(\Sigma_{i=1}{}^{N}\nu_i{}''\mu_i/R\theta),\end{aligned} \tag{44}$$

ϕ being a positive quantity. It is clear that Eq. (42) follows from this and

$$\rho'-\rho''=0, \tag{45}$$

but that Eq. (45) does not follow from the definition of thermostatic equilibrium. It is usually deduced from the principle of detailed balancing, but also follows from the Gibbsian criteria of equilibria.

If there are many possible reactions, these must be distinguished by an index (ϕ_s, $\rho_s{}'$, $n_{\alpha s}$, etc.). The rate of production of substance i is then

$$\Gamma_i=\Sigma_s(\nu_{is}{}''-\nu_{is}{}')(\rho_s{}'-\rho_s{}''), \tag{46}$$

and the definition of equilibrium is $\Gamma_i=0$. Eq. (45) cannot follow directly from this and Eq. (46) unless there are at least as many substances as possible reactions. It may, however, follow indirectly because of other considerations leading to the Gibbsian criteria of equilibrium.

From Eq. (25),

$$\begin{aligned}\rho_s{}' &= a_s \exp\,(\Sigma_{k=n+1}{}^{N}\nu_{ks}{}'\Delta_k/R\theta),\\ \rho_s{}'' &= a_s \exp\,(\Sigma_{k=n+1}{}^{N}\nu_{ks}{}''\Delta_k/R\theta),\end{aligned} \tag{47}$$

where

$$a_s=\phi_s \exp\,(\Sigma_{\alpha=1}{}^{n}n_{\alpha s}\mu_\alpha/R\theta)\geqslant 0.$$

Since ρ and Δ are invariant under an ϵ-substitution, a must also be; there is thus a presumption that the interpretation of a will be simpler than that of ϕ. Equation (46) then becomes

$$\begin{aligned}\Gamma_i=\Sigma_s(\nu_{is}{}''-\nu_{is}{}')a_s\{&\exp\,(\Sigma_{k=n+1}{}^{N}\nu_{ks}{}'\cdot\Delta_k/R\theta)\\ &-\exp\,(\Sigma_{k=n+1}{}^{N}\nu_{ks}{}''\Delta_k/R\theta)\}.\end{aligned} \tag{48}$$

For sufficiently small values of Δ_i,

$$\Gamma_i=-\Sigma_{s,\,k}(\nu_{is}{}''-\nu_{is}{}')a_s(\nu_{ks}{}''-\nu_{ks}{}')\Delta_k/R\theta,$$

so that

$$\begin{aligned}&\Sigma_{i=n+1}{}^{N}\Gamma_i(-\Delta_i/\theta)\\ &\qquad=(1/R)\Sigma_{s,\,k}a_s\{\Sigma_k(\nu_{ks}{}''-\nu_{ks}{}')(\Delta_k/\theta)\}^2.\end{aligned}$$

These last two equations are in complete accord with the general considerations leading to Eq. (34). The more general Eq. (48) is in accord with Eq. (31), and the Gibbsian criteria $\Delta_i=0$ are a sufficient condition for $\Gamma_i=0$. It is not easy to see whether they are also the necessary condition, as Gibbs asserts, nor whether

$$\Sigma_i\Gamma_i(-\Delta_i/\theta)\geqslant 0$$

for all values of Δ_i, as is required by the present assumption c.

Turning now to the conduction of heat and the diffusion of matter in the mixture, it may be supposed that the equations governing these processes are

$$\begin{aligned}\mathbf{q} &= \kappa_{00}\nabla(1/\theta)-\Sigma_{i=1}{}^{N}(\kappa_{0i}/\theta)\nabla\mu_i,\\ mc_j\mathbf{U}_j &= \kappa_{j0}\nabla(1/\theta)-\Sigma_{i=1}{}^{N}(\kappa_{ji}/\theta)\nabla\mu_i.\end{aligned} \tag{49}$$

In order that these equations be consistent with the general principles, it is necessary and sufficient that the matrix $\frac{1}{2}(\kappa_{ij}+\kappa_{ji})$ be positive

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[9] R. H. Fowler, *Statistical Mechanics* (Cambridge University Press, 1936) second edition, p. 700.

definite. Insofar as the mixture is an idealized one, there is no need to justify the assumption of Eq. (49), but the question of its departure from actual mixtures does arise.

