

TRANSACTIONS

84259

OF THE

CONNECTICUT ACADEMY

OF

ARTS AND SCIENCES.

VOLUME II.



NEW HAVEN:  
PUBLISHED BY THE ACADEMY.  
PRINTED BY TUTTLE, MOREHOUSE & TAYLOR.

1871 TO 1873.

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1870.



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## AMERICAN.

- ALBANY Institute. Transactions, vol. v, 1867. 8°. Manual, March, 1870. 8°, pp. 48.  
——— Dudley Observatory. Annals, vol. i, 1866. 8°.
- AMERICAN Association for the Advancement of Science. Proceedings at 15th, 16th, and 17th Meetings, 1866-8. Cambridge, 1867-70. 8°.
- BOSTON Society of Natural History. Memoirs, vol. i, parts 1, 2, and 4, 1866-9. 4°. Proceedings, vol. xi (wanting sig. 2), xii, xiii sigs. 1-17, 1866-70. 8°. Occasional Papers, vol. i, 1869, 8°. Annual Reports, May, 1869. 8°, pp. 76.
- CHICAGO Academy of Science. Transactions, vol. i, 1867-9. 8°.
- CINCINNATI Observatory. Adams, J. Q., Oration before the Cincinnati Astronomical Society, Nov. 10, 1843. 8°, pp. 72.  
Mansfield, E. D., Annual Address. June, 1845, with Reports. 8°, pp. 55.  
Reports of the Director, June, 1868, May, 1869. 8°, pp. 48.
- MONTREAL.—The Canadian Naturalist, with the Proceedings of the Natural History Society of Montreal. New Series, vol. iii. 1866-8. 8°.
- PHILADELPHIA.—Historical Society of Pennsylvania. Memoirs, vol. i (reprinted), iii, part 2, iv, part 1, v-vii. 1836-60. 8°.  
Garrard, L. H., Chambersburg in the Colony and the Revolution. 1856. 8°.  
Coles, E., History of the Ordinance of 1787. 1856. 8°, pp. 33.  
Mayer, B., Calvert and Penn. 1852. 8°, pp. 50.  
Ingersoll, J. R., Memoir of Samuel Breck. 1863. 8°, pp. 40.
- SALEM.—Essex Institute. Proceedings, vol. v, parts 2-4, 7, 8, vi, part 1. 1866-8. 8°. Bulletin, vol. i, 1869, ii, Nos. 1-3, 5. 8°.  
——— Peabody Academy of Science. Memoirs, vol. i, No. 1. 1869. 8°.
- SAVANNAH.—Georgia Historical Society. Collections, vols. ii, iii, part 1. 1842-8. 8°. Stevens, W. B., History of Georgia. New York and Phil., 1847-59. 2 vols., 8°.
- TORONTO.—Magnetical Observatory. Monthly Meteorological Register, 1869. 4°, pp. 12. General Meteorological Register, 1868, 1869. 8°, pp. 7, 6. Meteorological Summary, Nov., 1869. p. 1. Monthly Value of Magnetic Elements, 1865-8. 8°, pp. 2. On changes of barometric pressure, by G. T. Kingston. 8°, pp. 5.

## EUROPEAN.

- ALTENBURG.—Mitteltheilungen aus dem Osterlande, von den Gesellschaften zu Altenburg, Bd. xviii, Heft 1-2. 1867, 8°.
- BOLOGNA.—Accademia delle Scienze dell' Instituto di Bologna. Rendiconti, 1865-6, 1866-7, 1867-8. 8°.
- Galvani, L. Opere edito ed inedite, Bologna, 1841; Aggiunta, 1842. 4°.
- BRUSSELS.—Académie Royale des Sciences, des Lettres et des Beaux-Arts de Belgique. Mémoires, Tome xxxvii. 1869. 4°. Mémoires Couronnés et Mémoires des Savants Etrangers, Tome xxxiii. 1865-7. 4°. Mémoires Couronnés et autres Mémoires, Tomes xix, xx. 1867-8. 8°. Bulletins, 2<sup>e</sup> Série, Tomes xv-xxi, xxiii-xxvi. 1863-8, 8°. Annuaire, 1864-9. 12°.
- Observatoire Royal. Annales, Tome xviii. 1868. 4°. Annales Météorologiques, 1<sup>ère</sup> Année. 1870. 4°. Observations des Phénomènes Périodiques, 1861-2, 1864, 1865-6. 4°.
- CHEMNITZ.—Naturwissenschaftliche Gesellschaft. Erster Bericht, 1859-64. 1865. 8°, pp. 30. Zweiter Bericht, 1864-8. 1868. 8°, pp. 55.
- CHERBOURG.—Société Impériale des Sciences Naturelles. Mémoires, Tomes xviii, xix. Paris, 1868-9. 8°.
- CHRISTIANIA.—Videnskabs-Selskab. Forhandling, 1867. Register, 1858-67. 8°.
- Observatorium. Meteorologiske Iagttagelser, 1867. 4°.
- Norske Meteorologiske Institut. Aarboeg, 1867. 4°.
- Kongelige Norske Universitet. Aarsberetning. 1867. 8°. Index Scholarum, Feb., Aug., 1868. 4°.
- Sars, M., Mémoires pour servir à la connaissance des Crinoïdes vivants. 1868. 4°.
- Broch, O. J., Traité élémentaire des Fonctions elliptiques, second fasc. 1867. 8°. *From the University of Christiania.*
- COPENHAGEN.—Kongelige Danske Videnskabernes Selskab. Oversigt over Forhandling, 1866-8, 1869, Nos. 1, 2, 8°.
- DANZIG.—Naturforschende Gesellschaft. Schriften. Neue Folge, Bd. i, ii.
- DRESDEN.—Naturwissenschaftliche Gesellschaft Isis. Sitzungs-Berichte. Jahrg. 1868, No. 4-6. 8°.
- EDINBURGH Geological Society. Transactions, vol. i, 1868-70. 8°.
- HARLEM.—Musée Teyler. Archives. Vol. i, ii, Fasc. 1, 2, 1868-69. 8°. Catalogue Systématique de la Collection Paléontologique, par T. C. Winkler. Livr. 1-6, 1863-7. 8°.
- HELSINGFORS.—Societas Scientiarum Fennica. Acta, Tome viii. 1867, 4°. Ofversigt af Förhandlingar, Bd. ix, x, xi. 1867-9. 8°.
- Hjelt, O. E. A., Gedächtnisrede auf A. v. Nordmann. 1868. 8°, pp. 61.
- KRAKAU.—K. K. Sternwarte. Materialy do Klimatografii Galicyi. Rok 1867, 1868. 8°.
- Karlinski, F., Mittlere Temperatur zu Krakau 1826-1865. Wien, 1868. 4°.
- LEEDS.—Philosophical Society. Annual Report, 1867-8. 8°, pp. 32.
- LEYDEN.—Sternwarte. Annalen. Bd. i. Harlem, 1868. 4°.
- LONDON.—Museum of Practical Geology. Portlock, J. E., Report on the Geology of the County of Londonderry, and of parts of Tyrone and Fermanagh. Dublin, 1843. 8°.

- MADRID.**—Real Observatorio. Observaciones Meteorologicas, 1865-6, 1866-7. 8°. Observaciones Meteorologicas efectuadas en la Peninsula, 1865-6. 8°. Informe del Director. 1867. 8°.
- MANCHESTER.**—Literary and Philosophical Society. Memoirs, Third Series, vol. III. London, 1868. 8°. Proceedings, vols. v-vii, 1866-8. 8°.
- MANNHEIM.**—Verein für Naturkunde. Fünfunddreissigster Jahresbericht. 1869. 8°, pp. 75
- MILAN.**—Reale Istituto Lombardo. Rendiconti. Serie II, vol. I, II, fasc. 1-12. 8°. Amati, A., Dell' Australia e della fondazione d' una colonia con bandiera Italiana. Milano, 1868. 8°, pp. 50.
- Reale Osservatorio di Brera. Effemeridi Astronomiche, 1868, 1869. 8°. Schiaparelli, G. V., and Celoria, G., Sulle variazioni period. del barometro nel clima di Milano. 4°, pp. 31.
- MONCALIERI.**—Osservatorio del R. Collegio Carlo Alberto. Bulletino Meteorologico, Vol. I, II, III Nos. 1-9, 11-12. Denza, F., Le Stelle Cadenti dei periodi di Agosto e Novembre osservate in Piemonte, 1866-8, Memorie, I-IV. Torino, 1866-8. 8°. Sopra gli Aeroliti caduti, 29 Feb., 1868. Torino, 1868. 8°.
- MOSCOW.**—Société Impériale des Naturalistes. Bulletin, 1867, No. 4. 1868, Nos. 1-4. 8°.
- MUNICH.**—Königliche bayerische Akademie. Sitzungsberichte. 1866-1869, II, Heft 3 (wanting 1866, I, Heft 3). 8°. Almanach, 1867. 16°. Sternwarte. Annalen. Bde. XIV-XVII, 1865-9. 8°. Supplementbde. V-IX, 1866-9. 8°.
- Beiträge zur Geschichte der westlichen Araber, herausg. von M. J. Müller, Heft I. München, 1866. 8°.
- Bauernfeind, C. M., Die Bedeutung moderner Gradmessungen. München, 1866. 4°, pp. 41.
- Bischoff, Th. L. W., Resultate des Recrutirungs-Geschäftes. München, 1867. 8°, pp. 65.
- Giesebrecht, W. v., Ueber einige ältere Darstellungen der deutschen Kaiserzeit. München, 1867. 4°, pp. 20.
- Vogel, A., Denkrede auf H. A. von Vogel. München, 1868. 8°, pp. 72.
- “ “ Ueber die Entwicklung der Agriculturchemie. München, 1869. 4°, pp. 49.
- Voit, C., Ueber die Theorien der Ernährung der thiorischen Organismen. München, 1868. 4°, pp. 37.
- Meissner, C. F., Denkschrift auf C. F. P. von Martius. München, 1869. 4°, pp. 28.
- Schlagintweit, E., Die Gottesurtheile der Indier. München, 1866. 4°, pp. 36.
- Brunn, H., Ueber die Sogenannte Leukothea in der Glyptothek. München, 1867. 4°, pp. 25. *From the Royal Academy.*
- NUREMBERG.**—Naturhistorische Gesellschaft. Abhandlungen, Bd. IV. 1868. 8°.
- PARIS.**—Observatoire Météorologique de Montsouris. Bulletin, 1<sup>er</sup> Juillet, 1869—27 Avril, 1870. 4°.
- Société d' Ethnographie. Exposé Générale, 1869. 8°, pp. 24.
- PRAGUE.**—Königliche böhmische Gesellschaft der Wissenschaften. Abhandlungen. Fünfte Folge, Bd. XIV. Sechste Folge, Bd. I. 1866-8. 4°. Sitzungsberichte, 1865-7. 8°.

- RIGA.—Naturforschender Verein. Arbeiten. Neue Folge, Heft 2. 1868. 8°.
- ST. GALLEN.—Naturforschende Gesellschaft. Bericht, 1866–7, 1867–8. 8°.
- ST. PETERSBURG.—Académie Impériale des Sciences. Catalogue des livres publiés en langues étrangères par l'Académie. 1867. 8°.
- SCHWEIZERISCHE Naturforschende Gesellschaft. Verhandlungen, 51, 52, Jahresversammlungen. 1867, 1868. 8°.
- STOCKHOLM.—Kongliga Svenska Vetenskaps-Akademien. Handlingar, Ny Följd, Bd. VII, i, 1867. 4°. Ofversigt af Förhandlingar. Bd. xxv, 1868. 8°. Meteorologiska Iagttagelser, Bd. VIII. 1866. 4°. Lefnadsteckningar. Bd. I, i, 1869. 8°.
- Sundevall, C. J., Die Thierarten des Aristoteles, Stockholm, 1863. 8°.
- “ “ Conspectus Avium picinarum, Stockholm, 1866. 8°.
- Nordenskiöld, A. E., Sketch of the geology of Spitzbergen, Stockholm, 1867. 8°, pp. 55.
- Igelström, L. I., Rock of Nullaberg. 8°, pp. 11.
- STUTTGART.—Verein für vaterländische Naturkunde in Württemberg. Jahreshfte, Jahrg. xxiv, Heft. 3. 1868. 8°.
- UPSALA.—Regia Societas Scientiarum. Nova Acta. Ser. III, Vol. VI. 1868. 4°.
- VIENNA.—K. K. Geologische Reichsanstalt. Jahrbuch, 1867, Nos. 1–4, 1868, Nos. 1, 3, 4, 1869, Nos. 1–3. 8°. Verhandlungen, 1867, 1868, Nos. 1–6, 11–18, 1869, Nos. 6–13. 8°.
- ZURICH.—Naturforschende Gesellschaft. Vierteljahrsschrift, 1867, 1868. 8°.

- 
- Allen, J. A., Mammalia of Massachusetts. [Bulletin of the Museum of Comp. Zool., Cambridge, Mass., No. 8.]. *From the Author.*
- Barrande, J., Céphalopodes Siluriens de la Bohême, Introduction, Prague, 1867. 8°. pp. 48. *From the Author.*
- d'Elvert, C. Zur Geschichte der Pflege der Naturwissenschaften in Mähren und Schlesien, Brünn, 1868. 8°. *From the Author.*
- Galle, J. G., Ueber die Bahn des Pultusk Meteora. (From the Abh. d. Schles. Gesell.) Breslau, 1868. 8°. pp. 43. *From the Author.*
- Gore, G., On Hydrofluoric Acid. (From the Phil. Trans. 1869.) 4° pp. 27. *From the Author.*
- Quetelet, A., Physique Sociale, Tome I. Brux. 1869. 8°.
- Annales Météorol. de l'Observatoire de Bruxelles. 2<sup>e</sup> Année, 1868. 4°.
- Notices [extraits des Bulletins de l'Académie Royale]. 9 pamphlets 8°. *From M. A. Quetelet.*
- Quetelet, E., Sur l'état de l'atmosphère à Bruxelles, 1865. Brux., 1866. 8°. pp. 48.
- Mémoire sur le Température de Bruxelles. Brux., 1867. 4°. *From M. E. Quetelet.*

**XI. GRAPHICAL METHODS IN THE THERMODYNAMICS OF FLUIDS.**  
**By J. WILLARD GIBBS.**

ALTHOUGH geometrical representations of propositions in the thermodynamics of fluids are in general use, and have done good service in disseminating clear notions in this science, yet they have by no means received the extension in respect to variety and generality of which they are capable. So far as regards a general graphical method, which can exhibit at once all the thermodynamic properties of a fluid concerned in reversible processes, and serve alike for the demonstration of general theorems and the numerical solution of particular problems, it is the general if not the universal practice to use diagrams in which the rectilinear co-ordinates represent volume and pressure. The object of this article is to call attention to certain diagrams of different construction, which afford graphical methods co-extensive in their applications with that in ordinary use, and preferable to it in many cases in respect of distinctness or of convenience.

QUANTITIES AND RELATIONS WHICH ARE TO BE REPRESENTED BY THE DIAGRAM.

We have to consider the following quantities:—

$v$ ,	the volume,	}	of a given body in any state,	
$p$ ,	the pressure,			
$t$ ,	the (absolute) temperature,			
$\epsilon$ ,	the energy,			
$\eta$ ,	the entropy,			
also	$W$ ,	the work done,	}	by the body in passing from one state to another.
and	$H$ ,	the heat received,*		

These are subject to the relations expressed by the following differential equations:—

\* Work spent upon the body is as usual to be considered as a negative quantity of work done by the body, and heat given out by the body as a negative quantity of heat received by it.

