PRINCIPLES OF CLASSICAL THERMODYNAMICS

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> 'Then how should I begin,
> To spit out all the butt-ends of my days and ways?
> And how should I presume?' T. S. Eliot

ABSTRACT

The paper outlines the current presentation of thermodynamic principles to the combined Part I Engineering students at the University of Hong Kong. By considering all bodies taking part in a process, the first and second laws of thermodynamics are presented without the use of work or heat—terms which cannot be generally defined without anticipating the second law. The experimental data necessary to know substances thermodynamically are their internal energy functions, their isotherm functions, and their equations of chemical equilibrium—all in terms of pressure p, specific volume v, and the degree of advancement of chemical processes ξ. Thermodynamic temperature functions, affinity functions and entropy functions may be derived from these data. The paper concludes with a discussion of interactions between bodies in terms of work and heat.

1. INTRODUCTION

Neglecting metaphysical matters, we adopt the view that scientific principles are economical descriptions of events and processes. A new phenomenon is considered to be explained when it has been shown to conform to accepted principles. Thermodynamics is best regarded as an extension of rigid body Newtonian Mechanics, to deal generally with deformable bodies and chemical processes. The methodology of thermodynamics is in terms of simply measurable quantities, through relationships between functions of such quantities to the prediction of future values of the simple quantities. It is convenient to call the simple quantities coordinates. External coordinates are best taken relative to the astronomical frame of reference and include spatial coordinates x, y, z, and velocity coordinates q_x, q_y, q_z, with resultant velocity q. Confining our attention to a simple fluid, internal coordinates are conveniently taken as pressure (p) (specific force), specific volume (v) and the degree of advancement of any chemical process ξ. In addition we need the mass of each chemical species m_1, m_2, etc. Internal and external coordinates are conveniently embraced in the term thermodynamical coordinates. To make useful predictions we must include changes in all bodies which influenced each other. An isolated system of bodies is one which does not respond to changes in the environment outside the isolating wall.

2. FIRST LAW

A class of functions of the thermodynamic coordinates are called energy functions. The kinetic energy function is defined by

$$\mathrm{Kin} = \int_0^m \tfrac{1}{2}q^2\,\mathrm{d}m \tag{2.1}$$

Any other functions which when added to the kinetic energy function give a valid relationship between the coordinates are also called energy functions. In a constant long range field of strength k parallel to the z axis, a potential energy function is appropriate. This is defined as

$$\mathrm{Pot} = \int_0^m kz\,\mathrm{d}m \tag{2.2}$$

A valid description of the motion of a rigid body α in such a force field is

$$[\mathrm{Pot} + \mathrm{Kin}]^\alpha = N^\alpha = \text{constant} \tag{2.3}$$

We note that Pot and Kin are relative to external axes, and their sum may be called the external energy N. An imagined body so isolated that only changes in its external coordinates occur is conveniently called a Newtonian body.

When deformable bodies have relative motion of their parts (other than isotropic rotations), or when deformable bodies interact, the numerical value of their external energy changes. Experiment shows, however, that a valid description of the variation of the thermodynamic coordinates of an isolated system of bodies is obtained by introducing a function U of the internal coordinates. U is called the internal energy function. The behaviour of two interacting bodies α, β in an isolating envelope can be described by

$$[U + N]^\alpha + [U + N]^\beta = E^\alpha + E^\beta = \text{constant} \tag{2.4}$$

where E is the total energy function. The first law states that changes in the thermodynamic coordinates of an isolated system of bodies can be described in terms of constancy of the sum of the energy functions of all parts of the system; or more succinctly, but less informatively, 'the energy of an isolated system of bodies remains constant'. The functional form of the internal energy must be found from experiments.

2.1. To find $(\delta u/\delta p)_{v\xi}$

Let the specific internal energy be u. Let unit mass of fluid be divided into two equal parts and let these be projected horizontally at each other with equal and opposite velocities q, while contained in isolating envelopes. Let v and ξ remain constant and let the pressure rise Δp after the disturbance has died away be measured. Applying equation 2.4

$$\left(\frac{\delta u}{\delta p}\right)_{v\xi} = \underset{\Delta p \to 0}{Lt}\ \frac{\frac{1}{2}q^2}{\Delta p} \tag{2.5}$$

2.2. To find $(\delta u/\delta v)_{p\xi}$

Let a small evacuated space Δv be annexed to the fluid and let the fluid be allowed to enter it. Let the pressure change Δp be measured when the disturbance has died away. Then the energy is unchanged and with $d\xi = 0$ equation 2.4 gives

$$0 = \left(\frac{\delta u}{\delta p}\right)_{v\xi} \Delta p + \left(\frac{\delta u}{\delta v}\right)_{p\xi} \Delta v \tag{2.6}$$

Proceeding to the limit

$$\left(\frac{\delta u}{\delta v}\right)_{p\xi} = -\left(\frac{\delta u}{\delta p}\right)_{v\xi}\left(\frac{\delta p}{\delta v}\right)_{u\xi} \tag{2.7}$$

Since $(\delta u/\delta p)_{v\xi}$ has already been found from equation 2.5 and $(\delta p/\delta v)_{u\xi}$ is obtained from experiment, equation 2.7 evaluates $(\delta u/\delta v)_{p\xi}$.

