

or non-reacting gas mixtures, thus enabling values of $\left(\frac{\partial \chi}{\partial p}\right)_T$ for such mixtures to be used to guide the equation of state theory for mixtures. This is of interest, for a complete knowledge of the van der Waals forces in mixtures is of profound importance in the application of thermodynamics to chemical equilibria at finite pressures.

¹ J. W. Gibbs, *Scientific Papers*, Vol. I, p. 87.

² J. A. Beattie, *Proc. Amer. Acad.*, **63**, 229 (1928); *J. Math. and Phys. M.I.T.*, **9**, 11 (1930).

³ K. F. Herzfeld Muller Pouillet, *Lehrbuch der Physik*, **3**, 161; also F. G. Keyes, *Chem. Rev.*, **6**, 175 (1929).

⁴ J. G. Kirkwood and F. G. Keyes, *Phys. Rev.*, **38**, 516 (1931).

⁵ J. G. Kirkwood, *Phys. Zeit.*, **33**, 39 (1932).

⁶ An innovation in the technique of measuring the Joule-Thomson effect to be reported later has been developed which is adapted to low temperatures and low pressures. From the two effects $\left(\frac{\partial T}{\partial p}\right)_\chi$ and $\left(\frac{\partial \chi}{\partial p}\right)_T$ the value of c_p is immediately deducible. (Eq. 3.)

PROOF OF GIBBS' HYPOTHESIS ON THE TENDENCY TOWARD STATISTICAL EQUILIBRIUM.

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In this paper the author applies the circle of ideas due to B. O. Koopman¹ and J. v. Neumann² to the proof of Gibbs' fundamental hypothesis concerning the tendency of an ensemble of independent systems toward statistical equilibrium.³ The motions of the systems are described by a Hamiltonian differential system,

$$\dot{q}_i = \frac{\partial H}{\partial p_i}, \quad \dot{p}_i = - \frac{\partial H}{\partial q_i}.$$

The ensemble is represented by a certain distribution in phase $f(P)dm$, where $P = (p_i, q_i)$, and where $dm = \pi dq_i dp_i$ is the invariant volume element in the phase space. The distribution is carried by the phase flow associated with (H) and will, in general, alter in time. Under what conditions has (H) the property that any initial distribution tend toward a permanent one (not affected by the motions, i.e., being invariant under the flow)? Simple examples show that this tendency does not always exist.³ After giving an appropriate mathematical formulation of the tendency toward permanent distributions the author derives various necessary and sufficient conditions that a given flow show that tendency.

Let P denote the points of a general space Ω (not necessarily associated with (H)), and let $T_t(P)$,

$$T_s T_t = T_{s+t},$$

be a linear one parameter group of one to one transformations of Ω into itself (steady flow on Ω) preserving a certain measure m on Ω in the sense of Lebesgue. We set

$$(f, g) = \int_{\Omega} f(P)g(P)dm, \quad \|f\| = \sqrt{(f, f)},$$

for any two q. s. f. (quadratically summable functions) $f(P)$, $g(P)$. Only functions with real values are considered in this paper. All integrals are to be understood in the sense of Lebesgue. According to B. O. Koopman¹ the symbol U_t , where $U_t f$ signifies the function $f(T_t(P))$, defines a linear one parameter group of unitary operators in the Hilbert space of all q. s. f. $f(P)$,

$$U_s U_t = U_{s+t}, \quad (U_t f, U_t g) = (f, g).$$

A function f is called invariant under the group T_t if, for any given t , $U_t f = f$ holds almost everywhere on Ω . We shall use the following theorem proved by v. Neumann:²

Time-Average Theorem.—Every q. s. f. $f(P)$ possesses a time-average $f^*(P)$ such that

$$\lim_{T \rightarrow \infty} \left\| \frac{1}{T} \int_{\alpha}^{\alpha+T} U_t f dt - f^* \right\| = 0,⁴$$

independently of $\alpha = \alpha(T)$. $f^*(P)$ is q. s. and invariant under the group.