It is taken for granted that the body has a uniform temperature throughout, and that the pressure (or expansive force) has a uniform value both for all points in the body and for all directions. This, it will be observed, will exclude irreversible processes, but will not entirely exclude solids, although the condition of equal pressure in all directions renders the case very limited, in which they come within the scope of the discussion.

$$dW = \alpha p dv, \quad (a)$$

$$d\varepsilon = \beta dH - dW, \quad (b)$$

$$d\eta = \frac{dH^*}{t}, \quad (c)$$

where  $\alpha$  and  $\beta$  are constants depending upon the units by which  $v$ ,  $p$ ,  $W$  and  $H$  are measured. We may suppose our units so chosen that  $\alpha=1$  and  $\beta=1$ ,<sup>†</sup> and write our equations in the simpler form,

$$d\varepsilon = dH - dW, \quad (1)$$

$$dW = p dv, \quad (2)$$

$$dH = t d\eta. \quad (3)$$

Eliminating  $dW$  and  $dH$ , we have

$$d\varepsilon = t d\eta - p dv. \quad (4)$$

The quantities  $v$ ,  $p$ ,  $t$ ,  $\varepsilon$  and  $\eta$  are determined when the state of the body is given, and it may be permitted to call them *functions of the state of the body*. The state of a body, in the sense in which the term is used in the thermodynamics of fluids, is capable of two independent variations, so that between the five quantities  $v$ ,  $p$ ,  $t$ ,  $\varepsilon$  and  $\eta$  there exist relations expressible by three finite equations, different in general for different substances, but always such as to be in harmony with the differential equation (4). This equation evidently signifies that if  $\varepsilon$  be expressed as function of  $v$  and  $\eta$ , the partial differential co-efficients of this function taken with respect to  $v$  and to  $\eta$  will be equal to  $-p$  and to  $t$  respectively.<sup>‡</sup>

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\* Equation (a) may be derived from simple mechanical considerations. Equations (b) and (c) may be considered as defining the energy and entropy of any state of the body, or more strictly as defining the differentials  $d\varepsilon$  and  $d\eta$ . That functions of the state of the body exist, the differentials of which satisfy these equations, may easily be deduced from the first and second laws of thermodynamics. The term *entropy*, it will be observed, is here used in accordance with the original suggestion of Clausius, and not in the sense in which it has been employed by Professor Tait and others after his suggestion. The same quantity has been called by Professor Rankine the *Thermodynamic function*. See Clausius, *Mechanische Wärmetheorie*, Abhnd. ix, § 14; or Pogg. Ann., Bd. cxxv (1865), p. 390; and Rankine, *Phil. Trans.*, vol. 144, p. 126.

† For example, we may choose as the unit of volume, the cube of the unit of length,—as the unit of pressure the unit of force acting upon the square of the unit of length,—and as the unit of heat the thermal equivalent of the unit of work. The units of length and of force would still be arbitrary as well as the unit of temperature.

‡ An equation giving  $\varepsilon$  in terms of  $\eta$  and  $v$ , or more generally any finite equation between  $\varepsilon$ ,  $\eta$  and  $v$  for a definite quantity of any fluid, may be considered as the fundamental thermodynamic equation of that fluid, as from it by aid of equations (2), (3) and (4) may be derived all the thermodynamic properties of the fluid (so far as reversible

On the other hand  $W$  and  $H$  are not functions of the state of the body (or functions of any of the quantities  $v$ ,  $p$ ,  $t$ ,  $\epsilon$  and  $\eta$ ), but are determined by the whole series of states through which the body is supposed to pass.

FUNDAMENTAL IDEA AND GENERAL PROPERTIES OF THE DIAGRAM.

Now if we associate a particular point in a plane with every separate state, of which the body is capable, in any continuous manner, so that states differing infinitely little are associated with points which are infinitely near to each other,\* the points associated with states of equal volume will form lines, which may be called *lines of equal volume*, the different lines being distinguished by the numerical value of the volume, (as lines of volume 10, 20, 30, etc.) In the same way we may conceive of *lines of equal pressure, of equal temperature, of equal energy, and of equal entropy*. These lines we may also call *isometric, isopiestic, isothermal, isodynamic, isentropic*,† and if necessary use these words as substantives.

Suppose the body to change its state, the points associated with the states through which the body passes will form a line, which we may call the *path* of the body. The conception of a path must include the idea of direction, to express the order in which the body passes through the series of states. With every such change of state there is connected in general a certain amount of work done,  $W$ , and of heat received,  $H$ , which we may call the *work* and the *heat* of the *path*.‡

processes are concerned,) viz: the fundamental equation with equation (4) gives the three relations existing between  $v$ ,  $p$ ,  $t$ ,  $\epsilon$  and  $\eta$ , and these relations being known, equations (2) and (3) give the work  $W$  and heat  $H$  for any change of state of the fluid.

\* The method usually employed in treatises on thermodynamics, in which the rectangular co-ordinates of the point are made proportional to the volume and pressure of the body, is a single example of such an association.

† These lines are usually known by the name given them by Rankine, *adiabatic*. If, however, we follow the suggestion of Clausius and call that quantity *entropy*, which Rankine called the *thermodynamic function*, it seems natural to go one step farther, and call the lines in which this quantity has a constant value *isentropic*.

‡ For the sake of brevity, it will be convenient to use language which attributes to the diagram properties which belong to the associated states of the body. Thus it can give rise to no ambiguity, if we speak of the volume or the temperature of a point in the diagram, or of the work or heat of a line, instead of the volume or temperature of the body in the state associated with the point, or the work done or the heat received by the body in passing through the states associated with the points of the line. In like manner also we may speak of the body moving along a line in the diagram, instead of passing through the series of states represented by the line.

The value of these quantities may be calculated from equations (2) and (3),

$$\begin{aligned} dW &= pdv \\ dH &= td\eta, \\ \text{i. e.,} \quad W &= \int pdv & (5) \\ H &= \int td\eta, & (6) \end{aligned}$$

the integration being carried on from the beginning to the end of the path. If the direction of the path is reversed,  $W$  and  $H$  change their signs, remaining the same in absolute value.

If the changes of state of the body form a cycle, i. e., if the final state is the same as the initial, the path becomes a *circuit*, and the work done and heat received are equal, as may be seen from equation (1), which when integrated for this case becomes  $0 = H - W$ .

The circuit will enclose a certain area, which we may consider as positive or negative according to the direction of the circuit which circumscribes it. The direction in which areas must be circumscribed in order that their value may be positive, is of course arbitrary. In other words, if  $x$  and  $y$  are the rectangular co-ordinates, we may define an area either as  $\int y dx$ , or as  $\int x dy$ .

If an area be divided into any number of parts, the work done in the circuit bounding the whole area is equal to the sum of the work done in all the circuits bounding the partial areas. This is evident from the consideration, that the work done in each of the lines which separate the partial areas appears twice and with contrary signs in the sum of the work done in the circuits bounding the partial areas. Also the heat received in the circuit bounding the whole area is equal to the sum of the heat received in all the circuits bounding the partial areas.\*

If all the dimensions of a circuit are infinitely small, the ratio of the included area to the work or heat of the circuit is independent of the shape of the circuit and the direction in which it is described, and varies only with its position in the diagram. That this ratio is independent of the direction in which the circuit is described, is evident from the consideration that a reversal of this direction simply changes the sign of both terms of the ratio. To prove that the ratio

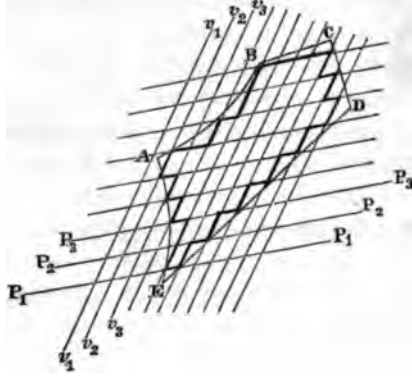
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\* The conception of areas as positive or negative renders it unnecessary in propositions of this kind to state explicitly the direction in which the circuits are to be described. For the directions of the circuits are determined by the signs of the areas, and the signs of the partial areas must be the same as that of the area out of which they were formed.



is independent of the shape of the circuit, let us suppose the area ABCDE (fig. 1) divided up by an infinite number of isometrics  $v_1 v_1, v_2 v_2, \text{ etc.}$ , with equal differences of volume  $dv$ , and an infinite number of isopiestic  $p_1 p_1, p_2 p_2, \text{ etc.}$ , with equal differences of pressure  $dp$ . Now from the principle of continuity, as the whole figure is infinitely small, the ratio of the area of one of the small quadrilaterals into which the figure is divided to the work done in passing around it is approximately the same for all the different quadrilaterals. Therefore the area of the figure composed of all the complete quadrilaterals which fall within the given circuit has to the work done in circumscribing this figure the same ratio, which we will call  $\gamma$ . But the area of this figure is approximately the same as that of the given circuit, and the work done in describing this figure is approximately the same as that done in describing the given circuit, (eq. 5). Therefore the area of the given circuit has to the work done or heat received in that circuit this ratio  $\gamma$ , which is independent of the shape of the circuit.

Fig. 1.



Now if we imagine the systems of equidifferent isometrics and isopiestic, which have just been spoken of, extended over the whole diagram, the work done in circumscribing one of the small quadrilaterals, so that the increase of pressure directly precedes the increase of volume, will have in every part of the diagram a constant value, viz., the product of the differences of volume and pressure ( $dv \times dp$ ), as may easily be proved by applying equation (2) successively to its four sides. But the area of one of these quadrilaterals, which we could consider as constant within the limits of the infinitely small circuit, may vary for different parts of the diagram, and will indicate proportionally the value of  $\gamma$ , which is equal to the area divided by  $dv \times dp$ .

In like manner, if we imagine systems of isentropics and isothermals drawn throughout the diagram for equal differences  $d\eta$  and  $dt$ , the heat received in passing around one of the small quadrilaterals, so that the increase of  $t$  shall directly precede that of  $\eta$ , will be the constant product  $d\eta \times dt$ , as may be proved by equation (3), and the

value of  $\gamma$ , which is equal to the area divided by the heat, will be indicated proportionally by the areas.\*

This quantity  $\gamma$ , which is the ratio of the area of an infinitely small circuit to the work done or heat received in that circuit, and which we may call the scale on which work and heat are represented by areas, or more briefly, the *scale of work and heat*, may have a constant value throughout the diagram or it may have a varying value. The diagram in ordinary use affords an example of the first case, as the area of a circuit is everywhere proportional to the work or heat. There are other diagrams which have the same property, and we may call all such *diagrams of constant scale*.

In any case we may consider the scale of work and heat as known for every point of the diagram, so far as we are able to draw the isometrics and isopiestic or the isentropics and isothermals. If we

\* The indication of the value of  $\gamma$  by systems of equidifferent isometrics and isopiestic, or isentropics and isothermals, is explained above, because it seems in accordance with the spirit of the graphical method, and because it avoids the extraneous consideration of the co-ordinates. If, however, it is desired to have analytical expressions for the value of  $\gamma$  based upon the relations between the co-ordinates of the point and the state of the body, it is easy to deduce such expressions as the following, in which  $x$  and  $y$  are the rectangular co-ordinates, and it is supposed that the sign of an area is determined in accordance with the equation  $A = \int y dx$  :—

$$\frac{1}{\gamma} = \frac{dv}{dx} \cdot \frac{dp}{dy} - \frac{dp}{dx} \cdot \frac{dv}{dy} = \frac{d\eta}{dx} \cdot \frac{dt}{dy} - \frac{dt}{dx} \cdot \frac{d\eta}{dy},$$

where  $x$  and  $y$  are regarded as the independent variables;—or

$$\gamma = \frac{dx}{dv} \cdot \frac{dy}{dp} - \frac{dy}{dv} \cdot \frac{dx}{dp},$$

where  $v$  and  $p$  are the independent variables;—or

$$\gamma = \frac{dx}{d\eta} \cdot \frac{dy}{dt} - \frac{dy}{d\eta} \cdot \frac{dx}{dt},$$

where  $\eta$  and  $t$  are the independent variables;—or

$$\frac{1}{\gamma} = \frac{d^2 \epsilon}{dv d\eta} \cdot \frac{dx}{dv} \cdot \frac{dy}{d\eta} - \frac{dy}{dv} \cdot \frac{dx}{d\eta},$$

where  $v$  and  $\eta$  are the independent variables.

These and similar expressions for  $\frac{1}{\gamma}$  may be found by dividing the value of the work or heat for an infinitely small circuit by the area included. This operation can be most conveniently performed upon a circuit consisting of four lines, in each of which one of the independent variables is constant. E. g., the last formula can be most easily found from an infinitely small circuit formed of two isometrics and two isentropics.

write  $\delta W$  and  $\delta H$  for the work and heat of an infinitesimal circuit, and  $\delta A$  for the area included, the relations of these quantities are thus expressed:—\*

$$\delta W = \delta H = \frac{1}{\gamma} \delta A. \tag{7}$$

We may find the value of  $W$  and  $H$  for a circuit of finite dimensions by supposing the included area  $A$  divided into areas  $\delta A$  infinitely small in all directions, for which therefore the above equation will hold, and taking the sum of the values of  $\delta H$  or  $\delta W$  for the various areas  $\delta A$ . Writing  $W^c$  and  $H^c$  for the work and heat of the circuit  $C$ , and  $\Sigma^c$  for a summation or integration performed within the limits of this circuit, we have

$$W^c = H^c = \Sigma^c \frac{1}{\gamma} \delta A. \tag{8}$$

We have thus an expression for the value of the work and heat of a circuit involving an integration extending over an area instead of one extending over a line, as in equations (5) and (6).

Similar expressions may be found for the work and the heat of a path which is not a circuit. For this case may be reduced to the preceding by the consideration that  $W=0$  for a path on an isometric or on the line of no pressure (eq. 2), and  $H=0$  for a path on an isentropic or on the line of absolute cold. Hence the work of any path  $S$  is equal to that of the circuit formed of  $S$ , the isometric of the final state, the line of no pressure and the isometric of the initial state, which circuit may be represented by the notation  $[S, v'', p^0, v']$ . And the heat of the same path is the same as that of the circuit  $[S, \eta'', t^0, \eta']$ . Therefore using  $W^s$  and  $H^s$  to denote the work and heat of any path  $S$ , we have

$$W^s = \Sigma [S, v'', p^0, v'] \frac{1}{\gamma} \delta A, \tag{9}$$

$$H^s = \Sigma [S, \eta'', t^0, \eta'] \frac{1}{\gamma} \delta A, \tag{10}$$

where as before the limits of the integration are denoted by the ex-

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\* To avoid confusion, as  $dW$  and  $dH$  are generally used and are used elsewhere in this article to denote the work and heat of an infinite short path, a slightly different notation,  $\delta W$  and  $\delta H$ , is here used to denote the work and heat of an infinitely small circuit. So  $\delta A$  is used to denote an element of area which is infinitely small in all directions, as the letter  $d$  would only imply that the element was infinitely small in one direction. So also below the integration or summation which extends to all the elements written with  $\delta$  is denoted by the character  $\Sigma$ , as the character  $\int$  naturally refers to elements written with  $d$ .

pression occupying the place of an index to the sign  $\Sigma$ .\* These equations evidently include equation (8) as a particular case.

It is easy to form a material conception of these relations. If we imagine, for example, mass inherent in the plane of the diagram with a varying (superficial) density represented by  $\frac{1}{\gamma}$ , then  $\Sigma \frac{1}{\gamma} \delta A$  will evidently denote the mass of the part of the plane included within the limits of integration, this mass being taken positively or negatively according to the direction of the circuit.

Thus far we have made no supposition in regard to the nature of the law, by which we associate the points of a plane with the states of the body, except a certain condition of continuity. Whatever law we may adopt, we obtain a method of representation of the thermodynamic properties of the body, in which the relations existing between the functions of the state of the body are indicated by a net-work of lines, while the work done and the heat received by the body when it changes its state are represented by integrals extending over the elements of a line, and also by an integral extending over the elements of certain areas in the diagram, or, if we choose to introduce such a consideration, by the mass belonging to these areas.

