

GIBBS' THERMODYNAMICAL MODEL.

BY W. P. BOYNTON.

IN Maxwell's Theory of Heat, p. 207, is a drawing showing some of the principal lines on a thermodynamical model, suggested by Professor J. Willard Gibbs, of Yale University. I have been told that Professor Maxwell had two of these models constructed, one of which remained at Cambridge, England, the other being sent to Professor Gibbs at Yale. There is also a copy of this model at Clarke University, Worcester, the only one which I have seen. While there may be others in existence, these are the only ones which I have known of, and I suspect that very few have ever been constructed.

This year, in connection with a course in thermodynamics, two of my pupils are attempting to construct one of these models, but are met by various serious difficulties, which may interest others.

In the diagram of which I speak, which is here reproduced, the directions chosen for the different coördinates are not immediately evident. Even by the aid of the description in the text I have not been able to locate them satisfactorily. In the attempt so to do, I have been guided by the following general considerations. Using Maxwell's notation, in which

- v = volume.
- p = pressure.
- T = absolute temperature.
- e = energy.
- φ = entropy.

The equation relating these quantities is

$$Td\varphi = de + pdv$$

which transposed gives

$$de = Td\varphi - pdv = \frac{\partial e}{\partial \varphi} d\varphi + \frac{\partial e}{\partial v} dv$$

the differential equation of the thermodynamical surface of which the coördinates are the entropy, volume and energy, and whose slope at each point in the principal directions gives the temperature and pressure, by the identities

$$T = \frac{\partial e}{\partial \phi}, \quad p = - \frac{\partial e}{\partial v}.$$

These are subject to the conditions that T is always positive, and p

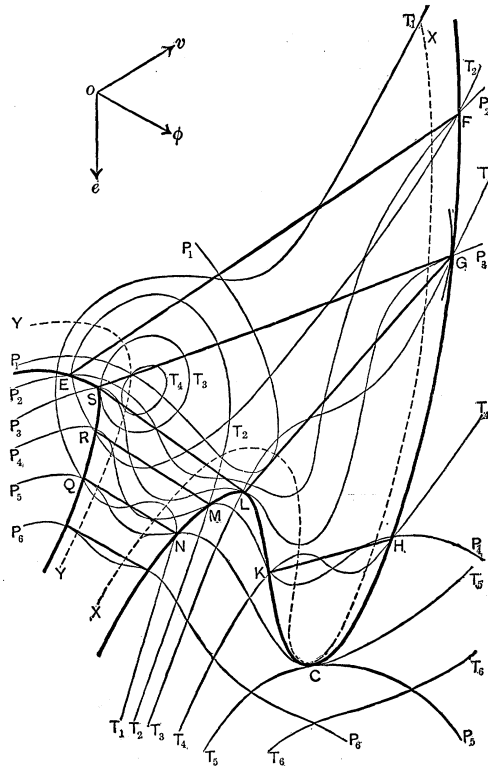


Fig. 1.

is usually positive, always so for the gaseous state, usually for the liquid and solid states.

If then e is taken vertically downward and v and ϕ horizontal, passing along a section of the surface by a plane of constant volume, in the direction of increasing entropy the slope will always be

downward, and generally convex, as the addition of heat, that is energy to a substance at constant volume increases its entropy, and generally its temperature, never decreasing it. A section by a plane of constant entropy will have a slope in the direction of increasing volume which is in general upward, corresponding to a positive pressure, and in all parts of the model referring to stable states of the substance this will be convex, since increase of volume is then accompanied by decrease of pressure.

I have attempted to determine the choice of coördinates by the properties of the critical state. In the two diagrams the broken line separates the parts representing stable or homogeneous states from parts representing unstable or non-homogeneous states.

In the pressure-volume diagram lines of constant pressure, vol-

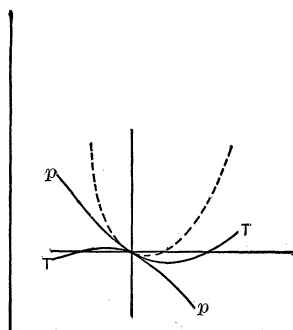


Fig. 2.

