NOTE ON THERMODYNAMIC SURFACES

BY J. E. TREVOR

Conditions of stability

In his investigation of the energy surface for a one-component system,¹ Gibbs has given an ingenious and convincing demonstration of the theorem that, when p, θ are the pressure and absolute temperature of a thermodynamic system in a state of dissipated energy determined by the volume v and the entropy η , and $v + \delta v, \eta + \delta \eta$ is another state, not a state of dissipated energy at p, θ , it is true that

$$\delta e + p\delta v - \theta\delta\eta > 0.$$

Otherwise stated, in all variations of state imagined as occurring from a state of stable equilibrium at p, θ to a state not in stable equilibrium at p, θ ,

$$\delta e > -p\delta v + \theta\delta\eta.$$

It is possible, however, to have a succession of univariant states or of invariant states that are all states of stable equilibrium at p, θ . In such a case, no one state of the succession will spontaneously pass into another, the equilibrium of each state will be 'neutral'. If the change through the succession of stable states be reversibly effected, Gibbs's demonstration yields

$$\delta e = -p\delta v + \theta\delta\eta.$$

For a state to be one of stable equilibrium at the pressure and temperature p, θ , it is therefore necessary that, in all variations of the state,

$$\delta e \geq -p\delta v + \theta\delta\eta.$$

On passing from any point v, η on the energy surface

$$e = e(v, \eta)$$

for one-phase states, or for states of two given phases, or of three given phases, to an adjacent point $v + \delta v, \eta + \delta \eta$ on the surface,

¹ Trans. Conn. Acad. 2, 382 (1873).

$$\delta e = \frac{\partial e}{\partial v} \delta v + \frac{\partial e}{\partial \eta} \delta \eta + \frac{1}{2} \left(\frac{\partial^2 e}{\partial v^2} (\delta v)^2 + 2 \frac{\partial^2 e}{\partial v \partial \eta} \delta v \delta \eta + \frac{\partial^2 e}{\partial \eta^2} (\delta \eta)^2 \right) + \dots;$$

whence, because of the above criterion of stability, which may be written

$$\delta e \geq \frac{\partial e}{\partial v} \delta v + \frac{\partial e}{\partial \eta} \delta \eta,$$

it appears that the condition that the point v, η , shall represent a state of equilibrium is

$$\frac{\partial^2 e}{\partial v^2} (\delta v)^2 + 2 \frac{\partial^2 e}{\partial v \partial \eta} \delta v \delta \eta + \frac{\partial^2 e}{\partial \eta^2} (\delta \eta)^2 \geq 0$$

for all values of v, η . This condition expresses that no portion of the surface may lie below the tangent plane passing through the point v, η . It expresses, in particular, that a succession of states in neutral equilibrium is represented by the points on a line common to the surface and the plane tangent thereto at the point v, η ; and that, at a point representing a state of stable equilibrium that is not also a state of neutral equilibrium, the surface is convex downward in all directions. All portions of the surface that do not satisfy these conditions must represent thermodynamically instable states.

When

$$e = e(v, \eta)$$

is the equation of the continuous succession of stable and instable one-phase states, a point representing a state of stable equilibrium must satisfy the condition

$$\frac{\partial^2 e}{\partial v^2} (\delta v)^2 + 2 \frac{\partial^2 e}{\partial v \partial \eta} \delta v \delta \eta + \frac{\partial^2 e}{\partial \eta^2} (\delta \eta)^2 > 0.$$

The necessary and sufficient conditions for this quadratic expression to be positive, i. e., for the surface to be convex downward in every direction at v, η , are

$$H(e) > 0, \quad \partial^2 e / \partial v^2 > 0,$$

where $H(e)$ denotes the hessian of the function $e(v, \eta)$. A con-

sequence of these 'conditions of stability' is the further inequality

$$\frac{\partial^2 e}{\partial \eta^2} > 0.$$

A problem

It was further pointed out by Gibbs that the thermodynamic properties represented by the surface