The conduction of heat is usually supposed to be given by Fourier's law that q is proportional to $\nabla\theta$; similarly, Fick's law that $\mathbf{U}_i$ is proportional to $\nabla(mc_i)$ is supposed to govern diffusion. However, more general cases have been considered, in which $\mathbf{U}_i$ is a linear function of all the concentration gradients. Such "diffusion-drag" forces have been invoked to explain certain biophysical phenomena, and it seems likely that they are important in the separation of isotopes. Except for a difference in notation, and the terms in κ_{0i}, the Eq. (49) are identical with those considered in the diffusion-drag theories.

To see this, note that because of Eq. (39) and $m=1/v$

$$\nabla\mu_i=\theta\alpha_i\nabla\theta+(R\theta/mc_i)\nabla(mc_i), \tag{50}$$

where

$$\theta\alpha_i=du_i/d\theta+R\log(mc_i),$$

so that Eq. (49) becomes

$$\begin{aligned} -\mathbf{q}&=k_{00}\nabla\theta+\Sigma_{i=1}{}^N k_{0i}\nabla(mc_i),\\ -mc_j\mathbf{U}_j&=k_{j0}\nabla\theta+\Sigma_{i=1}{}^N k_{ji}\nabla(mc_i), \end{aligned} \tag{51}$$

with

$$\begin{aligned} k_{j0}&=\kappa_{j0}/\theta^2+\Sigma_{i=1}{}^N\kappa_{ji}\alpha_i,\\ k_{ji}&=R\kappa_{ji}/mc_i. \end{aligned} \tag{52}$$

The coefficient k_{00} is the thermal conductivity, the k_{ii} $(i=1\cdots N)$ are the diffusion coefficients, while the k_{ij} $(i\neq j=1\cdots N)$ are the drag coefficients. If the coefficients $k_{j0}\neq 0$, this amounts to assuming that a temperature gradient tends to produce a diffusion of matter; similarly, if $k_{0i}\neq 0$ the concentration gradients tend to produce a flow of heat. Both of these phenomena occur; they are closely related to the various thermoelectric effects.

Since the matrix κ_{ij} is positive definite, the thermal conductivity and diffusion coefficients must be positive quantities, and

$$4c_ic_jk_{ii}k_{jj}\geqslant(k_{ij}c_j+k_{ji}c_i)^2,$$

etc. However, these particular inequalities are based on Eq. (40); they may have different forms for liquid mixtures. The general conclusion that the numerical values of the drag coefficients are restricted by the numerical values of the diffusion coefficients is valid in all cases.

Finally, it would be possible to consider generalizations of the usual formulae for the viscous stresses, but this seems of slight interest here.

SUMMARY

The restrictions imposed by the second law of thermodynamics on the equations governing irreversible changes have been investigated, first somewhat generally, and then for the particular case of a mixture of ideal gases. It was found that they are automatically fulfilled by the usual law of mass action for chemical reaction velocities. In the case of general diffusion processes, the diffusion coefficients must be positive, and certain other inequalities must be satisfied. The general methods used can be applied to other irreversible processes, and will always yield such inequalities. The experience of the author suggests that many of these inequalities have already found their place in physical theories, having been introduced on the basis of "physical intuition," but that the latter cannot deal with the more elaborate cases.

Note added April 26, 1940. Since writing the above, my attention has been called to the work of E. Lohr on similar problems.* A first reading of his extensive papers shows that some of his conclusions practically coincide with mine, though there seem to be appreciable differences in our points of view. The entropy law has also been formulated as a differential equation by R. C. Tolman,†, independently of the work of Lohr.

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* E. Lohr, Wiener Denkschriften, **93**, 339–421 (1917); **99**, 11–37, 59–91 (1924). Vektor- und Dyadenrechnung, p. 312 (Berlin, 1939).

† Literature references in R. C. Tolman and H. P. Robertson, Phys. Rev. **43**, 564 (1933).