

The Thermodynamics of Irreversible Processes

I. The Simple Fluid

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The rate of increase of the entropy of a simple viscous fluid, capable of conducting heat, is investigated in greater detail than has hitherto been customary. It is shown that, if Kelvin's hypothesis concerning the absolute temperature be adopted, and the usual law of viscosity be assumed, the requirements of the second law are satisfied.

SINCE the publication of Gibbs' "Equilibrium of heterogeneous substances,"¹ it has been obvious that the greater part of the existing thermodynamic theory would more appropriately be called thermostatics, the term thermodynamics being reserved for the rather unorganized lot of equations that govern irreversible changes in which heat plays a part. Examples of such equations are Fourier's law of heat conduction, Ohm's law, Fick's law of diffusion, etc., etc. Although this usage is dictated by the close analogy to mechanics, there has been no tendency to adopt it. This reluctance has been partly due to the chaotic state of thermodynamics proper, and partly to the belief that the laws mentioned above are much less fundamental than Newton's laws of motion or than the energy and entropy laws, and require derivation from kinetic theory. The purpose of the present investigation has been to find the general equation of which the foregoing are special cases. The problem of providing a kinetic theory derivation has not been considered. The major part of the discussion will be presented in such a manner as to bring out the connection with Gibbs' work, but by way of introduction, the case of a simple viscous fluid, conducting heat, will be discussed from a pre-Gibbsian standpoint.

Let m be the mass density of the fluid, \mathbf{V} its velocity, so that the conservation of mass leads to the equation of continuity

$$\partial m / \partial t + \nabla \cdot (m\mathbf{V}) = 0. \quad (1)$$

Defining the specific volume $v = 1/m$ and the operator

$$D/Dt = \partial/\partial t + \mathbf{V} \cdot \nabla$$

¹J. W. Gibbs, *Scientific Papers* (Longmans, 1906), Vol. I., p. 55.

we may also write

$$mDv/Dt = \nabla \cdot \mathbf{V}. \quad (2)$$

Let S be any closed surface moving with the fluid, so that an element of its area, $d\sigma$, sweeps out the volume $\mathbf{V} \cdot d\sigma dt$ in time dt . If f is any function of position and time

$$\begin{aligned} (d/dt) \int \int \int_S m f d\tau &= \int \int \int_S [\partial(mf)/\partial t] d\tau + \int \int \int_S m f \mathbf{V} \cdot d\sigma \\ &= \int \int \int_S \{ \partial(mf)/\partial t + \nabla \cdot (mf\mathbf{V}) \} d\tau \\ &= \int \int \int_S m (Df/Dt) d\tau. \end{aligned} \quad (3)$$

In the absence of external volume forces, the motion of the fluid will be governed by the hydrodynamic equation

$$mD\mathbf{V}/Dt = -\nabla p + \nabla \cdot \mathfrak{p}, \quad (4)$$

where p is the hydrostatic pressure, and \mathfrak{p} is the tensor of the viscous stresses. The precise expression for the latter will not be needed until later.

The kinetic energy of the fluid enclosed by S is

$$K = \int \int \int_S \frac{1}{2} m V^2 d\tau$$

and by Eq. (3)

$$\begin{aligned} dK/dt &= \int \int \int_S m \mathbf{V} \cdot (D\mathbf{V}/Dt) d\tau \\ &= \int \int \int_S \mathbf{V} \cdot (-\nabla p + \nabla \cdot \mathfrak{p}) d\tau \end{aligned}$$

or, on using the divergence theorem

$$dK/dt = - \int_S (\rho \mathbf{V} - \mathbf{p} \cdot \nabla) \cdot d\boldsymbol{\sigma} \\ + \int \int \int_S \{ \rho \nabla \cdot \mathbf{V} - (\mathbf{p} \cdot \nabla) \cdot \mathbf{V} \} d\tau. \quad (5)$$

The surface integral is the rate at which the fluid inside S does work on the fluid outside S .

The energy law as applied to this simple fluid, states that there is a function $w(p, v)$ (the internal energy per gram) and a vector \mathbf{q} (the heat flow) such that

$$(d/dt) \int \int \int_S \{ \frac{1}{2} m V^2 + m w \} d\tau \\ = - \int \int \int_S \mathbf{q} \cdot d\boldsymbol{\sigma} - \int \int \int_S (\rho \mathbf{V} - \mathbf{p} \cdot \nabla) \cdot d\boldsymbol{\sigma}. \quad (6)$$

The first integral on the right is the rate at which heat enters S and the other has already been identified. Subtracting Eq. (5) from Eq. (6) gives

$$\int \int \int_S \{ m(Dw/Dt) + \rho \nabla \cdot \mathbf{V} - (\mathbf{p} \cdot \nabla) \cdot \mathbf{V} \\ + \nabla \cdot \mathbf{q} \} d\tau = 0, \quad (7)$$

and since this must be true for all closed surfaces, it follows that the integrand itself must vanish.