$$e = e(v, \eta)$$

are represented by the surfaces

$$f = f(v, \theta)$$

$$g = g(p, \eta)$$

$$h = h(p, \theta);$$

the functions f, g, h being defined by the equations

$$f(v, \theta) = e - \theta \eta$$

$$g(p, \eta) = e + p v$$

$$h(p, \theta) = e + p v - \theta \eta;$$

wherefore we have the set of differential equations

$$de = -p dv + \theta d\eta$$

$$df = -p dv - \eta d\theta$$

$$dg = v dp + \theta d\eta$$

$$dh = v dp - \eta d\theta.$$

We may now seek to determine the curvatures of those portions of the f, g, h surfaces that represent one-phase stable states, i. e., that correspond to the convex portions of the primitive energy surface.

Auxiliary equations

In this search we shall require to use a series of equations, which shall now be assembled for reference. We have

$$-dp = \frac{\partial^2 e}{\partial v^2} dv + \frac{\partial^2 e}{\partial v \partial \eta} d\eta$$

$$d\theta = \frac{\partial^2 e}{\partial v \partial \eta} dv + \frac{\partial^2 e}{\partial \eta^2} d\eta;$$

whence, by successive elimination of $d\eta$ and dv ,

$$H(e) \cdot dv = \begin{vmatrix} -dp & \frac{\partial^2 e}{\partial v \partial \eta} \\ d\theta & \frac{\partial^2 e}{\partial \eta^2} \end{vmatrix}, \quad H(e) \cdot d\eta = \begin{vmatrix} \frac{\partial^2 e}{\partial v^2} & -dp \\ \frac{\partial^2 e}{\partial v \partial \eta} & d\theta \end{vmatrix};$$

whence follow the desired equations,

$$(a) \quad \left(\frac{\partial v}{\partial p} \right)_\theta = \frac{-1}{H(e)} \frac{\partial^2 e}{\partial \eta^2} \quad \left| \quad \left(\frac{\partial \eta}{\partial \theta} \right)_p = \frac{1}{H(e)} \frac{\partial^2 e}{\partial v^2} \quad (c)$$

$$(b) \quad \left(\frac{\partial v}{\partial \theta} \right)_p = \frac{-1}{H(e)} \frac{\partial^2 e}{\partial v \partial \eta} \quad \left| \quad \left(\frac{\partial \eta}{\partial p} \right)_\theta = \frac{1}{H(e)} \frac{\partial^2 e}{\partial v \partial \eta} \quad (d)$$

and from these, by division,

$$(e) \quad \left(\frac{\partial v}{\partial \eta} \right)_\theta = - \frac{\partial^2 e}{\partial \eta^2} : \frac{\partial^2 e}{\partial v \partial \eta} \quad \left| \quad \left(\frac{\partial \eta}{\partial v} \right)_p = - \frac{\partial^2 e}{\partial v^2} : \frac{\partial^2 e}{\partial v \partial \eta} \quad (f)$$

The second derivatives

We now require to determine the signs of the second derivatives, and of the hessian, of each of the functions f, g, h at points representing stable one-phase states.

For $\partial^2 f / \partial v^2$, we have

$$\begin{aligned} \frac{\partial f}{\partial v} &= -p \\ \frac{\partial^2 f}{\partial v^2} &= - \left(\frac{\partial p}{\partial v} \right)_\theta \\ &= H(e) : \frac{\partial^2 e}{\partial \eta^2} \\ &> 0, \end{aligned}$$

by equation (a).

For $\partial^2 f / \partial \theta^2$, we have

$$\begin{aligned} \frac{\partial f}{\partial \theta} &= -\eta \\ \frac{\partial^2 f}{\partial \theta^2} &= - \left(\frac{\partial \eta}{\partial \theta} \right)_v \\ &= -1 : \left(\frac{\partial \theta}{\partial \eta} \right)_v \\ &= -1 : \frac{\partial^2 e}{\partial \eta^2} \\ &< 0. \end{aligned}$$

For $H(f)$, we have

$$\begin{aligned}\frac{\partial^2 f}{\partial v \partial \theta} &= - \left(\frac{\partial p}{\partial \theta} \right)_v \\ &= - \left(\frac{\partial p}{\partial \eta} \right)_v : \left(\frac{\partial \theta}{\partial \eta} \right)_v \\ &= \frac{\partial^2 e}{\partial v \partial \eta} : \frac{\partial^2 e}{\partial \eta^2}.\end{aligned}$$