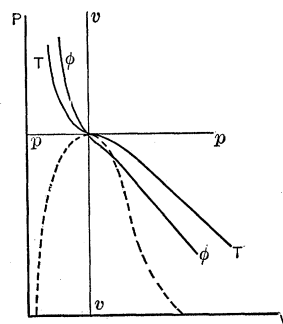


Fig. 3.

ume, entropy and temperature are drawn. On the other are drawn lines of constant pressure and temperature, taken from Maxwell. In both diagrams these lines are tangent to the broken line. In Fig. 2, the line $v = \text{const.}$ cuts sharply through the broken line. I have attempted to find the behavior of a line of constant entropy in the following way :

For a substance following van der Waals' equation

$$\left(p + \frac{a}{v^2}\right) (v - b) = RT$$

the equation of an isentropic can be shown to be

$$\left(p + \frac{a}{v^2}\right) (v - b)^{\gamma} = \text{const.}$$

where k is the ratio of the specific heats at constant pressure and constant volume. The slope of this curve is found to be

$$\frac{dp}{dv} = \frac{2a}{v^3} - \frac{k\left(p + \frac{a}{v^2}\right)}{v-b},$$

which becomes, substituting the values of the critical pressure and volume

$$\left(\frac{dp}{dv}\right)_{\text{crit.}} = \frac{2a(1-k)}{27b^3},$$

which is negative for real positive values of a and b . Hence the isentropic appears also to cut through the broken line, but less sharply.

Still further, we believe that the line of constant volume does not again cut out of this non-homogeneous or unstable area, while the isentropic may. Hence it has seemed to me necessary to consider the vertical line of Fig. 3 a line of constant volume, and the

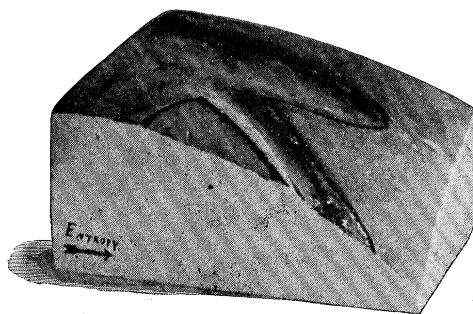


Fig. 4.

horizontal line an isentropic, while the critical point lies a little to the left of the vertex of the curve, so that the isentropic slightly cuts through the broken line.

The choice of coördinates will then be, energy, vertically downward, in the three-dimensional model, volume, measured to the right, in the diagram, Fig. 1, and entropy vertically downward, in the same diagram. This choice is not inconsistent with the arrows in the lower left-hand corner of Fig. 1. The model which has been

constructed in accordance with these considerations is shown in the accompanying figure.

It satisfies the general requirements as to slope and convexity. It represents the gaseous or vapor state as having in general the greatest volume and a great range of pressure, etc. One property, however, does not seem to be indicated by this model, nor do I see how to satisfactorily change it so that this can be done.

It has been deduced mathematically and shown experimentally that if a saturated vapor be expanded adiabatically, or isentropically, it may either become superheated or partially condense to liquid; in fact both phenomena can be shown with one substance, as for instance, chloroform above 127° C. becomes superheated, and below this temperature condenses, by sudden expansion, while at this temperature no visible effect is produced by either expansion or compression. That is, there is an isentropic which is at a particular point tangent to the "steam line," those on one side of it not touching it at all, while those on the other cut both in and out. This particular property is not shown by the model as constructed, with the present choice of coördinates. If, however, we had measured entropy horizontally in Fig. 1, then the isentropics, being vertical, might be tangent to, or cut through the steam line. This choice of coördinates has, however, seemed impossible for the reasons previously given.

We may, if we wish, discuss the question by a different method. The lines drawn in Figs. 1, 2 and 3 are all lines through the critical point. In Fig 2 the lines of constant pressure and temperature are tangent to the broken line; Fig. 3 shows the same property. In Fig. 2 the line of constant entropy cuts the broken line twice, but no other pair of lines has more than one intersection. Fig. 3 does not, as drawn, show the same property. In Fig. 2, passing from the water-line around the critical point in the homogeneous region to the steam-line, one cuts the lines in the following order: water-line, pressure, temperature, entropy, volume, pressure, temperature, entropy, steam-line. Fig. 3 gives the same order, with the choice of coördinates which we have adopted, if we let the temperature lines always slope downwards as do the pressure lines. With this change the two diagrams seem to agree, but otherwise their disagreement seems hopeless.

I shall be very glad to receive from anyone any suggestion which will help to remove the apparent disagreement between the two diagrams, or so modify the model that it may more completely represent the possible properties of actual bodies than it now seems to do.

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Fig. 4.