Since w is a function of p and v only, and because of Eq. (2), the first two terms may be transformed:

$$m(Dw/Dt) + \rho \nabla \cdot \mathbf{V} \\ = m \{ [(\partial w/\partial v) + p](Dv/Dt) \\ + (\partial w/\partial p)(Dp/Dt) \}. \quad (8)$$

Now, there are always two functions θ and η such that

$$(\partial w/\partial v) + p = \theta(\partial \eta/\partial v), \quad (\partial w/\partial p) = \theta(\partial \eta/\partial p), \quad (9)$$

so that finally

$$m(Dw/Dt) + \rho \nabla \cdot \mathbf{V} = m\theta(D\eta/Dt),$$

whence

$$m\theta(D\eta/Dt) + \nabla \cdot \mathbf{q} = (\mathbf{p} \cdot \nabla) \cdot \mathbf{V}. \quad (10)$$

Before making use of this equation, it is worth while to consider this definition of θ and η , despite the fact that it is discussed in all standard texts on thermostatics. Differentiating the first

of Eq. (9) with respect to p and the second with respect to v , and subtracting gives:

$$(\partial \theta/\partial p)(\partial \eta/\partial v) - (\partial \theta/\partial v)(\partial \eta/\partial p) = 1.$$

Elimination of η by means of Eq. (9) results in

$$(\partial \log \theta/\partial p)[(\partial w/\partial v) + p] \\ - (\partial \log \theta/\partial v)(\partial w/\partial p) = 1, \quad (11)$$

which can be solved for $\log \theta$, since w is supposed known. If $\theta = \theta_0(p, v)$ is one solution of Eq. (11) and $\phi(p, v)$ is any solution of

$$(\partial \phi/\partial p)[(\partial w/\partial v) + p] - (\partial \phi/\partial v)(\partial w/\partial p) = 0, \quad (12)$$

then the most general solution of Eq. (11) is

$$\theta = \theta_0 f(\phi), \quad (13)$$

where f is arbitrary. To complete the definition of θ , this function must be determined in some way.

Thereafter, the function η is determined except for an additive constant. From Eq. (9)

$$\eta(p, v) = \eta(p_0, v_0) \\ + \int_{p_0, v_0}^{p, v} (1/\theta) \{ [(\partial w/\partial v) + p] dv + (\partial w/\partial p) dp \}$$

and Eq. (11) is the condition that the integral be independent of the path.

The definition of θ is completed on the basis of what may be called the Kelvin hypothesis:

The arbitrary function f may be chosen so that the heat flow \mathbf{q} is related to θ by Fourier's equation

$$\mathbf{q} = -k \nabla \theta, \quad (14)$$

where k is a function of p and v that does not change sign.

When f is so chosen, θ is unique except for sign and unit. For, let θ_0 also satisfy the equation

$$\mathbf{q} = -k_0 \nabla \theta_0$$

then it follows that

$$\theta = F(\theta_0)$$

or

$$f(\phi) = F(\theta_0)/\theta_0.$$

But, because of Eqs. (11) and (12), ϕ cannot be a proper function of θ_0 , so that both sides of the equality must be constants; hence

$$\theta = a\theta_0.$$

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

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

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

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

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 $\mathbf{p} = 0$ (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 \mathbf{p} are²

$$\begin{aligned} p_{xx} &= (2\lambda/3)[2(\partial V_x/\partial x) - (\partial V_y/\partial y) - (\partial V_z/\partial z)], \\ p_{xy} &= p_{yx} = \lambda[(\partial V_x/\partial y) + (\partial V_y/\partial x)], \text{ etc.}, \end{aligned}$$

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

$$\begin{aligned} (\mathbf{p} \cdot \nabla) \cdot \mathbf{V} &= (2\lambda/3) \{ [(\partial V_x/\partial x) - (\partial V_y/\partial y)]^2 + \dots \} \\ &\quad + \lambda \{ [(\partial V_x/\partial y) + (\partial V_y/\partial x)]^2 + \dots \} \geq 0. \end{aligned}$$

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

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

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

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

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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