Hence we find

$$\begin{aligned}H(f) &= \frac{\partial^2 f}{\partial v^2} \frac{\partial^2 f}{\partial \theta^2} - \left(\frac{\partial^2 f}{\partial v \partial \theta} \right)^2 \\ &= \frac{\frac{\partial^2 e}{\partial v^2} \frac{\partial^2 e}{\partial \eta^2} - \left(\frac{\partial^2 e}{\partial v \partial \eta} \right)^2}{\frac{\partial^2 e}{\partial \eta^2}} \cdot \frac{-1}{\frac{\partial^2 e}{\partial \eta^2}} - \frac{\left(\frac{\partial^2 e}{\partial v \partial \eta} \right)^2}{\left(\frac{\partial^2 e}{\partial \eta^2} \right)^2} \\ &= - \frac{\partial^2 e}{\partial v^2} : \frac{\partial^2 e}{\partial \eta^2} \\ &< 0.\end{aligned}$$

For $\partial^2 g / \partial p^2$, we have

$$\begin{aligned}\frac{\partial g}{\partial p} &= v \\ \frac{\partial^2 g}{\partial p^2} &= \left(\frac{\partial v}{\partial p} \right)_\eta \\ &= 1 : \left(\frac{\partial p}{\partial v} \right)_\eta \\ &= -1 : \frac{\partial^2 e}{\partial v^2} \\ &< 0.\end{aligned}$$

For $\partial^2 g / \partial \eta^2$, we have

$$\begin{aligned}\frac{\partial g}{\partial \eta} &= \theta \\ \frac{\partial^2 g}{\partial \eta^2} &= \left(\frac{\partial \theta}{\partial \eta} \right)_p \\ &= (H)e : \frac{\partial^2 e}{\partial v^2} \\ &> 0,\end{aligned}$$

by equation (c).

For $H(g)$, we have

$$\begin{aligned}\frac{\partial^2 g}{\partial \rho \partial \eta} &= \left(\frac{\partial v}{\partial \eta} \right)_\rho \\ &= - \frac{\partial^2 e}{\partial v \partial \eta} : \frac{\partial^2 e}{\partial v^2},\end{aligned}$$

by equation (f). Hence we have

$$\begin{aligned}H(g) &= \frac{\partial^2 g}{\partial \rho^2} \frac{\partial^2 g}{\partial \eta^2} - \left(\frac{\partial^2 g}{\partial \rho \partial \eta} \right)^2 \\ &= - \frac{1}{\frac{\partial^2 e}{\partial v^2}} \cdot \frac{\frac{\partial^2 e}{\partial v^2} \frac{\partial^2 e}{\partial \eta^2} - \left(\frac{\partial^2 e}{\partial v \partial \eta} \right)^2}{\frac{\partial^2 e}{\partial v^2}} - \frac{\left(\frac{\partial^2 e}{\partial v \partial \eta} \right)^2}{\left(\frac{\partial^2 e}{\partial v^2} \right)^2} \\ &= - \frac{\partial^2 e}{\partial \eta^2} : \frac{\partial^2 e}{\partial v^2} \\ &< 0.\end{aligned}$$

For $\partial^2 h / \partial \rho^2$, we have

$$\begin{aligned}\frac{\partial h}{\partial \rho} &= v \\ \frac{\partial^2 h}{\partial \rho^2} &= \left(\frac{\partial v}{\partial \rho} \right)_\theta \\ &= \frac{-1}{H(e)} \frac{\partial^2 e}{\partial \eta^2} \\ &< 0,\end{aligned}$$

by equation (a).

For $\partial^2 h / \partial \theta^2$, we have

$$\begin{aligned}\frac{\partial h}{\partial \theta} &= -\eta \\ \frac{\partial^2 h}{\partial \theta^2} &= - \left(\frac{\partial \eta}{\partial \theta} \right)_\rho \\ &= \frac{-1}{H(e)} \frac{\partial^2 e}{\partial v^2} \\ &< 0,\end{aligned}$$

by equation (c).