The equation

$$(f, h) = (f^*, h) \tag{1}$$

is fulfilled by any q. s. and invariant $h(P)$.⁵

Let $f(P)dm$ be any initial ($t = 0$) distribution on Ω . If T_t is interpreted as a steady flow of a colorless and incompressible liquid, $f(P)$ may be regarded as an initial distribution of coloring matter in the liquid. At the time t its distribution will be given by $U_{-t} f dm$, since dm is invariant. The amount of coloring matter contained in a volume A at the time t will be $(U_{-t} f, \chi_A)$, where $\chi_A(P) = 1$ if $P \in A$, $\chi_A(P) = 0$ if $P \in \Omega - A$. If that content tends toward a limit, we infer from the time-average theorem

$$\lim_{t \rightarrow \infty} (U_{-t} f, \chi_A) = \lim_{T \rightarrow \infty} \frac{1}{T} \int_{-T}^0 (U_t f, \chi_A) dt = (f^*, \chi_A) = \int_A f^*(P) dm.$$

Thus, if convergence takes place for any finite volume A , the density of the limiting distribution of the coloring matter is given by $f^*(P)$ being invariant under the flow, i.e., the distribution becomes stationary in the

long run. The necessary and sufficient condition for that tendency toward stationarity is that the equation

$$\lim_{|t| \rightarrow \infty} (U_t f, g) = (f^*, g) \tag{2}$$

holds for any two q. s. f. $f(P), g(P)$.

The equation

$$\lim_{T \rightarrow \infty} \frac{1}{2T} \int_{-T}^{+T} [(U_t f, g) - (f^*, g)] dt = 0 \tag{3}$$

is a weaker interpretation of the tendency toward stationarity. However, there seem to be some indications that (3) is a more appropriate interpretation. Moreover, the integral average on the left side of (3) is the square of the dispersion of the function $(U_t f, g)$ about the value

$$(f^*, g) = (f^*, g^*)$$

so that (3) still represents "observable" convergence.

In his paper on "Complete Transitivity and the Ergodic Principle,"⁶ the author has treated the case of uniform distribution in the long run. The content of this paper admits of immediate generalization and leads to the

THEOREM 1. *A necessary and sufficient condition that (3) be true for any two q. s. f. is that the invariance under a transformation $T_a, a \neq 0$, of a measurable point set, imply its invariance under the whole group T_t .*

In connection with the spectral representation of the unitary group, the obvious condition is that $\lambda = 0$ be the only characteristic value of the spectrum. If there is no tendency of any initial distribution toward a stationary one, $(U_t f, g)$ fluctuates about (f^*, g) in an asymptotically almost-periodic manner (loc. cit.⁶).

The problem may, however, be treated from another and, in the author's belief, more natural point of view. We consider the product space $\Omega \times \Omega$ of the pairs

$$\pi = (P, Q) = (Q, P)$$

of two points of Ω , *disregarding their order*. Any point set on $\Omega \times \Omega$ is then a symmetric set in the space of the ordered pairs, and any function $F(\pi)$ is a symmetric function of the ordered pair, $F(P, Q) = F(Q, P)$. The flow $T_t(P)$ on Ω implies a "product flow"

$$T_t(\pi) = (T_t(P), T_t(Q)) = (T_t(Q), T_t(P))$$

on $\Omega \times \Omega$. Furthermore, the invariant volume element dm on Ω implies an invariant volume element

$$d\mu = d\mu_\pi = dm_P dm_Q$$

on $\Omega \times \Omega$, thus yielding an invariant measure μ over $\Omega \times \Omega$ in the sense of Lebesgue. We set

$$\langle F, G \rangle = \int_{\Omega \times \Omega} F(\pi)G(\pi)d\mu, \quad \Delta(F) = \sqrt{\langle F, F \rangle},$$

for any two q. s. f. $F(\pi), G(\pi)$ over $\Omega \times \Omega$, and

$$U_t F = F(T_t(\pi)).$$

Strong convergence of functions on $\Omega \times \Omega$ means as usually convergence in the sense of the distance Δ .