2.3. To find $(\delta u/\delta\xi)_{pv}$

Let a small quantity of the fluid be separated by a partition and let the chemical process be catalysed in this quantity. Let the partititon then be broken and thorough mixing permitted. Let Δp and $\Delta\xi$ be measured. Then with u and v constant

$$0 = \left(\frac{\delta u}{\delta p}\right)_{v\xi} \Delta p + \left(\frac{\delta u}{\delta \xi}\right)_{pv} \Delta \xi \tag{2.8}$$

Thus

$$\left(\frac{\delta u}{\delta \xi}\right)_{pv} = -\left(\frac{\delta u}{\delta p}\right)_{v\xi}\left(\frac{\delta p}{\delta \xi}\right)_{uv} \tag{2.9}$$

2.4. The internal energy function

Having obtained the derivatives experimentally we have

$$du = \left(\frac{\delta u}{\delta p}\right)_{v\xi} dp + \left(\frac{\delta u}{\delta v}\right)_{p\xi} dv + \left(\frac{\delta u}{\delta \xi}\right)_{pv} d\xi \tag{2.10}$$

By repeating the experimental process a table of $u - u_0$ in terms of p, v, ξ may be enumerated or if simple, the function $u(pv\xi)$ may be found. For gases of low density experiment shows that

$$U = m[pv(a\xi + b) + u_0(1 + c\xi)] \tag{2.11}$$

where m is a measure of quantity; v is the volume per mole and a, b and c are constants for given atomic content, and over a useful range of the variables. If ξ is constant

$$U = m\frac{pv}{\gamma - 1} + u_0 = \frac{pV}{\gamma - 1} + U_0 \tag{2.12}$$

where γ is a constant.

3. THE SECOND LAW

We may imagine many impossible processes which would satisfy the energy accounting system of the first law. The admissibility or otherwise of processes may be expressed as an inequality. A burning match does not reconstitute itself, so that the process may be described as $d\xi \geqslant 0$. If otherwise in equilibrium with a constant environment, the air pressure in an inflated motor car tyre never rises so that $dp \leqslant 0$. A blackboard duster freely sliding on a horizontal table does not draw from its internal energy and increase in speed, so that $dq \leqslant 0$, or $du \geqslant 0$. The second law states that not all imagined processes actually happen and that not all imagined future states are realizable even though they would satisfy the energy accounting system of the first law.

Following Guggenheim[1], let us suppose that for any system of interacting bodies α, β etc. there is a possibility function S of the thermodynamic coordinates such that for an isolated system

$$\frac{dS}{dt} = \frac{dS^{\alpha}}{dt} + \frac{dS^{\beta}}{dt} \geqslant 0 \tag{3.1}$$

Here t is time, and it is in the second law that later and sooner enter scientific principles. Unfortunately Clausius gave S the confusing name of entropy. S would be much better called the Clausius function. Our proposition is illustrated in *Figure 1*.

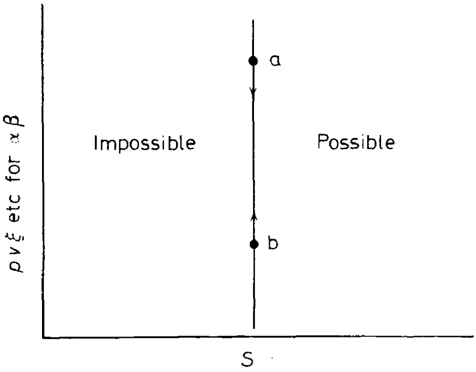

Figure 1. Possible future states of an isolated system.

Possible future states lie to the right of the line S = constant. Considering states on the line itself, any state (a) can be reached from any state (b) and vice versa. The line $dS = 0$ therefore represents reversible processes. Experience suggests that interchange in forms of external energy is unrestricted. We therefore guess that S is a function of internal coordinates only. Our statement of the second law then becomes 'changes in the internal coordinates of an isolated system of bodies are such that the sum of the entropy functions of all bodies is stationary or increases'.