The different diagrams which we obtain by different laws of association are all such as may be obtained from one another by a process of *deformation*, and this consideration is sufficient to demonstrate

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\* A word should be said in regard to the sense in which the above propositions should be understood. If beyond the limits, within which the relations of  $v$ ,  $p$ ,  $t$ ,  $\epsilon$  and  $\eta$  are known and which we may call the limits of the known field, we continue the isometrics, isopiestic, &c., in any way we please, only subject to the condition that the relations of  $v$ ,  $p$ ,  $t$ ,  $\epsilon$  and  $\eta$  shall be consistent with the equation  $d\epsilon = td\eta - pdv$ , then in calculating the values of quantities  $W$  and  $H$  determined by the equations  $dW = pdv$  and  $dH = td\eta$  for paths or circuits in any part of the diagram thus extended, we may use any of the propositions or processes given above, as these three equations have formed the only basis of the reasoning. We will thus obtain values of  $W$  and  $H$ , which will be identical with those which would be obtained by the immediate application of the equations  $dW = pdv$  and  $dH = td\eta$  to the path in question, and which in the case of any path which is entirely contained in the known field will be the true values of the work and heat for the change of state of the body which the path represents. We may thus use lines outside of the known field without attributing to them any physical signification whatever, without considering the points in the lines as representing any states of the body. If however, to fix our ideas, we choose to conceive of this part of the diagram as having the same physical interpretation as the known field, and to enunciate our propositions in language based upon such a conception, the unreality or even the impossibility of the states represented by the lines outside of the known field cannot lead to any incorrect results in regard to paths in the known field.

their properties from the well-known properties of the diagram in which the volume and pressure are represented by rectangular co-ordinates. For the relations indicated by the net-work of isometrics, isopiestic etc., are evidently not altered by deformation of the surface upon which they are drawn, and if we conceive of mass as belonging to the surface, the mass included within given lines will also not be effected by the process of deformation. If, then, the surface upon which the ordinary diagram is drawn has the uniform superficial density 1, so that the work and heat of a circuit, which are represented in this diagram by the included area, shall also be represented by the mass included, this latter relation will hold for any diagram formed from this by deformation of the surface on which it is drawn.

The choice of the method of representation is of course to be determined by considerations of simplicity and convenience, especially in regard to the drawing of the lines of equal volume, pressure, temperature, energy and entropy, and the estimation of work and heat. There is an obvious advantage in the use of diagrams of constant scale, in which the work and heat are represented simply by areas. Such diagrams may of course be produced by an infinity of different methods, as there is no limit to the ways of deforming a plane figure without altering the magnitude of its elements. Among these methods, two are especially important,—the ordinary method in which the volume and pressure are represented by rectilinear co-ordinates, and that in which the entropy and temperature are so represented. A diagram formed by the former method may be called, for the sake of distinction, a *volume-pressure* diagram,—one formed by the latter, an *entropy-temperature* diagram. That the latter as well as the former satisfies the condition that  $\gamma=1$  throughout the whole diagram, may be seen by reference to page 313.

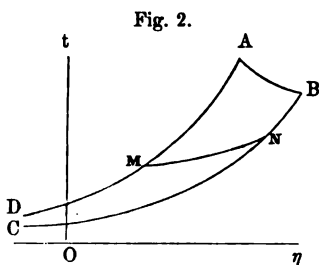
THE ENTROPY-TEMPERATURE DIAGRAM COMPARED WITH THAT IN ORDINARY USE.

*Considerations independent of the nature of the body in question.*

As the general equations (1), (2), (3) are not altered by interchanging  $v$ ,  $-p$  and  $-W$  with  $\eta$ ,  $t$  and  $H$  respectively, it is evident that, so far as these equations are concerned, there is nothing to choose between a volume-pressure and an entropy-temperature diagram. In the former, the work is represented by an area bounded by the path which represents the change of state of the body, two ordinates and the axis of abscissas. The same is true of the heat received in the latter diagram. Again, in the former diagram the heat received is represented by an area bounded by the path and certain lines, the

character of which depends upon the nature of the body under consideration. Except in the case of an ideal body, the properties of which are determined by assumption, these lines are more or less unknown in a part of their course, and in any case the area will generally extend to an infinite distance. Very much the same inconveniences attach themselves to the areas representing work in the entropy-temperature diagram.\* There is, however, a consideration of a general character, which shows an important advantage on the side of the entropy-temperature diagram. In thermodynamic problems, heat received at one temperature is by no means the equivalent of the same amount of heat received at another temperature. For example, a supply of a million calories at  $150^{\circ}$  is a very different thing from a supply of a million calories at  $50^{\circ}$ . But no such distinction exists in regard to work. This is a result of the general law, that heat can only pass from a hotter to a colder body, while work can be transferred by mechanical means from one fluid to any other, whatever may be

\* In neither diagram do these circumstances create any serious difficulty in the estimation of areas representing work or heat. It is always possible to divide these areas into two parts, of which one is of finite dimensions, and the other can be calculated in the simplest manner. Thus, in the entropy-temperature diagram, the work done in a path AB



(fig. 2) is represented by the area included by the path AB, the isometric BC, the line of no pressure and the isometric DA. The line of no pressure and the adjacent parts of the isometrics in the case of an actual gas or vapor are more or less undetermined in the present state of our knowledge, and are likely to remain so; for an ideal gas the line of no pressure coincides with the axis of abscissas, and is an asymptote to the isometrics.

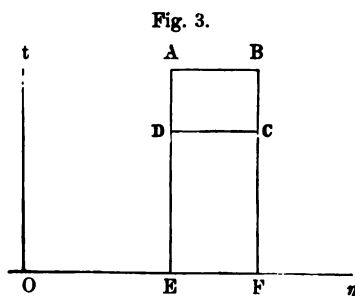
But, be this as it may, it is not necessary to examine the form of the remoter parts of the diagram. If we draw an isopiestic MN, cutting AD and BC, the area MNCD, which represents the work done in MN, will be equal to  $p(v'' - v')$ , where  $p$  denotes the pressure in MN, and  $v''$  and  $v'$  denote the volumes at B and A respectively (eq. 5). Hence the work done in AB will be represented by  $ABNM + p(v'' - v')$ . In the volume-pressure diagram, the areas representing heat may be divided by an isothermal, and treated in a manner entirely analogous.

Or, we may make use of the principle, that, for a path which begins and ends on the same isodynamic, the work and heat are equal, as appears by integration of equation (1). Hence, in the entropy-temperature diagram, to find the work of any path, we may extend it by an isometric (which will not alter its work), so that it shall begin and end on the same isodynamic, and then take the heat (instead of the work) of the path thus extended. This method was suggested by that employed by Cazin (*Théorie élémentaire des Machines à Air Chaud*, p. 11) and Zeuner (*Mechanische Wärmetheorie*, p. 80) in the reverse case, viz: to find the heat of a path in the volume-pressure diagram.

the pressures. Hence, in thermodynamic problems, it is generally necessary to distinguish between the quantities of heat received or given out by the body at different temperatures, while as far as work is concerned, it is generally sufficient to ascertain the total amount performed. If, then, several heat-areas and one work-area enter into the problem, it is evidently more important that the former should be simple in form, than that the latter should be so. Moreover, in the very common case of a circuit, the work-area is bounded entirely by the path, and the form of the isometrics and the line of no pressure are of no especial consequence.

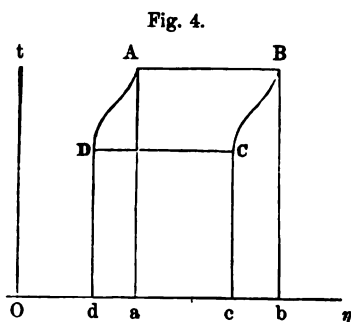
It is worthy of notice that the simplest form of a perfect thermodynamic engine, so often described in treatises on thermodynamics, is represented in the entropy-temperature diagram by a figure of extreme simplicity, viz: a rectangle of which the sides are parallel to the co-ordinate axes.

Thus in figure 3, the circuit ABCD may represent the series of states through which the fluid is made to pass in such an engine, the included area representing the work done, while the area ABFE represents the heat received from the heater at the highest temperature AE, and the area CDEF represents the heat transmitted to the cooler at the lowest temperature DE.



There is another form of the perfect thermodynamic engine, viz: one with a perfect regenerator as defined by Rankine (Phil. Trans. vol. 144, p. 140), the representation of which becomes peculiarly simple in the entropy-temperature diagram.

The circuit consists of two equal straight lines AB and CD (fig. 4) parallel to the axis of abscissas, and two precisely similar curves of any form BC and AD. The included area ABCD represents the work done, and the areas ABba and CDdc represent respectively the heat received from the heater and that transmitted to the cooler.



The heat imparted by the fluid to the regenerator in passing from B to C, and afterward restored to the fluid in its passage from D to A, is represented by the areas BCeb and DAad.

It is often a matter of the first importance in the study of any thermodynamic engine, to compare it with a perfect engine. Such a comparison will obviously be much facilitated by the use of a method in which the perfect engine is represented by such simple forms.

The method in which the co-ordinates represent volume and pressure has a certain advantage in the simple and elementary character of the notions upon which it is based, and its analogy with Watt's indicator has doubtless contributed to render it popular. On the other hand, a method involving the notion of *entropy*, the very existence of which depends upon the second law of thermodynamics, will doubtless seem to many far-fetched, and may repel beginners as obscure and difficult of comprehension. This inconvenience is perhaps more than counter-balanced by the advantages of a method which makes the second law of thermodynamics so prominent, and gives it so clear and elementary an expression. The fact, that the different states of a fluid can be represented by the positions of a point in a plane, so that the ordinates shall represent the temperatures, and the heat received or given out by the fluid shall be represented by the area bounded by the line representing the states through which the body passes, the ordinates drawn through the extreme points of this line, and the axis of abscissas,—this fact, clumsy as its expression in words may be, is one which presents a clear image to the eye, and which the mind can readily grasp and retain. It is, however, nothing more nor less than a geometrical expression of the second law of thermodynamics in its application to fluids, in a form exceedingly convenient for use, and from which the analytical expression of the same law can, if desired, be at once obtained. If, then, it is more important for purposes of instruction and the like to familiarize the learner with the second law, than to defer its statement as long as possible, the use of the entropy-temperature diagram may serve a useful purpose in the popularizing of this science.

The foregoing considerations are in the main of a general character, and independent of the nature of the substance to which the graphical method is applied. On this, however, depend the forms of the isometrics, isopiestic and isodynamics in the entropy-temperature diagram, and of the isentropics, isothermals and isodynamics in the volume-pressure diagram. As the convenience of a method depends largely upon the ease with which these lines can be drawn, and upon the peculiarities of the fluid which has its properties represented in the diagram, it is desirable to compare the methods under consideration in some of their most important applications. We will commence with the case of a perfect gas.



*Case of a perfect gas.*

A perfect or ideal gas may be defined as such a gas, that for any constant quantity of it the product of the volume and the pressure varies as the temperature, and the energy varies as the temperature, i. e.,

$$pv = at, \tag{A)*}$$

$$\epsilon = ct. \tag{B)}$$

The significance of the constant  $a$  is sufficiently indicated by equation (A). The significance of  $c$  may be rendered more evident by differentiating equation (B) and comparing the result

$$d\epsilon = c dt$$

with the general equations (1) and (2), viz:

$$d\epsilon = dH - dW, \quad dW = p dv.$$

If  $dv = 0$ ,  $dW = 0$ , and  $dH = c dt$ , i. e.,

$$\left(\frac{dH}{dt}\right)_v = c, \dagger \tag{C)}$$

i. e.,  $c$  is the quantity of heat necessary to raise the temperature of the body one degree under the condition of constant volume. It will be observed, that when different quantities of the same gas are considered,  $a$  and  $c$  both vary as the quantity, and  $c \div a$  is constant; also, that the value of  $c \div a$  for different gases varies as their specific heat determined for equal volumes and for constant volume.

With the aid of equations (A) and (B) we may eliminate  $p$  and  $t$  from the general equation (4), viz:

$$d\epsilon = t d\eta - p dv,$$

which is then reduced to

$$\frac{d\epsilon}{\epsilon} = \frac{1}{c} d\eta - \frac{a}{c} \frac{dv}{v},$$

and by integration to

$$\log \epsilon = \frac{\eta}{c} - \frac{a}{c} \log v. \ddagger \tag{D)}$$

\* In this article, all equations which are designated by arabic numerals subsist for any body whatever (subject to the condition of uniform pressure and temperature), and those which designated by small capitals subsist for any quantity of a perfect gas as defined above (subject of course to the same conditions).

† A subscript letter after a differential co-efficient is used in this article to indicate the quantity which is made constant in the differentiation.

‡ If we use the letter  $e$  to denote the base of the Naperian system of logarithms, equation (D) may also be written in the form

$$\epsilon = e^{\frac{\eta}{c} - \frac{a}{c} \log v}$$

This may be regarded as the fundamental thermodynamic equation of an ideal gas. See

The constant of integration becomes 0, if we call the entropy 0 for the state of which the volume and energy are both unity.

Any other equations which subsist between  $v$ ,  $p$ ,  $t$ ,  $\varepsilon$  and  $\eta$  may be derived from the three independent equations (A), (B) and (D). If we eliminate  $\varepsilon$  from (B) and (D), we have

$$\eta = a \log v + c \log t + c \log c. \quad (\text{E})$$

Eliminating  $v$  from (A) and (E), we have

$$\eta = (a+c) \log t - a \log p + c \log c + a \log a. \quad (\text{F})$$

Eliminating  $t$  from (A) and (E), we have

$$\eta = (a+c) \log v + c \log p + c \log \frac{c}{a}. \quad (\text{G})$$

If  $v$  is constant, equation (E) becomes

$$\eta = c \log t + \text{Const.},$$

i. e., the isometrics in the entropy-temperature diagram are logarithmic curves identical with one another in form,—a change in the value of  $v$  having only the effect of moving the curve parallel to the axis of  $\eta$ . If  $p$  is constant, equation (F) becomes

$$\eta = (a+c) \log t + \text{Const.},$$

so that the isopiestic in this diagram have similar properties. This identity in form diminishes greatly the labor of drawing any considerable number of these curves. For if a card or thin board be cut in the form of one of them, it may be used as a pattern or ruler to draw all of the same system.

The isodynamics are straight in this diagram (eq. B).

To find the form of the isothermals and isentropics in the volume-pressure diagram, we may make  $t$  and  $\eta$  constant in equations (A) and (G) respectively, which will then reduce to the well-known equations of these curves:—

$$pv = \text{Const.},$$

and

$$p^c v^{a+c} = \text{Const.}$$

The equation of the isodynamics is of course the same as that of the isothermals. None of these systems of lines have that property of identity of form, which makes the systems of isometrics and isopiestic so easy to draw in the entropy-temperature diagram.

the last note on page 310. It will be observed, that there would be no real loss of generality if we should choose, as the body to which the letters refer, such a quantity of the gas that one of the constants  $a$  and  $c$  should be equal to unity.

*Case of condensable vapors.*

The case of bodies which pass from the liquid to the gaseous condition is next to be considered. It is usual to assume of such a body, that when sufficiently superheated it approaches the condition of a perfect gas. If, then, in the entropy-temperature diagram of such a body we draw systems of isometrics, isopiestic and isodynamics, as if for a perfect gas, for proper values of the constants  $a$  and  $c$ , these will be asymptotes to the true isometrics, etc., of the vapor, and in many cases will not vary from them greatly in the part of the diagram which represents vapor unmixed with liquid, except in the vicinity of the line of saturation. In the volume-pressure diagram of the same body, the isothermals, isentropics and isodynamics, drawn for a perfect gas for the same values of  $a$  and  $c$ , will have the same relations to the true isothermals, etc.

In that part of any diagram which represents a mixture of vapor and liquid, the isopiestic and isothermals will be identical, as the pressure is determined by the temperature alone. In both the diagrams which we are now comparing, they will be straight and parallel to the axis of abscissas. The form of the isometrics and isodynamics in the entropy-temperature diagram, or that of the isentropics and isodynamics in the volume-pressure diagram, will depend upon the nature of the fluid, and probably cannot be expressed by any simple equations. The following property, however, renders it easy to construct equidifferent systems of these lines, viz: any such system will divide any isothermal (isopiestic) into equal segments.

It remains to consider that part of the diagram which represents the body when entirely in the condition of liquid. The fundamental characteristic of this condition of matter is that the volume is very nearly constant, so that variations of volume are generally entirely inappreciable when represented graphically on the same scale on which the volume of the body in the state of vapor is represented, and both the variations of volume and the connected variations of the connected quantities may be, and generally are, neglected by the side of the variations of the same quantities which occur when the body passes to the state of vapor.

