

THEORY OF HEAT

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WITH CORRECTIONS AND ADDITIONS (1891).

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REPRESENTATION OF THE PROPERTIES OF A SUBSTANCE BY
MEANS OF A SURFACE.

Professor J. Willard Gibbs, of Yale College, U.S., to whom we are indebted for a careful examination of the different methods of representing thermodynamic relations by plane diagrams, has introduced an exceedingly valuable method of studying the properties of a substance by means of a surface.¹

According to this method, the volume, entropy, and energy of the body in a given state are represented by the three rectangular coordinates of a point in the surface, and this point on the surface is said to correspond to the given state of the body. We shall suppose the volume measured towards the east from the meridian plane corresponding to no volume, the entropy measured towards the north from a vertical plane perpendicular to the meridian, whose position is entirely arbitrary, and the energy measured downwards from the horizontal plane of no energy, the position of which may be considered as arbitrary, because we cannot measure the whole energy existing in a body.

¹ *Transactions of the Academy of Sciences of Connecticut*, vol. ii.

The section of this surface by a vertical plane perpendicular to the meridian represents the relation between volume and energy when the entropy is constant, that is, when no **heat** enters or leaves the body.

If the pressure is positive, then the body, by expanding, would do work against external resistance, and its intrinsic energy would diminish. The rate at which the energy diminishes as the volume increases is represented by the tangent of the angle which the curve of section makes with the horizon.

The pressure is therefore represented by the tangent of the angle of slope of the curve of section. The pressure is positive when the curve slopes downwards towards the west. When the slope of the curve is towards the east the corresponding pressure is negative.

A tension or negative pressure cannot exist in a gas. It may, however, exist in a liquid, such as mercury. Thus, if a barometer tube is well filled with clean mercury, and then placed in a vertical position, with its closed end uppermost, the mercury sometimes does not fall in the tube to the point corresponding to the atmospheric pressure, but remains suspended in the tube, so as to fill it completely.

The pressure in this case is negative in that part of the mercury which is above the level of the ordinary barometric column.

In solid bodies, as we know, tensions of considerable magnitude may exist.

Hence in our thermodynamic model the pressure of the substance is indicated by the tangent of the slope of the curve of constant entropy, and is reckoned positive when the energy diminishes as the volume increases.

The section of the surface by a vertical plane parallel to the meridian is a curve of constant volume. In this curve the temperature is represented by the rate at which the

energy increases as the entropy increases, that is to say, by the tangent of the slope of the curve.

Since the temperature, reckoned from absolute zero, is an essentially positive quantity, the curve of constant volume must be such that the entropy and energy always increase together.

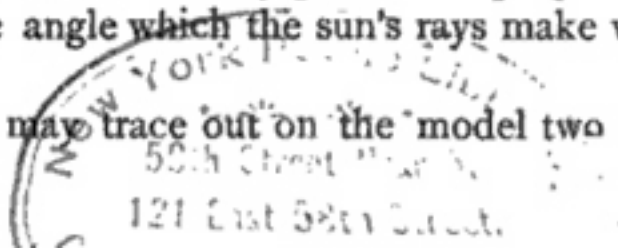
To ascertain the pressure and temperature of the substance in a given state, we may draw a tangent plane to the corresponding point of the surface. The normal to this plane through the origin will cut a horizontal plane at unit of distance above the origin at a point whose coordinates represent the pressure and temperature, the pressure being represented by the coordinate drawn towards the west, and the temperature by the coordinate drawn towards the north.

The pressure and temperature are thus represented by the direction of this normal, and if, at any two points of the surface, the directions of the normals are parallel, then in the two states of the substance corresponding to these two points the pressure and temperature must be the same.

If we wish to trace out on a model of the surface a series of lines of equal pressure, we have only to place it in the sunshine and to turn it so that the sun's rays are parallel to the plane of volume and energy, and make an angle with the line of volume whose tangent is proportional to the pressure. Then, if we trace on the surface the boundary of light and shadow, the pressure at all points of this line will be the same.

In like manner, if we place the model so that the sun's rays are parallel to the plane of entropy and energy, the boundary of light and shadow will be a line such that the temperature is the same at every point, and proportional to the tangent of the angle which the sun's rays make with the line of entropy.

In this way we may trace out on the model two series of



lines: lines of equal pressure, which Professor Gibbs calls Isopiestic; and lines of equal temperature, or Isothermals.