As the entropy approaches a maximum, a time invariant state is reached, which is called equilibrium. We proceed to discover the entropy function, by considering a fairly general system approaching equilibrium.

Consider a fluid (α), filling a constant volume isolating cylindrical vessel, mounted on a frictionless axial vertical pivot, and in a gravitational field of strength k. Initially, let $q\ p\ v\ \xi$ all be irregular. Then changes occurring are such that the entropy of α increases to a maximum, subject to its energy, its angular momentum about the pivot, and its mass remaining constant. Taking the z axis as vertical, and using cylindrical coordinates $r\ \theta\ z$, the author[2] has shown that the equilibrium state is described by maximizing

$$I = \int_0^V J\,\mathrm{d}V = \int_0^V [s + \lambda\{u + \tfrac{1}{2}(q_\theta^2 + q_r^2 + q_z^2) + kz\} + \mu q_\theta r + \nu]\frac{\mathrm{d}V}{v} \tag{3.2}$$

where λ, μ and ν are Lagrangian multipliers, and the lower case letters are specific quantities. A stationary value entails equating to zero the partial differentials of J with respect to the independent variables conveniently chosen as $qs\xi$ and v. Differentiating with respect to the velocities yields

$$q_r = q_z = 0; \qquad \frac{q_\theta}{r} = -\frac{\mu}{\lambda} = \omega \tag{3.3}$$

where ω is angular velocity. We therefore see that the final state is a rigid body rotation. Differentiation with respect to internal coordinates yields:

$$\frac{\delta J}{\delta s} = \frac{1}{v}\left[1 + \lambda\left(\frac{\delta u}{\delta s}\right)_{v\xi}\right] = 0; \qquad \left(\frac{\delta u}{\delta s}\right)_{v\xi} = -\frac{1}{\lambda} \tag{3.4}$$

$$\frac{\delta J}{\delta \xi} = \frac{\lambda}{v}\left(\frac{\delta u}{\delta \xi}\right)_{vs} = 0; \qquad \left(\frac{\delta u}{\delta \xi}\right)_{vs} = 0 \tag{3.5}$$

$$\frac{\delta J}{\delta v} = -\frac{J}{v} + \frac{\lambda}{v}\left(\frac{\delta u}{\delta v}\right)_{s\xi} = 0 \tag{3.6}$$

These three relationships define three components of equilibrium. Equation 3.4 defines thermal equilibrium, and it is convenient to give $(\delta u/\delta s)_{v\xi}$ the symbol T, and to call T the thermodynamic temperature function. We see that at equilibrium the temperature is uniform. Equation 3.5 defines chemical equilibrium. It is convenient to give $-(\delta u/\delta\xi)_{vs}$ the symbol a and $-m(\delta u/\delta\xi)_{vs}$ the symbol A and to call A the affinity function. Chemical equilibrium is described by $A = 0$.

Equation 3.6 which includes ω^2 may be identified as describing dynamic equilibrium. Applying Newtonian mechanics to this steady state forced vortex we obtain

$$\left(\frac{\delta p}{\delta z}\right)_r = -\frac{k}{v}; \qquad v\left(\frac{\delta p}{\delta r}\right)_z = \omega^2 r \tag{3.7}$$

Comparing 3.7 with 3.6, it may be shown that identity is obtained for $(\delta u/\delta v)_{s\xi} = -p + p_0$. The constant p_0 arises as only pressure differences occur in dynamics. Putting $p_0 = 0$ defines absolute pressure.

From these identifications the generating function for S with constant quantity of matter is

$$T\,\mathrm{d}S = m[\mathrm{d}u + p\,\mathrm{d}v + a\,\mathrm{d}\xi] = \mathrm{d}U + p\,\mathrm{d}V + A\,\mathrm{d}\xi \tag{3.8}$$

and to generate the function S it remains to discover A and T as functions of the coordinates. We do this by considering cases of partial equilibrium. For many substances, chemical equilibrium may be indefinitely delayed, and experimental sets of values of $pv\xi$ for which thermal and mechanical, but not chemical, equilibrium exist, may be described by $\theta(pv\xi) = \text{constant}$. Then $T(pv\xi)$ is a function of θ and can be found from an expression due to Planck[3].

$$\ln \frac{T}{T_0} = \int_{\theta_0}^{\theta} \frac{(\delta p/\delta\theta)_{v\xi}\, \mathrm{d}\theta}{(\delta u/\delta v)_{\theta\xi} + p} \tag{3.9}$$