Let us make, then, the usual assumption that  $v$  is constant, and see how the general equations (1), (2), (3) and (4) are thereby affected. We have first,

$$\begin{aligned} dv &= 0, \\ \text{then } dW &= 0, \\ \text{and } d\varepsilon &= t d\eta. \\ \text{If we add } dH &= t d\eta, \end{aligned}$$

these four equations will evidently be equivalent to the three independent equations (1), (2) and (3), combined with the assumption which we have just made. For a liquid, then,  $\epsilon$ , instead of being a function of two quantities  $v$  and  $\eta$ , is a function of  $\eta$  alone,— $t$  is also a function of  $\eta$  alone, being equal to the differential co-efficient of the function  $\epsilon$ ; that is, the value of one of the three quantities  $t$ ,  $\epsilon$  and  $\eta$ , is sufficient to determine the other two. The value of  $v$ , moreover, is fixed without reference to the values of  $t$ ,  $\epsilon$  and  $\eta$  (so long as these do not pass the limits of values possible for liquidity); while  $p$  does not enter into the equations, i. e.,  $p$  may have any value (within certain limits) without affecting the values of  $t$ ,  $\epsilon$ ,  $\eta$  or  $v$ . If the body change its state, continuing always liquid, the value of  $W$  for such a change is 0, and that of  $H$  is determined by the values of any one of the three quantities  $t$ ,  $\epsilon$  and  $\eta$ . It is, therefore, the relations between  $t$ ,  $\epsilon$ ,  $\eta$  and  $H$ , for which a graphical expression is to be sought; a method, therefore, in which the co-ordinates of the diagram are made equal to the volume and pressure, is totally inapplicable to this particular case;  $v$  and  $p$  are indeed the only two of the five functions of the state of the body,  $v$ ,  $p$ ,  $t$ ,  $\epsilon$  and  $\eta$ , which have no relations either to each other, or to the other three, or to the quantities  $W$  and  $H$ , to be expressed.\* The values of  $v$  and  $p$  do not really determine the state of an incompressible fluid,—the values of  $t$ ,  $\epsilon$  and  $\eta$  are still left undetermined, so that through every point in the volume-pressure diagram which represents the liquid there must pass (in general) an infinite number of isothermals, isodynamics and isentropics. The character of this part of the diagram is as follows:—the states of liquidity are represented by the points of a line parallel to the axis of pressures, and the isothermals, isodynamics and isentropics, which cross the field of partial vaporization and meet this line, turn upward and follow its course.†

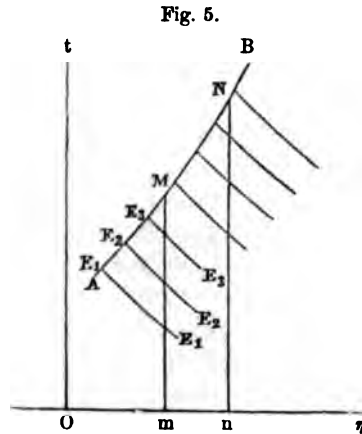
In the entropy-temperature diagram the relations of  $t$ ,  $\epsilon$  and  $\eta$  are distinctly visible. The line of liquidity is a curve AB (fig. 5) determined by the relation between  $t$  and  $\eta$ . This curve is also an iso-

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\* That is,  $v$  and  $p$  have no such relations to the other quantities, as are expressible by equations;  $p$ , however, cannot be less than a certain function of  $t$ .

† All these difficulties are of course removed when the differences of volume of the liquid at different temperatures are rendered appreciable on the volume-pressure diagram. This can be done in various ways,—among others, by choosing as the body to which  $v$ , etc., refer, a sufficiently large quantity of the fluid. But, however we do it, we must evidently give up the possibility of representing the body in the state of vapor in the same diagram without making its dimensions enormous.

metric. Every point of it has a definite volume, temperature, entropy and energy. The latter is indicated by the isodynamics  $E, E_1, E_2, E_3,$  etc., which cross the region of partial vaporization and terminate in the line of liquidity. (They do not in this diagram turn and follow the line.) If the body pass from one state to another, remaining liquid, as from  $M$  to  $N$  in the figure, the heat received is represented as usual by the area  $MNnm$ . That the work done is nothing, is indicated by the fact that the line  $AB$  is an isometric. Only the isopiestic in this diagram are superposed in the line of fluidity, turning downward where they meet this line and following its course, so that for any point in this line the pressure is undetermined. This is, however, no inconvenience in the diagram, as it simply expresses the fact of the case, that when all the quantities  $v, t, \epsilon$  and  $\eta$  are fixed, the pressure is still undetermined.



DIAGRAMS IN WHICH THE ISOMETRICS, ISOPIESTICS, ISOTHERMALS, ISODYNAMICS AND ISENTROPICS OF A PERFECT GAS ARE ALL STRAIGHT LINES.

There are many cases in which it is of more importance that it should be easy to draw the lines of equal volume, pressure, temperature, energy and entropy, than that work and heat should be represented in the simplest manner. In such cases it may be expedient to give up the condition that the scale ( $\gamma$ ) of work and heat shall be constant, when by that means it is possible to gain greater simplicity in the form of the lines just mentioned.

In the case of a perfect gas, the three relations between the quantities  $v, p, t, \epsilon$  and  $\eta$  are given on page 321, equations (A), (B) and (D). These equations may be easily be transformed into the three

$$\log p + \log v - \log t = \log a, \tag{H}$$

$$\log \epsilon - \log t = \log c, \tag{I}$$

$$\eta - c \log \epsilon - a \log v = 0; \tag{J}$$

so that the three relations between the quantities  $\log v, \log p, \log t, \log \epsilon,$  and  $\eta$  are expressed by linear equations, and it will be possible to make the five systems of lines all rectilinear in the same diagram, the distances of the isometrics being proportional to the differences

of the logarithms of the volumes, the distances of the isopiestic being proportional to the differences of the logarithms of the pressures, and so with the isothermals and the isodynamics,—the distances of the isentropics, however, being proportional to the differences of entropy simply.

The scale of work and heat in such a diagram will vary inversely as the temperature. For if we imagine systems of isentropics and isothermals drawn throughout the diagram for equal small differences of entropy and temperature, the isentropics will be equidistant, but the distances of the isothermals will vary inversely as the temperature, and the small quadrilaterals into which the diagram is divided will vary in the same ratio:  $\therefore \gamma \propto 1 \div t$ . (See page 313.)

So far, however, the form of the diagram has not been completely defined. This may be done in various ways: e. g., if  $x$  and  $y$  be the rectangular co-ordinates, we may make

$$\left\{ \begin{array}{l} x = \log v, \\ y = \log p; \end{array} \right. \text{ or } \left\{ \begin{array}{l} x = \eta, \\ y = \log t; \end{array} \right. \text{ or } \left\{ \begin{array}{l} x = \log v, \text{ etc.} \\ y = \eta; \end{array} \right.$$

Or we may set the condition that the logarithms of volume, of pressure and of temperature, shall be represented in the diagram on the same scale. (The logarithms of energy

are necessarily represented on the same scale as those of temperature.) This will require that the isometrics, isopiestic and isothermals cut one another at angles of  $60^\circ$ .

The general character of all these diagrams, which may be derived from one another by projection by parallel lines, may be illustrated by the case in which  $x = \log v$ , and  $y = \log p$ .

Through any point A (fig. 6) of such a diagram let there be drawn the isometric  $vv'$ , the isopiestic  $pp''$ , the isothermal  $tt'$  and the isentropic  $\eta\eta'$ . The lines  $pp'$  and

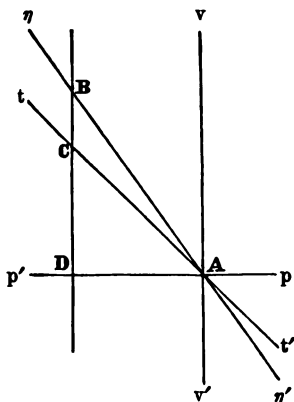
$vv'$  are of course parallel to the axes. Also by equation (H)

$$\tan tAp = \left( \frac{dy}{dx} \right)_t = \left( \frac{d \log p}{d \log v} \right)_t = -1,$$

and by (G)

$$\tan \eta Ap = \left( \frac{dy}{dx} \right)_\eta = \left( \frac{d \log p}{d \log v} \right)_\eta = -\frac{c+a}{c}.$$

Fig. 6.



Therefore, if we draw another isometric, cutting  $\eta\eta'$ ,  $tt'$ , and  $pp'$  in B, C and D,

$$\frac{BD}{CD} = \frac{c+a}{c}, \quad \frac{BC}{CD} = \frac{a}{c}, \quad \frac{CD}{BC} = \frac{c}{a}.$$

Hence, in the diagrams of different gases,  $CD \div BC$  will be proportional to the specific heat determined for equal volumes and for constant volume.

As the specific heat, thus determined, has probably the same value for most simple gases, the isentropics will have the same inclination in diagrams of this kind for most simple gases. This inclination may easily be found by a method which is independent of any units of measurement, for

$$BD : CD :: \left( \frac{d \log p}{d \log v} \right)_{\eta} : \left( \frac{d \log p}{d \log v} \right)_{t} :: \left( \frac{dp}{dv} \right)_{\eta} : \left( \frac{dp}{dv} \right)_{t},$$

i. e.,  $BD \div CD$  is equal to the quotient of the co-efficient of elasticity under the condition of no transmission of heat, divided by the co-efficient of elasticity at constant temperature. This quotient for a simple gas is generally given as 1.408 or 1.421. As  $CA \div CD = \sqrt{2} = 1.414$ ,  $BD$  is very nearly equal to  $CA$  (for simple gases), which relation it may be convenient to use in the construction of the diagram.

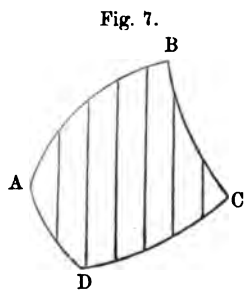
In regard to compound gases the rule seems to be, that the specific heat (determined for equal volumes and for constant volume) is to the specific heat of a simple gas inversely as the volume of the compound is to the volume of its constituents (in the condition of gas); that is, the value of  $BC \div CD$  for a compound gas is to the value of  $BC \div CD$  for a simple gas, as the volume of the compound is to the volume of its constituents. Therefore, if we compare the diagrams (formed by this method) for a simple and a compound gas, the distance  $DA$  and therefore  $CD$  being the same in each,  $BC$  in the diagram of the compound gas will be to  $BC$  in the diagram of the simple gas, as the volume of the compound is to the volume of its constituents.

Although the inclination of the isentropics is independent of the quantity of gas under consideration, the rate of increase of  $\eta$  will vary with this quantity. In regard to the rate of increase of  $t$ , it is evident that if the whole diagram be divided into squares by isopiestic and isometrics drawn at equal distances, and isothermals be drawn as diagonals to these squares, the volumes of the isometrics, the pressures of the isopiestic and the temperatures of the isothermals will each form a geometrical series, and in all these series the ratio of two contiguous terms will be the same.

The properties of the diagrams obtained by the other methods mentioned on page 326 do not differ essentially from those just described. For example, in any such diagram, if through any point we draw an isentropic, an isothermal and an isopiestic, which cut any isometric not passing through the same point, the ratio of the segments of the isometric will have the value which has been found for  $BC : CD$ .

In treating the case of vapors also, it may be convenient to use diagrams in which  $x = \log v$  and  $y = \log p$ , or in which  $x = \eta$  and  $y = \log t$ ; but the diagrams formed by these methods will evidently be radically different from one another. It is to be observed that each of these methods is what may be called a *method of definite scale* for work and heat; that is, the value of  $\gamma$  in any part of the diagram is independent of the properties of the fluid considered. In the first method  $\gamma = \frac{1}{e^{x+y}}$ , in the second  $\gamma = \frac{1}{e^y}$ . In this respect these methods have an advantage over many others. For example, if we should make  $x = \log v$ ,  $y = \eta$ , the value of  $\gamma$  in any part of the diagram would depend upon the properties of the fluid, and would probably not vary in any case, except that of a perfect gas, according to any simple law.

The conveniences of the entropy-temperature method will be found to belong in nearly the same degree to the method in which the coordinates are equal to the entropy and the logarithm of the temperature. No serious difficulty attaches to the estimation of heat and work in a diagram formed on the latter method on account of the variation of the scale on which they are represented, as this variation follows so simple a law. It may often be of use to remember that



such a diagram may be reduced to an entropy-temperature diagram by a vertical compression or extension, such that the distances of the isothermals shall be made proportional to their differences of temperature. Thus if we wish to estimate the work or heat of the circuit ABCD (fig. 7), we may draw a number of equidistant ordinates (isentropics) as if to estimate the included area, and for each of the ordinates take the differences of temperature of the points

where it cuts the circuit; these differences of temperature will be equal to the lengths of the segments made by the corresponding circuit in the entropy-temperature diagram upon a corresponding system of equidistant ordinates, and may be used to calculate the



area of the circuit in the entropy-temperature diagram, i. e., to find the work or heat required. We may find the work of any path by applying the same process to the circuit formed by the path, the isometric of the final state, the line of no pressure (or any isopiestic; see note on page 318), and the isometric of the initial state. And we may find the heat of any path by applying the same process to a circuit formed by the path, the ordinates of the extreme points and the line of absolute cold. That this line is at an infinite distance occasions no difficulty. The lengths of the ordinates in the entropy-temperature diagram which we desire are given by the temperature of points in the path determined (in either diagram) by equidistant ordinates.

The properties of the part of the entropy-temperature diagram representing a mixture of vapor and liquid, which are given on page 323, will evidently not be altered if the ordinates are made proportional to the logarithms of the temperatures instead of the temperatures simply.

The representation of specific heat in the diagram under discussion is peculiarly simple. The specific heat of any substance at constant volume or under constant pressure may be defined as the value of

$$\left(\frac{dH}{dt}\right)_v \text{ or } \left(\frac{dH}{dt}\right)_p, \text{ i. e., } \left(\frac{d\eta}{d \log t}\right)_v \text{ or } \left(\frac{d\eta}{d \log t}\right)_p,$$

for a certain quantity of the substance. Therefore, if we draw a diagram, in which  $x = \eta$  and  $y = \log t$ , for that quantity of the substance which is used for the determination of the specific heat, the tangents of the angles made by the isometrics and the isopiestic with the ordinates in the diagram will be equal to the specific heat of the substance determined for constant volume and for constant pressure respectively. Sometimes, instead of the condition of constant volume or constant pressure, some other condition is used in the determination of specific heat. In all cases, the condition will be represented by a line in the diagram, and the tangent of the angle made by this line with an ordinate will be equal to the specific heat as thus defined. If the diagram be drawn for any other quantity of the substance, the specific heat for constant volume or constant pressure, or for any other condition, will be equal to the tangent of the proper angle in the diagram, multiplied by the ratio of the quantity of the substance for which the specific heat is determined to the quantity for which the diagram is drawn.\*

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\* From this general property of the diagram, its character in the case of a perfect gas might be immediately deduced.

## THE VOLUME-ENTROPY DIAGRAM.

The method of representation, in which the co-ordinates of the point in the diagram are made equal to the volume and entropy of the body, presents certain characteristics which entitle it to a somewhat detailed consideration, and for some purposes give it substantial advantages over any other method. We might anticipate some of these advantages from the simple and symmetrical form of the general equations of thermodynamics, when volume and entropy are chosen as independent variables, viz:—\*

$$p = - \frac{d\varepsilon}{dv}, \quad (11)$$

$$t = \frac{d\varepsilon}{d\eta}, \quad (12)$$

$$dW = p \, dv,$$

$$dH = t \, d\eta.$$

Eliminating  $p$  and  $t$  we have also

$$dW = - \frac{d\varepsilon}{dv} \, dv, \quad (13)$$

$$dH = \frac{d\varepsilon}{d\eta} \, d\eta. \quad (14)$$

The geometrical relations corresponding to these equations are in the volume-entropy diagram extremely simple. To fix our ideas, let the axes of volume and entropy be horizontal and vertical respectively, volume increasing toward the right and entropy upward. Then the pressure taken negatively will equal the ratio of the difference of energy to the difference of volume of two adjacent points in the same horizontal line, and the temperature will equal the ratio of the difference of energy to the difference of entropy of two adjacent points in the same vertical line. Or, if a series of isodynamics be drawn for equal infinitesimal differences of energy, any series of horizontal lines will be divided into segments inversely proportional to the pressure, and any series of vertical lines into segments inversely proportional to the temperature. We see by equations (13) and (14), that for a motion parallel to the axis of volume, the heat received is 0, and the work done is equal to the decrease of the energy, while for

\* See page 310, equations (2), (3) and (4).