Besides these, we may trace the three systems of plane sections parallel to the coordinate planes, the isometrics or lines of equal volume, the isentropics or lines of equal entropy, which we formerly called, after Rankine, adiabatics, and the isenergics or lines of equal energy.

The network formed by these five systems of lines will form a complete representation of the relations between the five quantities, volume, entropy, energy, pressure, and temperature, for all states of the body.

The body itself need not be homogeneous either in chemical nature or in physical state. All that is necessary is that the whole should be at the same pressure and the same temperature.

By means of this model Professor Gibbs has solved several important problems relating to the thermodynamic relations between two portions of a substance, in different physical states, but at the same pressure and temperature.

Let a substance be capable of existing in two different states, say liquid and gaseous, at the same temperature and pressure. We wish to determine whether the substance will tend of itself to pass from one of these states to the other.

Let the substance be placed in a cylinder, under a piston, and surrounded by a medium at the given temperature and pressure, the extent of this medium being so great that its pressure and temperature are not sensibly altered by the changes of volume of the working substance, or by the **heat** which that body gives out or takes in.

The two physical states which are to be compared are represented by two points on the surface of the model; and since the pressure and temperature are the same, the tangent planes at these points are either coincident or parallel.

The surface representing the thermodynamic properties of the surrounding medium must be supposed to be constructed

on a scale proportional to the amount of this medium ; and as we assume that there is a very great mass of this medium, the scale of the surface will be so great that we may regard the portion of the surface with which we have to do as sensibly plane ; and since its pressure and temperature are those of the working substance in the given state, this plane surface is parallel to the tangent plane at the given point of the surface of the model.

Let $A B C$ be three points of the model at which the tangent planes are parallel, the energy being reckoned downwards.

Let $A a a$ be the tangent plane at A , and let us consider it as part of the model representing the external medium, this model being so placed that volume, entropy, and energy are reckoned in the opposite directions from those in the model of the working substance.

Now let us suppose the substance to pass from the state A to the state B , passing through the series of states represented by the points on the isothermal line joining the points of equal temperature A and B .

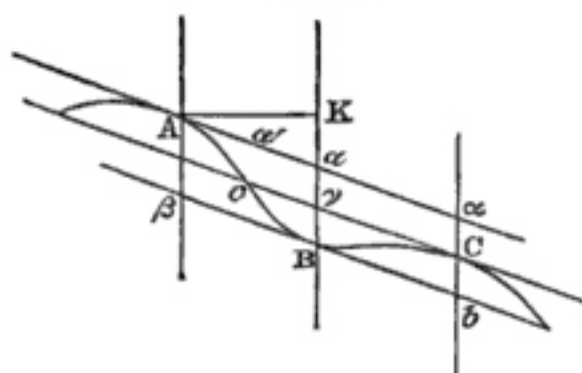
Then since the working substance and the external medium are always at the same temperature, the entropy lost by the one is equal to that gained by the other.

Also the one gains in volume what is lost by the other.

Hence, during the passage of the working substance from the state A to the state B , the state of the external medium is always represented by a point in the tangent plane in the same vertical line as the point representing the state of the working substance.

For the same horizontal motion which represents a gain of

FIG. 26b.



volume or entropy of the one substance represents an equal loss of volume or entropy in the other.

Hence, when the state of the working substance is represented by the point B , that of the external medium will be represented by the point a , where the vertical line through B meets the tangent plane through A .

Now the energy is reckoned downwards for the working substance and upwards for the external medium. Hence, drawing $A\kappa$ horizontal, κB represents the gain in energy of the working substance, and κa the loss of energy of the external medium.

The line Ba , or the vertical height of the tangent plane above the point B , represents the gain of energy in the whole system, consisting of the working substance and the external medium, during the passage from the state A to the state B . But the energy of the system can be increased only by doing work on it.

But if the system can of itself pass from one state to another, the work required to produce the corresponding changes of configuration must be drawn from the energy of the system, and the energy must therefore diminish.

The fact, therefore, that in the case before us the energy increases, shows that the passage from the state A to the state B in presence of a medium of constant temperature and pressure, cannot be effected without the expenditure of work by some external agent.

The working substance, therefore, cannot of itself pass from the state A to the state B , if B lies *below* the plane which touches the surface at A .

We have supposed the substance to pass from A to B by a process during which it is always at the same temperature as the external medium. In this case the entropy of the system remains constant.