THEOREM 2. (3) holds for any two q. s. f. $f(P), g(P)$, if and only if any q. s. f. $F(\pi)$ being invariant under the product flow is the limit in the sense of strong convergence of finite sums $\Sigma \varphi(P)\psi(Q)$, where φ, ψ are q. s. over Ω and invariant under the given flow.

The condition may easily be expressed in terms of invariant point sets instead in terms of invariant functions. Let \mathfrak{N} be a certain totality of measurable point sets on $\Omega \times \Omega$. We say that a measurable point set B is generated by the point sets A of \mathfrak{N} , if B can be approximated by finite sums ΣA such that $\mu(B + \Sigma A - B\Sigma A)$ can be made arbitrarily small. Theorem 2 may then be expressed as follows:

THEOREM 3. (3) holds for any pair of q. s. f. $f(P), g(P)$, if and only if every point set on $\Omega \times \Omega$ having a finite measure μ and being invariant under the product flow, can be generated by the invariant product sets $A \times A'$ where A and A' are any two invariant sets on Ω with a finite measure m .

The most interesting particular case is the case of an ergodic flow on Ω , i. e., the case where the time-average of any q. s. f. $f(P)$ is constant almost everywhere on Ω ,

$$f^*(P) = \frac{\int_{\Omega} f dm}{m(\Omega)}.$$

According to v. Neumann² the necessary and sufficient condition for ergodicity is that the flow be metrically transitive, i. e., that any invariant and measurable set has either the measure zero or the measure $m(\Omega)$. From Theorem 3 we infer therefore the

THEOREM 4. The equation

$$\lim_{T \rightarrow \infty} \frac{1}{2T} \int_{-T}^{+T} \left[(U_t f, g) - \frac{\int_{\Omega} f dm \int_{\Omega} g dm}{m(\Omega)^2} \right]^2 dt = 0$$

holds for any two q. s. f. f, g , if and only if the product flow is metrically transitive (condition for the tendency toward uniform distribution).

The proof of Theorem 3 is simplified by the use of the

THEOREM 5. *A necessary and sufficient condition that (3) be true for any two q. s. f. f, g , is that*

$$(f(P)f(Q))^* = f^*(P)f^*(Q)$$

holds for any $f(P)$ being q. s. over Ω .

Proof of Theorem 5.—According to

$$[(U_t f, g) - (f^*, g)]^2 = (U_t f, g)^2 + (f^*, g)^2 - 2(f^*, g)(U_t f, g)$$

and to

$$\lim_{T \rightarrow \infty} \frac{1}{2T} \int_{-T}^{+T} (U_t f, g) dt = (f^*, g)$$

the equation (3) is equivalent to the equation

$$\lim_{T \rightarrow \infty} \frac{1}{2T} \int_{-T}^{+T} (U_t f, g)^2 dt = (f^*, g)^2. \tag{4}$$

In setting

$$F(\pi) = f(P)f(Q), \quad G(\pi) = g(P)g(Q) \tag{5}$$

and

$$F(\pi) = f^*(P)f^*(Q), \tag{6}$$

we infer

$$\langle U_t F, G \rangle = (U_t f, g)^2; \quad \langle \tilde{F}, G \rangle = (f^*, g)^2.$$

Thus (4) may be written in the form

$$\lim_{T \rightarrow \infty} \frac{1}{2T} \int_{-T}^{+T} \langle U_t F, G \rangle dt = \langle \tilde{F}, G \rangle.$$

As this equation remains true if \tilde{F} is replaced by the time-average F^* of F , we conclude that the equation

$$\langle F^*, G \rangle = \langle \tilde{F}, G \rangle \tag{7}$$

together with (5) and (6) is equivalent to (3). The condition indicated in Theorem 5 is therefore sufficient.