In general, in this article, where differential co-efficients are used, the quantity which is constant in the differentiation is indicated by a subscript letter. In this discussion of the volume-entropy diagram, however,  $v$  and  $\eta$  are uniformly regarded as the independent variables, and the subscript letter is omitted.

a motion parallel to the axis of entropy, the work done is 0, and the heat received is equal to the increase of the energy. These two propositions are true either for elementary paths or for those of finite length. In general, the work for any element of a path is equal to the product of the pressure in that part of the diagram into the horizontal projection of the element of the path, and the heat received is equal to the product of the temperature into the vertical projection of the element of the path.

If we wish to estimate the value of the integrals  $\int p dv$  and  $\int t d\eta$ , which represent the work and heat of any path, by means of measurements upon the diagram, or if we wish to appreciate readily by the eye the approximate value of these expressions, or if we merely wish to illustrate their meaning by means of the diagram; for any of these purposes the diagram which we are now considering will have the advantage that it represents the differentials  $dv$  and  $d\eta$  more simply and clearly than any other.

But we may also estimate the work and heat of any path by means of an integration extending over the elements of an area, viz: by the formulæ of page 315,

$$\begin{aligned}
 W^c = H^c &= \sum^c \frac{1}{\gamma} \delta A, \\
 W^s &= \sum^{[S, v'', p^0, v']} \frac{1}{\gamma} \delta A, \\
 H^s &= \sum^{[S, \eta'', \epsilon, \tau]} \frac{1}{\gamma} \delta A.
 \end{aligned}$$

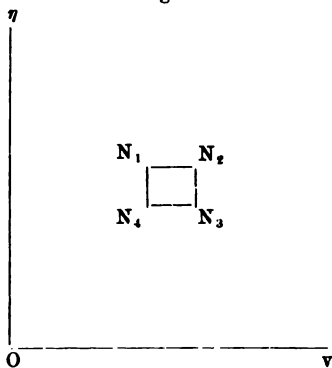
In regard to the limits of integration in these formulæ, we see that for the work of any path which is not a circuit, the bounding line is composed of the path, the line of no pressure and two vertical lines, and for the heat of the path, the bounding line is composed of the path, the line of absolute cold and two horizontal lines.

As the sign of  $\gamma$ , as well as that of  $\delta A$ , will be indeterminate until we decide in which direction an area must be circumscribed in order to be considered positive, we will call an area positive which is circumscribed in the direction in which the hands of a watch move. This choice, with the positions of the axes of volume and entropy which we have supposed, will make the value of  $\gamma$  in most cases positive, as we shall see hereafter.

The value of  $\gamma$ , in a diagram drawn according to this method, will depend upon the properties of the body for which the diagram is drawn. In this respect, this method differs from all the others which

have been discussed in detail in this article. It is easy to find an expression for  $\gamma$  depending simply upon the variations of the energy,

Fig. 8.



by comparing the area and the work or heat of an infinitely small circuit in the form of a rectangle having its sides parallel to the two axes.

Let  $N_1N_2N_3N_4$  (fig. 8) be such a circuit, and let it be described in the order of the numerals, so that the area is positive. Also let  $\varepsilon_1, \varepsilon_2, \varepsilon_3, \varepsilon_4$  represent the energy at the four corners. The work done in the four sides in order commencing at  $N_1$ , will be  $\varepsilon_1 - \varepsilon_2, 0, \varepsilon_3 - \varepsilon_4, 0$ . The total work, therefore, for the rectangular circuit is

$$\varepsilon_1 - \varepsilon_2 + \varepsilon_3 - \varepsilon_4.$$

Now as the rectangle is infinitely small, if we call its sides  $dv$  and  $d\eta$ , the above expression will be equivalent to

$$- \frac{d^2\varepsilon}{dv d\eta} dv d\eta.$$

Dividing by the area  $dv d\eta$ , and writing  $\gamma_{v, \eta}$  for the scale of work and heat in a diagram of this kind, we have

$$\frac{1}{\gamma_{v, \eta}} = - \frac{d^2\varepsilon}{dv d\eta} = \frac{dp}{d\eta} = - \frac{dt}{dv}. \quad (15)$$

The two last expressions for the value of  $1/\gamma_{v, \eta}$  indicate that the value of  $\gamma_{v, \eta}$  in different parts of the diagram will be indicated proportionally by the segments into which vertical lines are divided by a system of equidifferent isopiestic, and also by the segments into which horizontal lines are divided by a system of equidifferent isothermals. These results might also be derived directly from the propositions on page 313.

As, in almost all cases, the pressure of a body is increased when it receives heat without change of volume,  $\frac{dp}{d\eta}$  is in general positive, and the same will be true of  $\gamma_{v, \eta}$  under the assumptions which we have made in regard to the directions of the axes (page 330) and the definition of a positive area (page 331).

In the estimation of work and heat it may often be of use to consider the deformation necessary to reduce the diagram to one of constant scale for work and heat. Now if the diagram be so deformed,

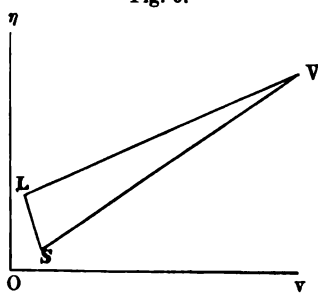
that each point remains in the same vertical line, but moves in this line so that all isopiestic become straight and horizontal lines, at distances proportional to their differences of pressure, it will evidently become a volume-pressure diagram. Again, if the diagram be so deformed that each point remains in the same horizontal line, but moves in it so that isothermals becomes straight and vertical lines at distances proportional to their differences of temperature, it will become a entropy-temperature diagram. These considerations will enable us to compute numerically the work or heat of any path which is given in a volume-entropy diagram, when the pressure and temperature are known for all points of the path, in a manner analogous to that explained on page 328.

The ratio of any element of area in the volume-pressure or the entropy-temperature diagram, or in any other in which the scale of work and heat is unity, to the corresponding element in the volume-entropy diagram is represented by  $\frac{1}{\gamma_{v,\eta}}$  or  $-\frac{d^2\varepsilon}{dv d\eta}$ . The cases in which this ratio is 0, or changes its sign, demand especial attention, as in such cases the diagrams of constant scale fail to give a satisfactory representation of the properties of the body, while no difficulty or inconvenience arises in the use of the volume-entropy diagram.

As  $-\frac{d^2\varepsilon}{dv d\eta} = \frac{dp}{d\eta}$ , its value is evidently zero in that part of the diagram which represents the body when in part solid, in part liquid, and in part vapor. The properties of such a mixture are very simply and clearly exhibited in the volume-entropy diagram.

Let the temperature and the pressure of the mixture, which are independent of the proportions of vapor, solid and liquid, be denoted by  $t'$  and  $p'$ . Also let V, L and S (fig. 9) be points of the diagram which indicate the volume and entropy of the body in three perfectly defined states, viz: that of a vapor of temperature  $t'$  and pressure  $p'$ , that of a liquid of the same temperature and pressure, and that of a solid of the same temperature and pressure. And let  $v_v, \eta_v, v_L, \eta_L, v_s, \eta_s$  denote the volume and entropy of these states. The position of the point which represents the body, when part is vapor, part liquid, and part solid, these parts being as  $\mu, \nu$ , and  $1-\mu-\nu$ , is determined by the equations

Fig. 9.



$$v = \mu v_V + \nu v_L + (1 - \mu - \nu) v_S,$$

$$\eta = \mu \eta_V + \nu \eta_L + (1 - \mu - \nu) \eta_S,$$

where  $v$  and  $\eta$  are the volume and entropy of the mixture. The truth of the first equation is evident. The second may be written

$$\eta - \eta_S = \mu (\eta_V - \eta_S) + \nu (\eta_L - \eta_S),$$

or multiplying by  $t'$ ,

$$t' (\eta - \eta_S) = \mu t' (\eta_V - \eta_S) + \nu t' (\eta_L - \eta_S).$$

The first member of this equation denotes the heat necessary to bring the body from the state S to the state of the mixture in question under the constant temperature  $t'$ , while the terms of the second member denote separately the heat necessary to vaporize the part  $\mu$ , and to liquefy the part  $\nu$  of the body.

The values of  $v$  and  $\eta$  are such as would give the center of gravity of masses  $\mu$ ,  $\nu$  and  $1 - \mu - \nu$  placed at the points V, L and S.\* Hence the part of the diagram which represents a mixture of vapor, liquid and solid, is the triangle VLS. The pressure and temperature are constant for this triangle, i. e., an isopiestic and also an isothermal here expand to cover a space. The isodynamics are straight and equidistant for equal differences of energy. For  $\frac{d\varepsilon}{dv} = -p'$ , and  $\frac{d\varepsilon}{d\eta} = t'$ , both of which are constant throughout the triangle.

This case can be but very imperfectly represented in the volume-pressure, or in the entropy-temperature diagram. For all points in the same vertical line in the triangle VLS will, in the volume-pressure diagram, be represented by a single point, as having the same volume and pressure. And all the points in the same horizontal line will be represented in the entropy-temperature diagram by a single point, as having the same entropy and temperature. In either diagram, the whole triangle reduces to a straight line. It must reduce to a line in any diagram whatever of constant scale, as its area must become 0 in such a diagram. This must be regarded as a defect in these diagrams, as essentially different states are represented by the same point. In consequence, any circuit within the triangle

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\* These points will not be in the same straight line unless

$$t' (\eta_V - \eta_S) : t' (\eta_L - \eta_S) :: v_V - v_S : v_L - v_S,$$

a condition very unlikely to be fulfilled by any substance. The first and second terms of this proportion denote the heat of vaporization (from the solid state) and that of liquefaction.

VLS will be represented in any diagram of constant scale by two paths of opposite directions superposed, the appearance being as if a body should change its state and then return to its original state by inverse processes, so as to repass through the same series of states. It is true that the circuit in question is like this combination of processes in one important particular, viz: that  $W = H = 0$ , i. e., there is no transformation of heat into work. But this very fact, that a circuit without transformation of heat into work is possible, is worthy of distinct representation.

A body may have such properties that in one part of the volume-entropy diagram  $\frac{1}{\gamma_{v,\eta}}$ , i. e.,  $\frac{dp}{d\eta}$  is positive and in another negative. These parts of the diagram may be separated by a line, in which  $\frac{dp}{d\eta} = 0$ , or by one in which  $\frac{dp}{d\eta}$  changes abruptly from a positive to a negative value.\* (In part, also, they may be separated by an area in which  $\frac{dp}{d\eta} = 0$ .) In the representation of such cases in any diagram of constant scale, we meet with a difficulty of the following nature.

Let us suppose that on the right of the line LL (fig. 10) in a volume-entropy diagram,  $\frac{dp}{d\eta}$  is positive, and on the left negative. Then, if we draw any circuit ABCD on the right side of LL, the direction being that of the hands of a watch, the work and heat of the circuit will be positive. But if we draw any circuit EFGH in the same direction on the other side of the line

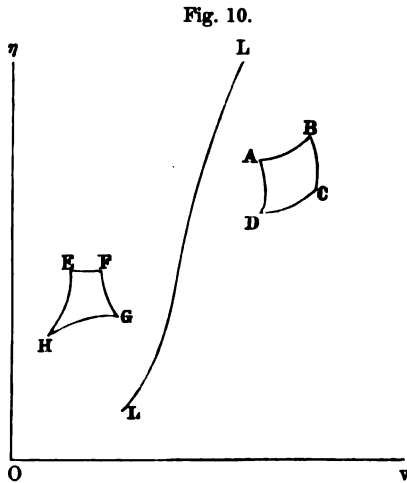


Fig. 10.

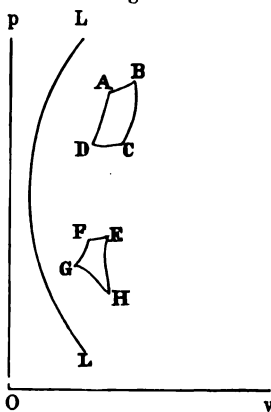
LL, the work and heat will be negative. For

$$W = H = \sum \frac{1}{\gamma_{v,\eta}} \delta A = \sum \frac{dp}{d\eta} \delta A,$$

\* The line which represents the various states of water at its maximum density for various constant pressures is an example of the first case. A substance which as a liquid has no proper maximum density for constant pressure, but which expands in solidifying, affords an example of the second case.

and the direction of the circuits makes the areas positive in both cases. Now if we should change this diagram into any diagram of constant scale, the areas of the circuits, as representing proportionally the work done in each case, must necessarily have opposite signs, i. e., the direction of the circuits must be opposite. We will suppose that the work done is positive in the diagram of constant scale, when the direction of the circuit is that of the hands of a watch. Then, in

Fig. 11.



that diagram, the circuit ABCD would have that direction, and the circuit EFGH the contrary direction, as in figure 11. Now if we imagine an indefinite number of circuits on each side of LL in the volume-entropy diagram, it will be evident that to transform such a diagram into one of constant scale, so as to change the direction of all the circuits on one side of LL, and of none on the other, the diagram must be *folded over* along that line; so that the points on one side of LL in a diagram of constant scale do not represent any states of the body, while on the other side of this line, each point, for a certain distance at least, represents two

different states of the body, which in the volume-entropy diagram are represented by points on opposite sides of the line LL. We have thus in a part of the field two diagrams superposed, which must be carefully distinguished. If this be done, as by the help of different colors, or of continuous and dotted lines, or otherwise, and it is remembered that there is no continuity between these superposed diagrams, except along the bounding line LL, all the general theorems which have been developed in this article can be readily applied to the diagram. But to the eye or to the imagination, the figure will necessarily be much more confusing than a volume-entropy diagram.

If  $\frac{dp}{d\eta} = 0$  for the line LL, there will be another inconvenience in the use of any diagram of constant scale, viz: in the vicinity of the line LL,  $\frac{dp}{d\eta}$ , i. e.,  $1 \div \gamma_{v, \eta}$  will have a very small value, so that areas will be very greatly reduced in the diagram of constant scale, as compared with the corresponding areas in the volume-entropy diagram. Therefore, in the former diagram, either the isometrics, or the isentropics, or both, will be crowded together in the vicinity of the line LL, so that this part of the diagram will be necessarily indistinct.



It may occur, however, in the volume-entropy diagram, that the same point must represent two different states of the body. This occurs in the case of liquids which can be vaporized. Let  $MM$  (fig. 12) be the line representing the states of the liquid bordering upon vaporization. This line will be near to the axis of entropy, and nearly parallel to it. If the body is in a state represented by a point of the line  $MM$ , and is compressed without addition or subtraction of heat, it will remain of course liquid. Hence, the points of the space immediately on the left of  $MM$  represent simple liquid. On the other hand, the body being in the original state, if its volume should be increased without addition or subtraction of heat, and if the conditions necessary for vaporization are present (conditions relative to the

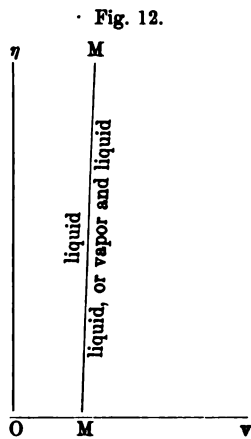


Fig. 12.

body enclosing the liquid in question, etc.), the liquid will become partially vaporized, but if these conditions are not present, it will continue liquid. Hence, every point on the right of  $MM$  and sufficiently near to it represents two different states of the body, in one of which it is partially vaporized, and in the other it is entirely liquid. If we take the points as representing the mixture of vapor and liquid, they form one diagram, and if we take them as representing simple liquid, they form a totally different diagram superposed on the first. There is evidently no continuity between these diagrams except at the line  $MM$ ; we may regard them as upon separate sheets united only along  $MM$ . For the body cannot pass from the state of partial vaporization to the state of liquid except at this line. The reverse process is indeed possible; the body can pass from the state of superheated liquid to that of partial vaporization, if the conditions of vaporization alluded to above are supplied, or if the increase of volume is carried beyond a certain limit, but not by gradual changes or reversible processes. After such a change, the point representing the state of the body will be found in a different position from that which it occupied before, but the change of state cannot be properly represented by any path, as during the change the body does not satisfy that condition of uniform temperature and pressure which has been assumed throughout this article, and which is necessary for the graphical methods under discussion. (See note on page 309.)