If, however, the communication of **heat** between the substances occurs when they are not at the same temperature,

the entropy of the system will increase; and if in the figure the gain of entropy of the working substance is represented by the horizontal component of AB , the loss of entropy of the external medium will be represented by a smaller quantity, such as the horizontal component of Aa' . Hence a' will be to the left of a , and therefore higher. The gain of entropy of the system will therefore be represented by the horizontal part of aa' .

Now since temperature is essentially positive, a gain of entropy at a given volume always implies a gain of energy. Hence the gain of energy is greater when there is a gain of entropy than when the entropy remains constant.

There is, therefore, no method by which the change from A to B can be effected without a gain of energy, and this implies the expenditure of work by an external agent.

If, therefore, the tangent plane at A is everywhere above the thermodynamic surface, the condition of the working substance represented by the point A is essentially stable, and the substance cannot of itself pass into any other state while exposed to the same external influences of pressure and temperature.

This will be the case if the surface is convexo-convex upwards.

If, on the other hand, the surface, as at the point B , is either concave upwards in all directions, or concave in one direction and convex in another, it will be possible to draw on the surface a line from the point of contact lying entirely above the tangent plane, and therefore representing a series of states through which the substance can pass of itself.

In this case the point of contact represents a state of the substance which, if physically possible for an instant, is essentially unstable, and cannot be permanent.

There is a third case, however, in which the surface, as at the point C , is convexo-convex, so that a line drawn on

the surface from the point of contact must lie below the tangent plane ; but the tangent plane, if produced far enough, cuts the surface at c, so that the point A lies above the tangent plane. In this case the substance cannot pass through any continuous series of states from c to A, because any line drawn on the surface from c to A begins by dipping below the tangent plane. But if a quantity, however small, of the substance in the state A is in physical contact with the rest of the substance in the state c, minute portions will pass at once from the state c to the state A without passing through the intermediate states.

The energy set at liberty by this transformation will accelerate the subsequent rate of transformation, so that the process will be of the nature of an explosion.

Instances of such a process occur when a liquid not in presence of its vapour is heated above its boiling point, and also when a liquid is cooled below its freezing point, or when a solution of a salt, or of a gas, becomes supersaturated.

In the first of these cases the contact of the smallest quantity of vapour will produce an explosive evaporation, in the second, the contact of ice will produce explosive freezing ; in the third, a crystal of the salt will produce explosive crystallization ; and in the fourth, a bubble of any gas will produce explosive effervescence.

Finally, when the tangent plane touches the surface at two or more points, and is above the surface everywhere else, portions of the substance in states corresponding to the points of contact can exist in presence of each other, and the substance can pass freely from one state to another in either direction.

The state of the whole body when part is in one physical state and part in another is represented by a point in the straight line joining the centre of gravity of two masses equal respectively to the masses of the substance in the two states, and placed at the points of the model corresponding to these states.

Hence, in addition to the surface already considered, which we may call the primitive surface, and which represents the properties of the substance when homogeneous, all the points of the line joining the two points of contact of the same tangent plane belong to a secondary surface, which represents the properties of the substance when part is in one state and part in another.

To trace out this secondary surface we may suppose the doubly tangent plane to be made to roll upon the surface, always touching it at two points called the node-couple.

The two points of contact will thus trace out two curves such that a point in the one corresponds to a point in the other. These two curves are called in geometry the *node-couple* curves.

The secondary surface is generated by a line which moves so as always to join corresponding points of contact. It is a developable surface, being the envelope of the rolling tangent plane.

To construct it, spread a film of grease on a sheet of glass and cause the sheet of glass to roll without slipping on the model, always touching it in two points at least.

The grease will be partly transferred from the glass to the model at the points of contact, and there will be traces on the model of the node-couple curves, and on the glass of corresponding plane curves.

If we now copy on paper the curve traced out on the glass and cut it out, we may bend the paper so that the cut edges shall coincide with the two node-couple curves, and the paper between these curves will form the derived surface representing the state of the body when part is in one physical state and part in another.

There is one position of the tangent plane in which it touches the primitive surface in three points. These points represent the solid, liquid, and gaseous states of the substance when the temperature and the pressure are such that the three states can exist together in equilibrium.

The plane triangle, of which these points are the angles, represents all possible mixtures of these three states. For instance, if there are s grammes in the solid state, L grammes in the liquid state, and v grammes in the state of vapour, this condition of the substance will be represented by a point in the triangle which is the centre of gravity of masses s , L , and v placed at the corresponding angular points.