In order to prove that the condition is necessary we use the following elementary

Lemma.—Every function $\phi(\pi)$ being q. s. over $\Omega \times \Omega$ is the limit in the sense of strong convergence of finite sums $\Sigma = \varphi(P)\varphi(Q)$, where the functions $\varphi(P)$ are q. s. over Ω .

This lemma is readily proved for sums $\Sigma \varphi(P)\psi(Q)$. ϕ , however, is necessarily symmetric in P, Q , thus being the strong limit of sums

$$= \frac{1}{2}\Sigma\{\varphi(P) + \psi(P)\}(\varphi(Q) + \psi(Q)) - \varphi(P)\varphi(Q) - \psi(P)\psi(Q).$$

The lemma shows immediately that (7) must be true for any q. s. f. $G(\pi)$, i.e., that $\tilde{F} = F^*$.

Proof of Theorem 3. We suppose the equation

$$(f(P)f(Q))^* = f^*(P)f^*(Q)$$

to hold for any q. s. $f(P)$. We set

$$d(\pi) = F(\pi) - \Sigma \mp f(P)f(Q).$$

If F is invariant, i.e., if $F = F^*$, we infer

$$d^*(\pi) = F(\pi) - \Sigma \mp f^*(P)f^*(Q).$$

The fundamental equation $\langle d^*, H \rangle = \langle d, H \rangle$, H being invariant, yields, for $H = d^*$,

$$\Delta(d^*)^2 = \langle d, d^* \rangle \leq \Delta(d)\Delta(d^*), \quad \Delta(d^*) \leq \Delta(d).$$

Since, according to the lemma, $\Delta(d)$ can be made arbitrarily small, we infer the same for $\Delta(d^*)$, i.e., F is the strong limit of sums of the required kind.

Conversely, let us suppose every invariant and q. s. f. $F(\pi)$ to be the strong limit of sums of functions

$$H' = \mp h(P)h(Q),$$

$h(P)$ being invariant and q. s. over Ω . We set

$$F(\pi) = f(P)f(Q), \quad \tilde{F}(\pi) = f^*(P)f^*(Q).$$

From the equations $\langle F^*, H' \rangle = \langle F, H' \rangle$ and $(f^*, h) = (f, h)$ we infer

$$\langle F^*, H' \rangle = (f, h)^2 = (f^*, h)^2 = \langle \tilde{F}, H' \rangle$$

for every H' . $\langle F^*, H' \rangle = \langle \tilde{F}, H' \rangle$ is therefore true for any invariant H , particularly for $H = F^* - \tilde{F}$, i.e., we have $\tilde{F} = \tilde{F}^*$.

v. Neumann² has proved that the totality of the measurable and invariant point sets on Ω possesses a basis,

$$\Omega_x, 0 \leq x \leq 1; \quad \Omega_0 = 0, \Omega_1 = \Omega; \quad \Omega_x \subset \Omega_{x'}, x < x',$$

such that every measurable and invariant set can be generated by the sets $\Omega_{x'} - \Omega_x$. Any measurable and invariant function reduces (apart from a set of measure zero on Ω) to a function of x , where, for given P , x is determined by the inequalities

$$P \text{ in } \Omega_{x'}, x' > x; \quad P \text{ not in } \Omega_{x'}, x' < x.$$

The proof of the following theorem offers no difficulty.

THEOREM 6. *A necessary and sufficient condition that (3) hold for any two q. s. f. f, g is that every measurable function $F(\pi)$ being invariant under the product flow reduces to a function of $(x, y) = (y, x)$.*

With regard to the particular kind of flow defined by a Hamiltonian differential system, let us apply our results to the following case. Ω is an analytic manifold and $T_t(P)$ depends analytically upon P and t . Let

$$S_x, a \leq x \leq b,$$

be an analytic one parameter family of analytic submanifolds being invariant under the flow (the manifolds of constant energy) and exhausting Ω altogether. The equation

$$dm = dx d\sigma_x$$

determines then an invariant volume element $d\sigma_x$ on S_x . $\sigma_x(S_x)$ is supposed to be bounded, $a \leq x \leq b$. The invariant volume element on the invariant product set $S_x \times S_y$ is furnished by $d\sigma_x d\sigma_y$.