Of the two superposed diagrams, that which represents simple liquid is a continuation of the diagram on the left of  $MM$ . The iso-

piestics, isothermals and isodynamics pass from one to the other without abrupt change of direction or curvature. But that which represents a mixture of vapor and liquid will be different in its character, and its isopiestic and isothermals will make angles in general with the corresponding lines in the diagram of simple liquid. The isodynamics of the diagram of the mixture, and those of the diagram of simple liquid, will differ in general in curvature at the line MM, but not in direction, for  $\frac{d\varepsilon}{dv} = -p$  and  $\frac{d\varepsilon}{d\eta} = t$ .

The case is essentially the same with some substances, as water, for example, about the line which separates the simple liquid from a mixture of liquid and solid.

In these cases the inconvenience of having one diagram superposed upon another cannot be obviated by any change of the principle on which the diagram is based. For no distortion can bring the three sheets, which are united along the line MM (one on the left and two on the right), into a single plane surface without superposition. Such cases, therefore, are radically distinguished from those in which the superposition is caused by an unsuitable method of representation.

To find the character of a volume-entropy diagram of a perfect gas, we may make  $\varepsilon$  constant in equation (D) on page 321, which will give for the equation of an isodynamic and isothermal

$$\eta = a \log v + \text{Const.},$$

and we may make  $p$  constant in equation (G), which will give for the equation of an isopiestic

$$\eta = (a + c) \log v + \text{Const.}$$

It will be observed that all the isodynamics and isothermals can be drawn by a single pattern and so also with the isopiestic.

The case will be nearly the same with vapors in a part of the diagram. In that part of the diagram which represents a mixture of liquid and vapor, the isothermals, which of course are identical with the isopiestic, are straight lines. For when a body is vaporized under constant pressure and temperature, the quantities of heat received are proportional to the increments of volume; therefore, the increments of entropy are proportional to the increments of volume.

As  $\frac{d\varepsilon}{dv} = -p$  and  $\frac{d\varepsilon}{d\eta} = t$ , any isothermal is cut at the same angle by all the isodynamics, and is divided into equal segments by equidifferent isodynamics. The latter property is useful in drawing systems of equidifferent isodynamics.

ARRANGEMENT OF THE ISOMETRIC, ISOPIESTIC, ISOTHERMAL AND ISENTROPIC ABOUT A POINT.

The arrangement of the isometric, the isopiestic, the isothermal and the isentropic drawn through any same point, in respect to the order in which they succeed one another around that point, and in respect to the sides of these lines toward which the volume, pressure, temperature and entropy increase, is not altered by any deformation of the surface on which the diagram is drawn, and is therefore independent of the method by which the diagram is formed.\* This arrangement is determined by certain of the most characteristic thermodynamic properties of the body in the state in question, and serves in turn to indicate these properties. It is determined, namely, by the value of  $\left(\frac{dp}{d\eta}\right)_v$  as positive, negative, or zero, i. e., by the effect of heat as increasing or diminishing the pressure when the volume is maintained constant, and by the nature of the internal thermodynamic equilibrium of the body as stable or neutral,—an unstable equilibrium, except as a matter of speculation, is of course out of the question.

Let us first examine the case in which  $\left(\frac{dp}{d\eta}\right)_v$  is positive and the equilibrium is stable. As  $\left(\frac{dp}{d\eta}\right)_v$  does not vanish at the point in question, there is a definite isopiestic passing through that point, on one side of which the pressures are greater, and on the other less, than on the line itself. As  $\left(\frac{dt}{dv}\right)_\eta = -\left(\frac{dp}{d\eta}\right)_v$ , the case is the same with the isothermal. It will be convenient to distinguish the sides of the isometric, isopiestic, etc., on which the volume, pressure, etc., increase, as the *positive* sides of these lines. The condition of stability requires that, when the pressure is constant, the temperature shall increase with the heat received,—therefore with the entropy. This may be written  $[dt : d\eta]_p > 0$ .† It also requires that, when there is no

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\* It is here assumed that, in the vicinity of the point in question, each point in the diagram represents only one state of the body. The propositions developed in the following pages cannot be applied to points of the line where two superposed diagrams are united (see pages 335-338) without certain modifications.

† As the notation  $\frac{dt}{d\eta}$  is used to denote the limit of the ratio of  $dt$  to  $d\eta$ , it would not be quite accurate to say that the condition of stability requires that  $\left(\frac{dt}{d\eta}\right)_p > 0$ . This

transmission of heat, the pressure should increase as the volume diminishes, i. e., that  $[dp : dv]_{\eta} < 0$ . Through the point in question, A (fig. 13), let there be drawn the isometric  $vv'$  and the isentropic  $\eta\eta'$ , and let the positive sides of these lines be indicated as in the figure. The conditions  $\left(\frac{dp}{d\eta}\right)_v > 0$  and  $[dp : dv]_{\eta} < 0$  require that the pressure at  $v$  and at  $\eta$  shall be greater than at A, and hence, that the isopiestic shall fall as  $pp'$  in the figure, and have its positive side turned as indicated. Again, the conditions

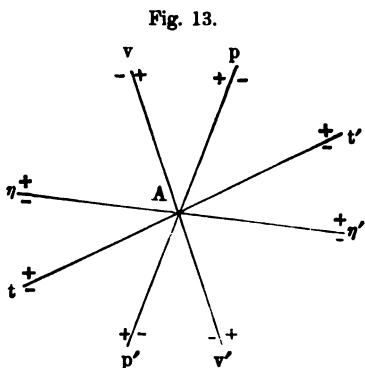


Fig. 13.

$\left(\frac{dt}{dv}\right)_{\eta} < 0$  and  $[dt : d\eta]_p > 0$  require that the temperature at  $\eta$  and at  $p$  shall be greater than at A, and hence, that the isothermal shall fall as  $tt'$  and have its positive side turned as indicated. As it is not necessary that

$\left(\frac{dt}{d\eta}\right)_p > 0$ , the lines  $pp'$  and  $tt'$  may be tangent to one another at A,

provided that they cross one another, so as to have the same order about the point A as is represented in the figure; i. e., they may have a contact of the second (or any even) order.\* But the condition that

$\left(\frac{dp}{d\eta}\right)_v > 0$ , and hence  $\left(\frac{dt}{dv}\right)_{\eta} < 0$ , does not allow  $pp'$  to be tangent to

$vv'$ , nor  $tt'$  to  $\eta\eta'$ .

If  $\left(\frac{dp}{d\eta}\right)_v$  be still positive, but the equilibrium be neutral, it will be possible for the body to change its state without change either of temperature or of pressure; i. e., the isothermal and isopiestic will be

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condition requires that the ratio of the differences of temperature and entropy between the point in question and any other infinitely near to it and upon the same isopiestic should be positive. It is not necessary that the limit of this ratio should be positive.

\* An example of this is doubtless to be found at the critical point of a fluid. See Dr. Andrews "On the continuity of the gaseous and liquid states of matter." Phil. Trans., vol. 159, p. 575.

If the isothermal and isopiestic have a simple tangency at A, on one side of that point they will have such directions as will express an unstable equilibrium. A line drawn through all such points in the diagram will form a boundary to the possible part of the diagram. It may be that the part of the diagram of a fluid, which represents the superheated liquid state, is bounded on one side by such a line.

identical. The lines will fall as in figure 13, except that the isothermal and isopiestic will be superposed.

In like manner, if  $\left(\frac{dp}{d\eta}\right)_v < 0$ , it may be proved that the lines will fall as in figure 14 for stable equilibrium, and in the same way for neutral equilibrium, except that  $pp'$  and  $tt'$  will be superposed.\*

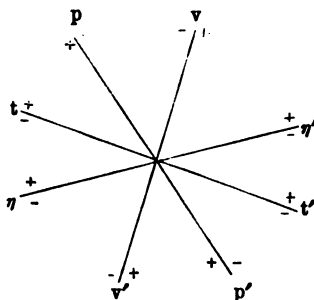
The case that  $\left(\frac{dp}{d\eta}\right)_v = 0$  includes a considerable number of conceivable cases, which would require to be distinguished. It will be sufficient to mention those most likely to occur.

In a field of stable equilibrium it may occur that  $\left(\frac{dp}{d\eta}\right)_v = 0$  along a line, on one side of which  $\left(\frac{dp}{d\eta}\right)_v > 0$ , and on the other side  $\left(\frac{dp}{d\eta}\right)_v < 0$ . At any point in such a line the isopiestic will be tangent to the isometrics and the isothermals to the isentropics. (See, however, note on page 339.)

In a field of neutral equilibrium representing a mixture of two different states of the substance, where the isothermals and isopiestic are identical, a line may occur which has the threefold character of an isometric, an isothermal and an isopiestic. For such a line  $\left(\frac{dp}{d\eta}\right)_v = 0$ . If  $\left(\frac{dp}{d\eta}\right)_v$  has opposite signs on opposite sides of this line, it will be an isothermal of maximum or minimum temperature.†

The case in which the body is partly solid, partly liquid and partly vapor has already been sufficiently discussed. (See page 333).

Fig. 14.



\* When it is said that the arrangement of the lines in the diagram must be like that in figure 13 or in figure 14, it is not meant to exclude the case in which the figure (13 or 14) must be turned over, in order to correspond with the diagram. In the case, however, of diagrams formed by any of the methods mentioned in this article, if the directions of the axes be such as we have assumed, the agreement with figure 13 will be *without inversion*, and the agreement with figure 14 will also be *without inversion* for volume-entropy diagrams, but *with inversion* for volume-pressure or entropy-temperature diagrams, or those in which  $x = \log v$  and  $y = \log p$ , or  $x = \eta$  and  $y = \log t$ .

† As some liquids expand and others contract in solidifying, it is possible that there are some which will solidify either with expansion, or without change of volume, or with contraction, according to the pressure. If any such there are, they afford examples of the case mentioned above.

The arrangement of the isometric, isopiestic, etc., as given in figure 13, will indicate directly the sign of any differential co-efficient of the form  $\left(\frac{du}{dv}\right)_z$ , where  $u$ ,  $v$  and  $z$  may be any of the quantities  $v$ ,  $p$ ,  $t$ ,  $\eta$  (and  $\epsilon$ , if the isodynamic be added in the figure). The value of such a differential co-efficient will be indicated, when the rates of increase of  $v$ ,  $p$ , etc., are indicated, as by isometrics, etc., drawn both for the values of  $v$ , etc., at the point A, and for values differing from these by a small quantity. For example, the value of  $\left(\frac{dp}{dv}\right)_\eta$  will be indicated by the ratio of the segments intercepted upon an isentropic by a pair of isometrics and a pair of isopiestic, of which the differences of volume and pressure have the same numerical value. The case in which  $W$  or  $H$  appears in the numerator or denominator instead of a function of the state of the body, can be reduced to the preceding by the substitution of  $p dv$  for  $dW$ , or that of  $t d\eta$  for  $dH$ .

In the foregoing discussion, the equations which express the fundamental principles of thermodynamics in an analytical form have been assumed, and the aim has only been to show how the same relations may be expressed geometrically. It would, however, be easy, starting from the first and second laws of thermodynamics as usually enunciated, to arrive at the same results without the aid of analytical formulæ,—to arrive, for example, at the conception of energy, of entropy, of absolute temperature, in the construction of the diagram without the analytical definitions of these quantities, and to obtain the various properties of the diagram without the analytical expression of the thermodynamic properties which they involve. Such a course would have been better fitted to show the independence and sufficiency of a graphical method, but perhaps less suitable for an examination of the comparative advantages or disadvantages of different graphical methods.

The possibility of treating the thermodynamics of fluids by such graphical methods as have been described evidently arises from the fact that the state of the body considered, like the position of a point in a plane, is capable of two and only two independent variations. It is, perhaps, worthy of notice, that when the diagram is only used to demonstrate or illustrate general theorems, it is not necessary, although it may be convenient, to assume any particular method of forming the diagram; it is enough to suppose the different states of the body to be represented continuously by points upon a sheet.

**XIV. A METHOD OF GEOMETRICAL REPRESENTATION OF THE THERMODYNAMIC PROPERTIES OF SUBSTANCES BY MEANS OF SURFACES. BY J. WILLARD GIBBS.**

THE leading thermodynamic properties of a fluid are determined by the relations which exist between the volume, pressure, temperature, energy, and entropy of a given mass of the fluid in a state of thermodynamic equilibrium. The same is true of a solid in regard to those properties which it exhibits in processes in which the pressure is the same in every direction about any point of the solid. But all the relations existing between these five quantities for any substance (three independent relations) may be deduced from the single relation existing for that substance between the volume, energy, and entropy. This may be done by means of the general equation,

$$d\varepsilon = t d\eta - p dv, \quad (1)^*$$

that is,

$$p = - \left( \frac{d\varepsilon}{dv} \right)_{\eta}, \quad (2)$$

$$t = \left( \frac{d\varepsilon}{d\eta} \right)_v, \quad (3)$$

where  $v$ ,  $p$ ,  $t$ ,  $\varepsilon$ , and  $\eta$  denote severally the volume, pressure, absolute temperature, energy, and entropy of the body considered. The subscript letter after the differential coefficient indicates the quantity which is supposed constant in the differentiation.

*Representation of Volume, Entropy, Energy, Pressure, and Temperature.*

Now the relation between the volume, entropy, and energy may be represented by a surface, most simply if the rectangular co-ordinates of the various points of the surface are made equal to the volume, entropy, and energy of the body in its various states. It may be interesting to examine the properties of such a surface, which we will call the thermodynamic surface of the body for which it is formed.†

\* For the demonstration of this equation, and in regard to the units used in the measurement of the quantities, the reader is referred to page 310 of this volume.

† Professor J. Thomson has proposed and used a surface in which the co-ordinates are proportional to the volume, pressure, and temperature of the body. (Proc. Roy. Soc., Nov. 16, 1871, vol. xx, p. 1; and Phil. Mag., vol. xliii, p. 227). It is evident,

To fix our ideas, let the axes of  $v$ ,  $\eta$ , and  $\epsilon$  have the directions usually given to the axes of X, Y, and Z ( $v$  increasing to the right,  $\eta$  forward, and  $\epsilon$  upward). Then the pressure and temperature of the state represented by any point of the surface are equal to the tangents of the inclinations of the surface to the horizon at that point, as measured in planes perpendicular to the axes of  $\eta$  and of  $v$  respectively. (Eqs. 2 and 3). It must be observed, however, that in the first case the angle of inclination is measured upward from the direction of *decreasing*  $v$ , and in the second, upward from the direction of *increasing*  $\eta$ . Hence, the tangent plane at any point indicates the temperature and pressure of the state represented. It will be convenient to speak of a plane as representing a certain pressure and temperature, when the tangents of its inclinations to the horizon, measured as above, are equal to that pressure and temperature.

Before proceeding farther, it may be worth while to distinguish between what is essential and what is arbitrary in a surface thus formed. The position of the plane  $v=0$  in the surface is evidently fixed, but the position of the planes  $\eta=0$ ,  $\epsilon=0$  is arbitrary, provided the direction of the axes of  $\eta$  and  $\epsilon$  be not altered. This results from the nature of the definitions of entropy and energy, which involve each an arbitrary constant. As we may make  $\eta=0$  and  $\epsilon=0$  for any state of the body which we may choose, we may place the origin of co-ordinates at any point in the plane  $v=0$ . Again, it is evident from the form of equation (1) that whatever changes we may make in the units in which volume, entropy, and energy are measured, it will always be possible to make such changes in the units of temperature and pressure, that the equation will hold true in its present form, without the introduction of constants. It is easy to see how a change of the units of volume, entropy, and energy would affect the surface. The projections parallel to any one of the axes of distances between points of the surface would be changed in the ratio inverse to that in which the corresponding unit had been changed. These considerations enable us to foresee to a certain extent the nature of the general properties of the surface which we are to investigate. They must be such, namely, as shall not be affected by any of the changes mentioned above. For example, we may find properties which concern

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however, that the relation between the volume, pressure, and temperature affords a less complete knowledge of the properties of the body than the relation between the volume, entropy, and energy. For, while the former relation is entirely determined by the latter, and can be derived from it by differentiation, the latter relation is by no means determined by the former.



the plane  $v=0$  (as that the whole surface must necessarily fall on the positive side of this plane), but we must not expect to find properties which concern the planes  $\eta=0$ , or  $\epsilon=0$ , in distinction from others parallel to them. It may be added that, as the volume, entropy, and energy of a body are equal to the sums of the volumes, entropies, and energies of its parts, if the surface should be constructed for bodies differing in quantity but not in kind of matter, the different surfaces thus formed would be similar to one another, their linear dimensions being proportional to the quantities of matter.