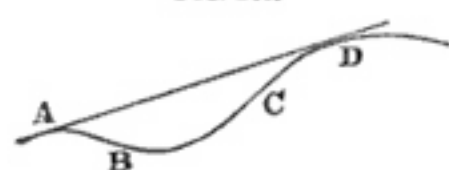
From this position of the tangent plane it may roll on the primitive surface in three directions so as in each case to touch it at two points. We thus obtain three sheets of the derived surface, the first connecting the solid and liquid states, the second the liquid and gaseous states, and the third the gaseous and solid states. These three developable surfaces, together with the plane triangle $sL v$, constitute what Professor Gibbs calls the Surface of Dissipated Energy.

Of the three developable surfaces the first and third, those which connect the solid state with the liquid and gaseous, have been experimentally investigated only to a short distance from the triangle $sL v$; but the sheet which connects the liquid and gaseous states has been thoroughly explored.

The experiments of Cagniard de la Tour and the numerical determinations of Andrews show that the curves traced out by the two points of contact of the doubly tangent plane unite in a point which represents what Andrews calls the critical state. At this point the two points of contact of the rolling tangent plane coalesce, and if the plane continues to roll on the surface it will touch it at one point only.

If the primitive surface forms a continuous sheet beneath the surface of dissipated energy, it cannot be at all points

FIG. 26c.



convexo-convex upwards. For let AD be the line joining two corresponding points of contact of the doubly tangent plane, and let $ABCD$ be the section of the

primitive surface by a vertical plane through AD , then it is

manifest that the curve $ABCD$ must in some part of its course be concave upwards.

Now a point on the primitive surface at which either of its principal curvatures is concave upwards, represents a state of the body which is essentially unstable. Part of the primitive surface, therefore, if it is continuous, must represent states of the body essentially unstable. If, therefore, the primitive surface is continuous, there must be a region representing states essentially unstable, because one or both of the principal curvatures is concave upwards. This region is bounded by what is called in geometry the *spinode* curve. Beyond this curve the surface is convexo-convex, but the tangent plane still cuts the surface at some more or less distant point till we come to the curve of the node-couple, at which the tangent plane touches the surface at two points. Beyond this the tangent plane lies entirely above the surface, and the corresponding state of the body is essentially stable.

The region between the spinode curve and the node-couple curve represents states of the body which, though stable when the whole substance is homogeneous, are liable to sudden change if a portion of the same substance in another state is present.

Since every vertical section through two corresponding points of contact must cut the spinode curve at the points of inflexion B and C , the chord AD of the node-couple curve and the chord BC of the spinode curve must coincide at the critical point, so that at this point the spinode curve and the two branches of the node-couple curve coalesce and have a common tangent. This point is called in geometry the *tacnodal* point.

Note.—For these geometrical names I am indebted to Professor Cayley.

THERMAL LINES ON THE THERMODYNAMIC SURFACE.

(FIG. 26d.)

- o Origin.
- o v Axis of volume.
- o ϕ Axis of entropy.
- o e Axis of energy.
- $P_1 \dots P_6$ Isopiestic or lines of equal pressure.

Of these P_1 represents a negative pressure, or, in other words, a tension, such as may exist in solids and in some liquids.

$T_1 \dots T_6$ Isothermals, or lines of equal temperature.

The curves T_3 and T_4 have branches in the form of closed loops.

FGHC. To the right of this line the substance is gaseous and absolutely stable. To the left of FG it may condense into the solid state, and to the left of GHC it may condense into the liquid state.

CKLMN. Below this line the substance is liquid and absolutely stable. To the right of LKC it may evaporate, to the left of LMN it may solidify.

QRSE. To the left of this line the substance is solid and absolutely stable. To the right of SRQ it may melt, and above SE it may evaporate.

c is the critical point of the liquid and gaseous states.

Below this point there is no discontinuity of states.