For $H(h)$, we have

$$\begin{aligned}\frac{\partial^2 h}{\partial p \partial \theta} &= \left(\frac{\partial v}{\partial \theta} \right)_p \\ &= -\frac{1}{H(e)} \frac{\partial^2 e}{\partial v \partial \eta},\end{aligned}$$

by equation (b). Hence we find

$$\begin{aligned}H(h) &= \frac{\partial^2 h}{\partial p^2} \frac{\partial^2 h}{\partial \theta^2} - \left(\frac{\partial^2 h}{\partial p \partial \theta} \right)^2 \\ &= \frac{-\frac{\partial^2 e}{\partial \eta^2}}{H(e)} \cdot \frac{-\frac{\partial^2 e}{\partial v^2}}{H(e)} - \frac{\left(\frac{\partial^2 e}{\partial v \partial \eta} \right)^2}{H^2(e)} \\ &= 1 : H(e) \\ &> 0.\end{aligned}$$

These results are assembled in the following table :

$H(e) > 0$	$\frac{\partial^2 e}{\partial v^2} > 0$	$\frac{\partial^2 e}{\partial \eta^2} > 0$
$H(f) < 0$	$\frac{\partial^2 f}{\partial v^2} > 0$	$\frac{\partial^2 f}{\partial \theta^2} < 0$
$H(g) < 0$	$\frac{\partial^2 g}{\partial p^2} < 0$	$\frac{\partial^2 g}{\partial \eta^2} > 0$
$H(h) > 0$	$\frac{\partial^2 h}{\partial p^2} < 0$	$\frac{\partial^2 h}{\partial \theta^2} < 0$

The curvatures

From these data it appears that the portions of the e, f, g, h -surfaces that represent stable one-phase states are convex in the case of the e -surface, concave in the case of the h -surface, and saddle-shaped in the other two cases. In particular, the f -surface is convex at v, θ in the section parallel to v , and concave in the section parallel to θ ; and the g -surface is convex at p, η in the section parallel to η , and concave in the section parallel to p .

It may be added that, whenever the primitive e -surface becomes concave at v, η , every curvature stated above will be changed into its opposite; and that, whenever the e -surface be-

comes convex in one coordinate section and concave in the other, the h -surface will be so also, while the f -surface and the g -surface will become dome-shaped. For when the hessian of a surface $z = z(x, y)$ is positive the surface is dome-shaped, and is convex or concave according as

$$\frac{\partial^2 z}{\partial x^2} \quad \text{and} \quad \frac{\partial^2 z}{\partial y^2}$$

are both positive or both negative. When the hessian is positive these derivatives must have the same sign.

Reciprocal character of the surfaces

It may be noted in the above that the Hessians of the e and h surfaces, and of the f and g surfaces, are the reciprocals of each other; that

$$H(e) \cdot H(h) = 1$$

$$H(f) \cdot H(g) = 1.$$

This is one aspect of the reciprocal relation between the e and h and the f and g surfaces, which appears most clearly when it is noted that the ordinate of a point in either surface of either pair appears in the other surface as the segment

$$z - \frac{\partial z}{\partial x} x - \frac{\partial z}{\partial y} y,$$

intercepted on the vertical axis by the tangent plane at the point; and that the horizontal coordinates of the one surface are the slopes of the other¹ (the changes of sign being due to taking $+p$ instead of $-p$ as a coordinate in two cases). This is exhibited in the tabulation:

Ordinate	Intercept	Coordinates	Slopes
e	h	v, η	$-p, \theta$
h	e	p, θ	$v, -\eta$
f	g	v, θ	$-p, -\eta$
g	f	p, η	v, θ

¹ With respect to the e and h surfaces, this has been pointed out by Gibbs.

This reciprocity appears again in the relation

$$e + h = f + g,$$

which follows from the definition equations

$$e = e$$

$$f = e - \theta\eta$$

$$h = e + pv - \theta\eta.$$

$$g = e + pv.$$

Cornell University.