*Nature of that Part of the Surface which represents States which are not Homogeneous.*

This mode of representation of the volume, entropy, energy, pressure, and temperature of a body will apply as well to the case in which different portions of the body are in different states (supposing always that the whole is in a state of thermodynamic equilibrium), as to that in which the body is uniform in state throughout. For the body taken as a whole has a definite volume, entropy, and energy, as well as pressure and temperature, and the validity of the general equation (1) is independent of the uniformity or diversity in respect to state of the different portions of the body.\* It is evident, therefore, that the thermodynamic surface, for many substances at least,

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\* It is, however, supposed in this equation that the variations in the state of the body, to which  $dv$ ,  $dn$ , and  $de$  refer, are such as may be produced *reversibly* by expansion and compression or by addition and subtraction of heat. Hence, when the body consists of parts in different states, it is necessary that these states should be such as can pass either into the other without sensible change of pressure or temperature. Otherwise, it would be necessary to suppose in the differential equation (1) that the proportion in which the body is divided into the different states remains constant. But such a limitation would render the equation as applied to a compound of different states valueless for our present purpose. If, however, we leave out of account the cases in which we regard the states as chemically different from one another, which lie beyond the scope of this paper, experience justifies us in assuming the above condition (that either of the two states existing in contact can pass into the other without sensible change of the pressure or temperature), as at least approximately true, when one of the states is fluid. But if both are solid, the necessary mobility of the parts is wanting. It must therefore be understood, that the following discussion of the compound states is not intended to apply without limitation to the exceptional cases, where we have two different solid states of the same substance at the same pressure and temperature. It may be added that the thermodynamic equilibrium which subsists between two such solid states of the same substance differs from that which subsists when one of the states is fluid, very much as in statics an equilibrium which is maintained by friction differs from that of a frictionless machine in which the

can be divided into two parts, of which one represents the homogeneous states, the other those which are not so. We shall see that, when the former part of the surface is given, the latter can readily be formed, as indeed we might expect. We may therefore call the former part the primitive surface, and the latter the derived surface.

To ascertain the nature of the derived surface and its relations to the primitive surface sufficiently to construct it when the latter is given, it is only necessary to use the principle that the volume, entropy, and energy of the whole body are equal to the sums of the volumes, entropies, and energies respectively of the parts, while the pressure and temperature of the whole are the same as those of each of the parts. Let us commence with the case in which the body is in part solid, in part liquid, and in part vapor. The position of the point determined by the volume, entropy, and energy of such a compound will be that of the center of gravity of masses proportioned to the masses of solid, liquid, and vapor placed at the three points of the primitive surface which represent respectively the states of complete solidity, complete liquidity, and complete vaporization, each at the temperature and pressure of the compound. Hence, the part of the surface which represents a compound of solid, liquid, and vapor is a plane triangle, having its vertices at the points mentioned. The fact that the surface is here plane indicates that the pressure and temperature are here constant, the inclination of the plane indicating the value of these quantities. Moreover, as these values are the same for the compound as for the three different homogeneous states corresponding to its different portions, the plane of the triangle is tangent at each of its vertices to the primitive surface, viz: at one vertex to that part of the primitive surface which represents solid, at another to the part representing liquid, and at the third to the part representing vapor.

When the body consists of a compound of two different homogeneous states, the point which represents the compound state will be at

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active forces are so balanced, that the slightest change of force will produce motion in either direction.

Another limitation is rendered necessary by the fact that in the following discussion the magnitude and form of the bounding and dividing surfaces are left out of account; so that the results are in general strictly valid only in cases in which the influence of these particulars may be neglected. When, therefore, two states of the substance are spoken of as in contact, it must be understood that the surface dividing them is plane. To consider the subject in a more general form, it would be necessary to introduce considerations which belong to the theories of capillarity and crystallization.

the center of gravity of masses proportioned to the masses of the parts of the body in the two different states and placed at the points of the primitive surface which represent these two states (i. e., which represent the volume, entropy, and energy of the body, if its whole mass were supposed successively in the two homogeneous states which occur in its parts). It will therefore be found upon the straight line which unites these two points. As the pressure and temperature are evidently constant for this line, a single plane can be tangent to the derived surface throughout this line and at each end of the line tangent to the primitive surface.\* If we now imagine the temperature

\* It is here shown that, if two different states of the substance are such that they can exist permanently in contact with each other, the points representing these states in the thermodynamic surface have a common tangent plane. We shall see hereafter that the converse of this is true,—that, if two points in the thermodynamic surface have a common tangent plane, the states represented are such as can permanently exist in contact; and we shall also see what determines the direction of the discontinuous change which occurs when two different states of the same pressure and temperature, for which the condition of a common tangent plane is not satisfied, are brought into contact.

It is easy to express this condition analytically. Resolving it into the conditions, that the tangent planes shall be parallel, and that they shall cut the axis of  $\epsilon$  at the same point, we have the equations

$$p' = p'', \quad (\alpha)$$

$$t' = t'', \quad (\beta)$$

$$\epsilon' - t'\eta' + p'v' = \epsilon'' - t''\eta'' + p''v'', \quad (\gamma)$$

where the letters which refer to the different states are distinguished by accents. If there are three states which can exist in contact, we must have for these states,

$$p' = p'' = p''',$$

$$t' = t'' = t''',$$

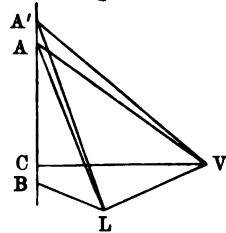
$$\epsilon' - t'\eta' + p'v' = \epsilon'' - t''\eta'' + p''v'' = \epsilon''' - t'''\eta''' + p'''v'''.$$

These results are interesting, as they show us how we might foresee whether two given states of a substance of the same pressure and temperature, can or cannot exist in contact. It is indeed true, that the values of  $\epsilon$  and  $\eta$  cannot like those of  $v$ ,  $p$ , and  $t$  be ascertained by mere measurements upon the substance while in the two states in question. It is necessary, in order to find the value of  $\epsilon'' - \epsilon'$  or  $\eta'' - \eta'$ , to carry out measurements upon a process by which the substance is brought from one state to the other, *but this need not be by a process in which the two given states shall be found in contact*, and in some cases at least it may be done by processes in which the body remains always homogeneous in state. For we know by the experiments of Dr. Andrews (Phil. Trans., vol. 159, p. 575), that carbonic acid may be carried from any of the states which we usually call liquid to any of those which we usually call gas, without losing its homogeneity. Now, if we had so carried it from a state of liquidity to a state of gas of the same pressure and temperature, making the proper measurements in the process, we should be able to foretell what would occur if these two states of the substance should be brought together,—whether evaporation would take place, or condensation, or whether they would remain unchanged in contact,—although we had

and pressure of the compound to vary, the two points of the primitive surface, the line in the derived surface uniting them, and the tangent plane will change their positions, maintaining the aforesaid relations. We may conceive of the motion of the tangent plane as produced by rolling upon the primitive surface, while tangent to it in two points, and as it is also tangent to the derived surface in the lines joining these points, it is evident that the latter is a developable and forms a part of the envelop of the successive positions of the rolling plane. We shall see hereafter that the form of the primitive surface is such that the double tangent plane does not cut it, so that this rolling is physically possible.

From these relations may be deduced by simple geometrical considerations, one of the principal propositions in regard to such compounds. Let the tangent plane touch the primitive surface at the two points L and V (fig. 1), which, to fix our ideas, we may suppose to represent liquid and vapor; let planes pass through these points perpendicular to the axes of  $v$  and  $\eta$  respectively, intersecting in the line AB, which will be parallel to the axis of  $\epsilon$ . Let the tangent plane cut this line at A, and let LB and VC be drawn at right angles to AB and parallel to the axes of  $\eta$  and  $v$ . Now the pressure and temperature represented by the tangent plane are evidently  $\frac{AC}{CV}$  and  $\frac{AB}{BL}$  respectively, and if we suppose the

Fig. 1.



never seen the phenomenon of the coexistence of these two states, or of any other two states of this substance.

Equation ( $\gamma$ ) may be put in a form in which its validity is at once manifest for two states which can pass either into the other at a constant pressure and temperature. If we put  $p'$  and  $t'$  for the equivalent  $p''$  and  $t''$ , the equation may be written

$$e'' - e' = t' (\eta'' - \eta') - p' (v'' - v').$$

Here the left hand member of the equation represents the difference of energy in the two states, and the two terms on the right represent severally the heat received and the work done when the body passes from one state to the other. The equation may also be derived at once from the general equation (1) by integration.

It is well known that when the two states being both fluid meet in a curved surface,

instead of (a) we have 
$$p'' - p' = T \left( \frac{1}{r} + \frac{1}{r'} \right),$$

where  $r$  and  $r'$  are the radii of the principal curvatures of the surface of contact at any point (positive, if the concavity is toward the mass to which  $p''$  refers), and  $T$  is what is called the *superficial tension*. Equation ( $\beta$ ), however, holds good for such cases, and it might easily be proved that the same is true of equation ( $\gamma$ ). In other words, the tangent planes for the points in the thermodynamic surface representing the two states cut the plane  $v=0$  in the same line.

tangent plane in rolling upon the primitive surface to turn about its instantaneous axis LV an infinitely small angle, so as to meet AB in A',  $dp$  and  $dt$  will be equal to  $\frac{AA'}{CV}$  and  $\frac{AA'}{BL}$  respectively. Therefore,

$$\frac{dp}{dt} = \frac{BL}{CV} = \frac{\eta'' - \eta'}{v'' - v'},$$

where  $v'$  and  $\eta'$  denote the volume and entropy for the point L, and  $v''$  and  $\eta''$  those for the point V. If we substitute for  $\eta'' - \eta'$  its equivalent  $\frac{r}{t}$  ( $r$  denoting the heat of vaporization), we have the equation in its usual form,  $\frac{dp}{dt} = \frac{r}{t(v'' - v')}$ .

*Properties of the Surface relating to Stability of Thermodynamic Equilibrium.*

We will now turn our attention to the geometrical properties of the surface, which indicate whether the thermodynamic equilibrium of the body is stable, unstable, or neutral. This will involve the consideration, to a certain extent, of the nature of the processes which take place when equilibrium does not subsist. We will suppose the body placed in a medium of constant pressure and temperature; but as, when the pressure or temperature of the body at its surface differs from that of the medium, the immediate contact of the two is hardly consistent with the continuance of the initial pressure and temperature of the medium, both of which we desire to suppose constant, we will suppose the body separated from the medium by an envelop which will yield to the smallest differences of pressure between the two, but which can only yield very gradually, and which is also a very poor conductor of heat. It will be convenient and allowable for the purposes of reasoning to limit its properties to those mentioned, and to suppose that it does not occupy any space, or absorb any heat except what it transmits, i. e., to make its volume and its specific heat 0. By the intervention of such an envelop, we may suppose the action of the body upon the medium to be so retarded as not sensibly to disturb the uniformity of pressure and temperature in the latter.

When the body is not in a state of thermodynamic equilibrium, its state is not one of those which are represented by our surface. The body, however, as a whole has a certain volume, entropy, and energy,

which are equal to the sums of the volumes, etc., of its parts.\* If, then, we suppose points endowed with mass proportional to the masses of the various parts of the body, which are in different thermodynamic states, placed in the positions determined by the states and motions of these parts, (i. e., so placed that their co-ordinates are equal to the volume, entropy, and energy of the whole body supposed successively in the same states and endowed with the same velocities as the different parts,) the center of gravity of such points thus placed will evidently represent by its co-ordinates the volume, entropy, and energy of the whole body. If all parts of the body are at rest, the point representing its volume, entropy, and energy will be the center of gravity of a number of points upon the primitive surface. The effect of motion in the parts of the body will be to move the corresponding points parallel to the axis of  $\epsilon$ , a distance equal in each case to the *vis viva* of the whole body, if endowed with the velocity of the part represented;—the center of gravity of points thus determined will give the volume, entropy, and energy of the whole body.

Now let us suppose that the body having the initial volume, entropy, and energy,  $v', \eta',$  and  $\epsilon'$ , is placed (enclosed in an envelop as aforesaid) in a medium having the constant pressure  $P$  and temperature  $T$ , and by the action of the medium and the interaction of its own parts comes to a final state of rest in which its volume, etc., are  $v'', \eta'', \epsilon''$ ;—we wish to find a relation between these quantities. If we regard, as we may, the medium as a very large body, so that imparting heat to it or compressing it within moderate limits will have no appreciable effect upon its pressure and temperature, and write  $V, H,$  and  $E,$  for its volume, entropy, and energy, equation (1) becomes

$$dE = TdH - PdV,$$

which we may integrate regarding  $P$  and  $T$  as constants, obtaining

$$E'' - E' = TH'' - TH' - PV'' + PV', \quad (a)$$

where  $E', E''$ , etc., refer to the initial and final states of the medium. Again, as the sum of the energies of the body and the surrounding medium may become less, but cannot become greater (this arises from the nature of the envelop supposed), we have

$$\epsilon'' + E'' \leq \epsilon' + E'. \quad (b)$$

\* As the discussion is to apply to cases in which the parts of the body are in (sensible) motion, it is necessary to define the sense in which the word *energy* is to be used. We will use the word as including the *vis viva* of sensible motions.

Again, as the sum of the entropies may increase but cannot diminish

$$\eta'' + H'' \geq \eta' + H'. \quad (c)$$

Lastly, it is evident that

$$v'' + V'' = v' + V'. \quad (d)$$

These four equations may be arranged with slight changes as follows :

$$-E'' + TH'' - PV'' = -E' + TH' - PV'$$

$$\varepsilon'' + E'' \leq \varepsilon' + E'$$

$$-T\eta'' - TH'' \leq -T\eta' - TH'$$

$$Pv'' + PV'' = Pv' + PV'.$$

By addition we have

$$\varepsilon'' - T\eta'' + Pv'' \leq \varepsilon' - T\eta' + Pv'. \quad (e)$$

Now the two members of this equation evidently denote the vertical distances of the points  $(v'', \eta'', \varepsilon'')$  and  $(v', \eta', \varepsilon')$  above the plane passing through the origin and representing the pressure  $P$  and temperature  $T$ . And the equation expresses that the ultimate distance is less or at most equal to the initial. It is evidently immaterial, whether the distances be measured vertically or normally, or that the fixed plane representing  $P$  and  $T$  should pass through the origin; but distances must be considered negative when measured from a point below the plane.

It is evident that the sign of inequality holds in (e) if it holds in either (b) or (c), therefore, it holds in (e) if there are any differences of pressure or temperature between the different parts of the body or between the body and the medium, or if any part of the body has sensible motion. (In the latter case, there would be an increase of entropy due to the conversion of this motion into heat). But even if the body is initially without sensible motion and has throughout the same pressure and temperature as the medium, the sign  $<$  will still hold if different parts of the body are in states represented by points in the thermodynamic surface at different distances from the fixed plane representing  $P$  and  $T$ . For it certainly holds if such initial circumstances are followed by differences of pressure or temperature, or by sensible velocities. Again, the sign of inequality would necessarily hold if one part of the body should pass, without producing changes of pressure or temperature or sensible velocities, into the state of another part represented by a point not at the same distance from the fixed plane representing  $P$  and  $T$ . But these are the only suppositions possible in the case, unless we suppose that equilibrium

subsists, which would require that the points in question should have a common tangent plane (page 386), whereas by supposition the planes tangent at the different points are parallel but not identical.