THEOREM 7. *A necessary and sufficient condition that (3) hold for any two q. s. f. f, g and that f^* depend but on x is that the product flow be metrically transitive on $S_x \times S_y$ for almost all $(x, y) = (y, x)$ (in the sense of the plane measure).*

This theorem indicates thus the precise condition under which any initial distribution in the phase-space tends toward a distribution whose density depends but on the energy (fundamental hypothesis of Gibbs-Lorentz).

The proof that ergodicity on $S_x \times S_y$ for almost all $(x, y) = (y, x)$ is equivalent to the fact that any measurable and invariant function $F(\pi)$ reduces to a function of x, y , offers no essential difficulties.

Let us illustrate Theorem 7 in the following well-known case (H. Poincaré, J. Kröð).³ x, φ are polar coordinates in the plane, and Ω is the circular region $x \leq 1$. We consider the circular flow

$$P: x, \varphi; T_t(P): x, \varphi + v(x)t,$$

where $v(x)$ is continuously differentiable in $0 \leq x \leq 1$. S_x is here the circle with the radius x , $d\sigma_x = d\varphi$ being the invariant element on S_x . The product flow on $S_x \times S_y$ is given by

$$\varphi, \psi \longrightarrow \varphi + v(x)t, \psi + v(y)t.$$

This flow is ergodic if and only if $v(x)/v(y)$ is an irrational number. The condition of Theorem 7 will therefore be fulfilled provided that $v'(x)$ has but a finite number of zeros.

The condition indicated in Theorem 7 cannot, however, be regarded as final. Tendency toward a stationary distribution depending but on x

(Gibb's canonical distribution) depends obviously upon properties in the small, i.e., upon the behavior of the flow in the shells between S_x and $S_{x+\delta}$, $a \leq x \leq b$, δ being arbitrarily small. The true condition for that tendency must therefore be an infinitesimal one. It is evidently of great interest to find such a condition.

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¹ Cf. B. O. Koopman, these PROCEEDINGS, 17, 315-318 (1931).

² Cf. J. v. Neumann, these PROCEEDINGS, 18, 70-82 (1932).

³ Cf. J. W. Gibbs, *Statistical Mechanics*, Chapter VII. We refer in particular to the sections 23 and 27 of P. and T. Ehrenfest's article, "Statistische Mechanik," in the *Encyclopaedie der math. Wiss.*, IV 2.

⁴ The actual existence of the limit except in a point set of zero measure has been proved by Birkhoff, these PROCEEDINGS, 17, 650-660 (1931). This fact is, however, not needed for our purposes.

⁵ An elementary proof has been given by the author, these PROCEEDINGS, 18, 93-100 (1932).

⁶ E. Hopf, these PROCEEDINGS, 18, 204-209 (1932). The same subject has been simultaneously and independently treated by Koopman and v. Neumann, these PROCEEDINGS, March, 1932. These authors have found another interesting form of the equation (3). Furthermore, they give an example of a unitary group U_t , for which (3) holds, whereas (2) is not fulfilled in general.

REGULAR FAMILIES OF CURVES. II*

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The purpose of this note is three-fold: (a) A new definition of the function μ is given.¹ (b) A condition for the regularity of a family of curves is stated. (c) If a closed set of "invariant points" be added to a regular family of curves, an "extended family of curves" is formed; theorems are stated on the covering of the curves by a set of "tubes," and on the introduction of a function continuous throughout the extended family.

1. *The New Function μ .*—Let R be any metric separable space, and let a_1, a_2, \dots , be a sequence of points dense in R . For any x in R , define $f_n(x)$ as follows:

$$f_n(x) = \frac{1}{1 + \rho(x, a_n)}. \quad (1)$$

Let S be any subset of R ; we put

$$\mu_n(S) = \max_{x \in S} f_n(x) - \min_{x \in S} f_n(x), \quad (2)$$