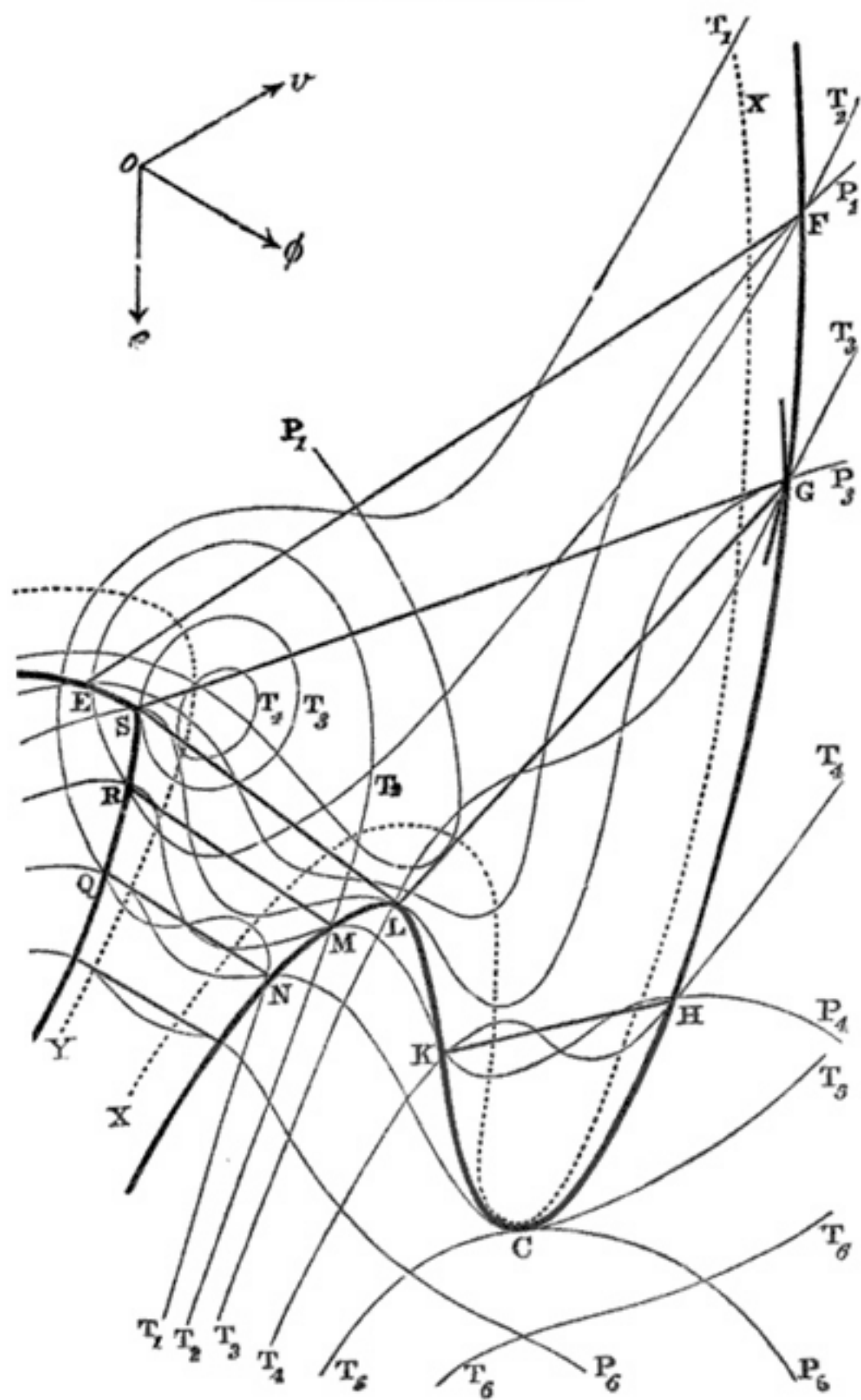
c is called in geometry the tacnodal point.

The curves FG, GHCKL, LMN, QRS, and SE are branches of what is called in geometry the node-couple curve.

The curves xcx and yy are branches of the spinode curve.

Above this curve the substance is absolutely unstable. Between it and the node-couple curve the substance is stable, but only if homogeneous.

FIG. 26d.
Thermodynamic Surface.



The plane triangle *s L G* represents that state of uniform pressure and temperature at which the substance can be partly solid, partly liquid, and partly gaseous.

The straight lines represent states of uniform pressure and temperature in which two different states are in equilibrium

s G and *e F* between solid and gaseous.

G L and *k H* between liquid and gaseous.

s L, *R M*, and *Q N* between solid and liquid.

The surface of dissipated energy consists of the plane triangle *s L G* and the three developable surfaces of which the generating lines are those above mentioned. This surface lies above the primitive thermodynamic surface and touches it along the node-couple curve.