For perfect gases not undergoing chemical processes, the isotherm function is found to be $\theta = pv = \text{constant}$. From 2.12 and 3.9 we easily find:

$$T = \frac{pv}{r}; \qquad S = \frac{mr}{\gamma - 1} \ln pv^{\gamma} + S_0 \tag{3.10}$$

where r is chosen so that the triple point of water–ice–vapour is allotted the temperature $T = 273{\cdot}16°$. Considering a non-ideal gas defined by 2.12 and $\theta = pv^{\beta}$, equations 3.8 and 3.9 yield:

$$T = B(pv^{\beta})^{\gamma - 1/\gamma - \beta}; \qquad s = \frac{\gamma - \beta}{B(\gamma - 1)(1 - \beta)}(pv^{\gamma})^{1 - \beta/\gamma - \beta} + S_0 \tag{3.11}$$

where B is a constant chosen as for r above.

By encapsulating different parts of the rotating fluid in light, flexible, thermally insulating walls, we may inhibit thermal equilibrium. Sets of experimental values of $pv\xi$ for which chemical and mechanical but not thermal equilibrium is attained may be described by a function $\alpha(pv\xi) = 0$. Then A must be chosen so that $\mathrm{d}S$ is an exact differential, and subject to $A = 0$ when $\alpha = 0$. These conditions are (J = Jacobian):

$$\frac{\delta}{\delta\alpha}\left(\frac{A}{T}\right) = \frac{1}{T^2} J\left(\frac{TU}{\alpha\xi}\right); \quad \frac{\delta}{\delta V}\left(\frac{A}{T}\right) = \frac{1}{T^2} J\left(\frac{TU}{V\xi}\right) + \frac{\delta}{\delta\xi}\left(\frac{p}{T}\right);$$

$$\frac{\delta}{\delta\alpha}\left(\frac{p}{T}\right) = \frac{1}{T^2} J\left(\frac{TU}{\alpha V}\right) \tag{3.12}$$

While generation of A from α is conceptually important, at present the entropy function with ξ as variable is not found. In current practice values of S at constant ξ are found by integration from $T = 0$. This process is made viable by the third law which states that $(\delta s/\delta\xi)_{TP} \approx 0\ (T \to 0)$. At standard pressure we may consider the entropy of all perfectly crystalline substances to approach zero as $T \to 0$. When matter is introduced from outside a body the function 3.8 does not apply, but it may rigorously be extended to show that variation in total quantity of each chemical element is accommodated by the relationship due to Gibbs

$$T\,\mathrm{d}S = \mathrm{d}U + p\,\mathrm{d}V - \sum_{1}^{n} \mu\, \mathrm{d}m \tag{3.13}$$

where μ is chemical potential and $m_1 m_2$ are quantities of each chemical substance.

So far we have only considered deductions from a statement of the stationary value of I. For a maximum in many variables see Apostol[4]. Important deductions from maximizing I are:

$$T > 0; \quad T\left(\frac{\delta S}{\delta T}\right)_{p\xi} > T\left(\frac{\delta S}{\delta T}\right)_{v\xi} > 0; \quad \left(\frac{\delta a}{\delta \xi}\right)_{vs} < 0; \quad \left(\frac{\delta p}{\delta v}\right)_{s\xi} < \left(\frac{\delta p}{\delta v}\right)_{T\xi} < 0 \tag{3.14}$$

If we have a body isolated from interaction with other than Newtonian bodies, we see from 3.1 and the first and second sets of 3.14, that only equal or higher temperatures are possible in the future, under conditions of $p\xi$ constant and $v\xi$ constant.

4. INTERACTIONS BETWEEN PARTS OF A SYSTEM

It is useful to partition interactions into work and heat, and the distinction between these quantities is the province of the second law. A heat interaction necessarily changes the entropy of a body, and thus affects the limits of its future states when subsequently isolated from other than Newtonian bodies. A work interaction may or may not generate entropy, depending on whether or not the processes occurring in the body as a result of the work interaction are reversible or not.

We may define the heat component (Q) of an interaction with an opaque body (α) of constant number of atoms and having surface temperature T^σ as

$$\mathrm{d}Q = [T^\sigma(\mathrm{d}S - \mathrm{d}S^+)]^\alpha$$

where $\mathrm{d}S^{+\alpha} \geqslant 0$. $\mathrm{d}S^{+\alpha}$ is all the entropy increment additional to that due to the heat interaction at the surface. Among factors which contribute to $\mathrm{d}S^{+\alpha}$ are surface frictional effects, temperature gradients within the body, viscous effects, plastic deformation of solids, irreversible chemical processes and diffusion of chemical substances.

The work component of the interaction may then be defined as the difference between the energy change and the heat component. For mechanical work, it may be shown that the above definition can be reduced to the scalar product of a vector force and its vector displacement.

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