The results of the preceding paragraph may be summed up as follows:—Unless the body is initially without sensible motion, and its state, if homogeneous, is such as is represented by a point in the primitive surface where the tangent plane is parallel to the fixed plane representing  $P$  and  $T$ , or, if the body is not homogeneous in state, unless the points in the primitive surface representing the states of its parts have a common tangent plane parallel to the fixed plane representing  $P$  and  $T$ , such changes will ensue that the distance of the point representing the volume, entropy, and energy of the body from that fixed plane will be diminished (distances being considered negative if measured from points beneath the plane). Let us apply this result to the question of the stability of the body when surrounded, as supposed, by a medium of constant temperature and pressure.

The state of the body in equilibrium will be represented by a point in the thermodynamic surface, and as the pressure and temperature of the body are the same as those of the surrounding medium, we may take the tangent plane at that point as the fixed plane representing  $P$  and  $T$ . If the body is not homogeneous in state, although in equilibrium, we may, for the purposes of this discussion of stability, either take a point in the derived surface as representing its state, or we may take the points in the primitive surface which represent the states of the different parts of the body. These points, as we have seen (page 386), have a common tangent plane, which is identical with the tangent plane for the point in the derived surface.

Now, if the form of the surface be such that it falls above the tangent plane except at the single point of contact, the equilibrium is necessarily stable; for if the condition of the body be slightly altered, either by imparting sensible motion to any part of the body, or by slightly changing the state of any part, or by bringing any small part into any other thermodynamic state whatever, or in all of these ways, the point representing the volume, entropy, and energy of the whole body will then occupy a position *above* the original tangent plane, and the proposition above enunciated shows that processes will ensue which will diminish the distance of this point from that plane, and that such processes cannot cease until the body is brought back into its original condition, when they will necessarily cease on account of the form supposed of the surface.



On the other hand, if the surface have such a form that any part of it falls below the fixed tangent plane, the equilibrium will be unstable. For it will evidently be possible by a slight change in the original condition of the body (that of equilibrium with the surrounding medium and represented by the point or points of contact) to bring the point representing the volume, entropy, and energy of the body into a position *below* the fixed tangent plane, in which case we see by the above proposition that processes will occur which will carry the point still farther from the plane, and that such processes cannot cease until all the body has passed into some state entirely different from its original state.

It remains to consider the case in which the surface, although it does not anywhere fall below the fixed tangent plane, nevertheless meets the plane in more than one point. The equilibrium in this case, as we might anticipate from its intermediate character between the cases already considered, is neutral. For if any part of the body be changed from its original state into that represented by another point in the thermodynamic surface lying in the same tangent plane, equilibrium will still subsist. For the supposition in regard to the form of the surface implies that uniformity in temperature and pressure still subsists, nor can the body have any necessary tendency to pass entirely into the second state or to return into the original state, for a change of the values of  $T$  and  $P$  less than any assignable quantity would evidently be sufficient to reverse such a tendency if any such existed, as either point at will could by such an infinitesimal variation of  $T$  and  $P$  be made the nearer to the plane representing  $T$  and  $P$ .

It must be observed that in the case where the thermodynamic surface at a certain point is concave upward in both its principal curvatures, but somewhere falls below the tangent plane drawn through that point, the equilibrium although unstable in regard to *discontinuous* changes of state is stable in regard to *continuous* changes, as appears on restricting the test of stability to the vicinity of the point in question; that is, if we suppose a body to be in a state represented by such a point, although the equilibrium would show itself unstable if we should introduce into the body a small portion of the same substance in one of the states represented by points below the tangent plane, yet if the conditions necessary for such a discontinuous change are not present, the equilibrium would be stable. A familiar example of this is afforded by liquid water when

heated at any pressure above the temperature of boiling water at that pressure.\*

*Leading Features of the Thermodynamic Surface for Substances which take the forms of Solid, Liquid and Vapor.*

We are now prepared to form an idea of the general character of the primitive and derived surfaces and their mutual relations for a substance which takes the forms of solid, liquid, and vapor. The primitive surface will have a triple tangent plane touching it at the three points which represent the three states which can exist in contact. Except at these three points, the primitive surface falls entirely above the tangent plane. That part of the plane which forms a triangle having its vertices at the three points of contact, is the derived surface which represents a compound of the three states of the substance. We may now suppose the plane to roll on the under side of the surface, continuing to touch it in two points without cutting it. This it may do in three ways, viz: it may commence by turning about any one of the sides of the triangle aforesaid. Any pair of points which the plane touches at once represent states which can exist permanently in contact. In this way six lines are traced upon the surface. These lines have in general a common property, that a tangent plane at any point in them will also touch the surface in another point. We must say *in general*, for, as we shall see hereafter, this statement does not hold good for the critical point. A tangent plane at any point of the surface *outside* of these lines has the surface entirely above it, except the single point of contact. A tangent plane at any point of the primitive surface *within* these lines will cut the surface. These lines, therefore, taken together may be called the *limit of absolute stability*, and the surface outside of them, the *surface of absolute stability*. That part of the envelop of the rolling plane, which lies between the pair of lines which the plane traces on the surface, is a part of the derived surface, and represents a mixture of two states of the substance.

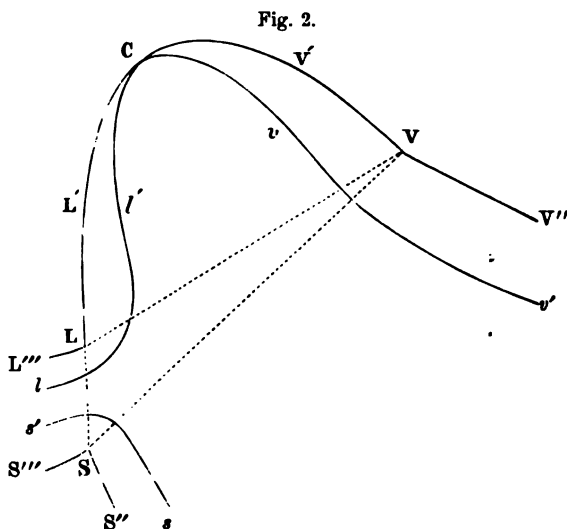
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\* If we wish to express in a single equation the necessary and sufficient condition of thermodynamic equilibrium for a substance when surrounded by a medium of constant pressure  $P$  and temperature  $T$ , this equation may be written

$$\delta(\epsilon - T\eta + Pv) = 0,$$

when  $\delta$  refers to the variation produced by any variations in the state of the parts of the body, and (when different parts of the body are in different states) in the proportion in which the body is divided between the different states. The condition of stable equilibrium is that the value of the expression in the parenthesis shall be a minimum.

The relations of these lines and surfaces are roughly represented in horizontal projection\* in figure 2, in which the full lines represent lines on the primitive surface, and the dotted lines those on the derived surface. S, L, and V are the points which have a common tangent plane and represent the states of solid, liquid, and vapor



which can exist in contact. The plane triangle SLV is the derived surface representing compounds of these states. LL' and VV' are the pair of lines traced by the rolling double tangent plane, between which lies the derived surface representing compounds of liquid and vapor. VV'' and SS'' are another such pair, between which lies the derived surface representing compounds of vapor and solid. SS''' and LL''' are the third pair, between which lies the derived surface representing a compound of solid and liquid. L''L', V'VV'' and S''SS''' are the boundaries of the surfaces which represent respectively the absolutely stable states of liquid, vapor, and solid.

The geometrical expression of the results which Dr. Andrews (Phil. Trans., vol. 159, p. 575) has obtained by his experiments with carbonic acid is that, in the case of this substance at least, the derived surface which represents a compound of liquid and vapor is terminated as follows: as the tangent plane rolls upon the primitive surface, the two points of contact approach one another and finally fall

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\* A horizontal projection of the thermodynamic surface is identical with the diagram described on pages 330-338 of this volume, under the name of the volume-entropy diagram.

together. The rolling of the double tangent plane necessarily comes to an end. The point where the two points of contact fall together is the *critical point*. Before considering farther the geometrical characteristics of this point and their physical significance, it will be convenient to investigate the nature of the primitive surface which lies between the lines which form the limit of absolute stability.

Between two points of the primitive surface which have a common tangent plane, as those represented by  $L'$  and  $V'$  in figure 2, if there is no gap in the primitive surface, there must evidently be a region where the surface is concave toward the tangent plane in one of its principal curvatures at least, and therefore represents states of unstable equilibrium in respect to continuous as well as discontinuous changes (see page 392).\* If we draw a line upon the primitive surface, dividing it into parts which represent respectively stable and unstable equilibrium, in respect to continuous changes, i. e., dividing the surface which is concave upward in both its principal curvatures from that which is concave downward in one or both, this line, which may be called the *limit of essential instability*, must have a form somewhat like that represented by  $U'CVV'SS'$  in figure 2. It touches the limit of absolute stability at the critical point  $C$ . For we may take a pair of points in  $LC$  and  $VC$  having a common tangent plane as near to  $C$  as we choose, and the line joining them upon the primitive surface made by a plane section perpendicular to the tangent plane, will pass through an area of instability.

The geometrical properties of the critical point in our surface may be made more clear by supposing the lines of curvature drawn upon the surface for one of the principal curvatures, that one, namely, which has different signs upon different sides of the limit of essential instability. The lines of curvature which meet this line will in general cross it. At any point where they do so, as the sign of their curvature changes, they evidently cut a plane tangent to the surface, and therefore the surface itself cuts the tangent plane. But where one of these lines of curvature touches the limit of essential instability without crossing it, so that its curvature remains always positive (curvatures being considered positive when the concavity is on the upper side of the surface), the surface evidently does not cut the tangent plane, but has a contact of the third order with it in the section of least curvature. The critical point, therefore, must be a point

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\* This is the same result as that obtained by Professor J. Thomson in connection with the surface referred to in the note on page 382.

where the line of that principal curvature which changes its sign is tangent to the line which separates positive from negative curvatures.

From the last paragraphs we may derive the following physical property of the critical state:—Although this is a limiting state between those of stability and those of instability in respect to continuous changes, and although such limiting states are in general unstable in respect to such changes, yet the critical state is stable in regard to them. A similar proposition is true in regard to absolute stability, i. e., if we disregard the distinction between continuous and discontinuous changes, viz: that although the critical state is a limiting state between those of stability and instability, and although the equilibrium of such limiting states is in general neutral (when we suppose the substance surrounded by a medium of constant pressure and temperature), yet the critical point is stable.

From what has been said of the curvature of the primitive surface at the critical point, it is evident, that if we take a point in this surface infinitely near to the critical point, and such that the tangent planes for these two points shall intersect in a line perpendicular to the section of least curvature at the critical point, the angle made by the two tangent planes will be an infinitesimal of the same order as the cube of the distance of these points. Hence, at the critical point

$$\begin{aligned} \left(\frac{dp}{dv}\right)_t = 0, & \quad \left(\frac{dp}{d\eta}\right)_t = 0, & \quad \left(\frac{dt}{dv}\right)_p = 0, & \quad \left(\frac{dt}{d\eta}\right)_p = 0, \\ \left(\frac{d^2p}{dv^2}\right)_t = 0, & \quad \left(\frac{d^2p}{d\eta^2}\right)_t = 0, & \quad \left(\frac{d^2t}{dv^2}\right)_p = 0, & \quad \left(\frac{d^2t}{d\eta^2}\right)_p = 0, \end{aligned}$$

and if we imagine the isothermal and isopiestic (line of constant pressure) drawn for the critical point upon the primitive surface, these lines will have a contact of the third order.

Now the elasticity of the substance at constant temperature and its specific heat at constant pressure may be defined by the equations,

$$e = -v \left(\frac{dp}{dv}\right)_t, \quad s = t \left(\frac{d\eta}{dt}\right)_p;$$

therefore at the critical point

$$\begin{aligned} e = 0, & \quad \frac{1}{s} = 0, \\ \left(\frac{de}{dv}\right)_t = 0, & \quad \left(\frac{de}{d\eta}\right)_t = 0, & \quad \left(\frac{d\frac{1}{s}}{dv}\right)_p = 0, & \quad \left(\frac{d\frac{1}{s}}{d\eta}\right)_p = 0. \end{aligned}$$

The last four equations would also hold good if  $p$  were substituted for  $t$ , and *vice versa*.

We have seen that in the case of such substances as can pass continuously from the state of liquid to that of vapor, unless the primitive surface is abruptly terminated and that in a line which passes through the critical point, a part of it must represent states which are essentially unstable (i. e., unstable in regard to continuous changes,) and therefore cannot exist permanently unless in very limited spaces. It does not necessarily follow that such states cannot be realized at all. It appears quite probable, that a substance initially in the critical state may be allowed to expand so rapidly, that, the time being too short for appreciable conduction of heat, it will pass into some of these states of essential instability. No other result is possible on the supposition of no transmission of heat, which requires that the points representing the states of all the parts of the body shall be confined to the isentropic (adiabatic) line of the critical point upon the primitive surface. It will be observed that there is no instability in regard to changes of state thus limited, for this line (the plane section of the primitive surface perpendicular to the axis of  $\eta$ ) is concave upward, as is evident from the fact that the primitive surface lies entirely above the tangent plane for the critical point.

We may suppose waves of compression and expansion to be propagated in a substance initially in the critical state. The velocity of propagation will depend upon the value of  $\left(\frac{dp}{dv}\right)_\eta$ , i. e., of  $-\left(\frac{d^2\varepsilon}{dv^2}\right)_\eta$ . Now for a wave of compression the value of these expressions is determined by the form of the isentropic on the primitive surface. If a wave of expansion has the same velocity approximately as one of compression, it follows that the substance when expanded under the circumstances remains in a state represented by the primitive surface, which involves the realization of states of essential instability.

The value of  $\left(\frac{d^2\varepsilon}{dv^2}\right)_\eta$  in the derived surface is, it will be observed, totally different from its value in the primitive surface, as the curvature of these surfaces at the critical point is different.

The case is different in regard to the part of the surface between the limit of absolute stability and the limit of essential instability. Here, we have experimental knowledge of some of the states represented. In water, for example, it is well known that liquid states can be realized beyond the limit of absolute stability,—both beyond the part of the limit where vaporization usually commences (LL' in figure 2), and beyond the part where congelation usually commences (LL''). That vapor may also exist beyond the limit of absolute stability, i. e.,

that it may exist at a given temperature at pressures greater than that of equilibrium between the vapor and its liquid meeting in a plane surface at that temperature, the considerations adduced by Sir W. Thomson in his paper "On the equilibrium of a vapor at the curved surface of a liquid" (Proc. Roy. Soc. Ed., Session 1869-1870, and Phil. Mag., vol. xlii, p. 448), leave no room for doubt. By experiments like that suggested by Professor J. Thomson in his paper already referred to, we may be able to carry vapors farther beyond the limit of absolute stability.\* As the resistance to deformation characteristic of solids evidently tends to prevent a discontinuous change of state from commencing within them, substances can doubtless exist in solid states very far beyond the limit of absolute stability.

The surface of absolute stability, together with the triangle representing a compound of three states, and the three developable surfaces which have been described representing compounds of two states, forms a continuous sheet, which is everywhere concave upward except where it is plane, and has only one value of  $\epsilon$  for any given values of  $v$  and  $\eta$ . Hence, as  $t$  is necessarily positive, it has only one value of  $\eta$  for any given values of  $v$  and  $\epsilon$ . If vaporization can take place at every temperature except 0,  $p$  is everywhere positive, and the surface has only one value of  $v$  for any given values of  $\eta$  and  $\epsilon$ . It forms the *surface of dissipated energy*. If we consider all the points representing the volume, entropy, and energy of the body in every possible state, whether of equilibrium or not, these points will

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\* If we experiment with a fluid which does not wet the vessel which contains it, we may avoid the necessity of keeping the vessel hotter than the vapor, in order to prevent condensation. If a glass bulb with a stem of sufficient length be placed vertically with the open end of the stem in a cup of mercury, the stem containing nothing but mercury and its vapor, and the bulb nothing but the vapor, the height at which the mercury rests in the stem, affords a ready and accurate means of determining the pressure of the vapor. If the stem at the top of the column of liquid should be made hotter than the bulb, condensation would take place in the latter, if the liquid were one which would wet the bulb. But as this is not the case, it appears probable, that if the experiment were conducted with proper precautions, there would be no condensation within certain limits in regard to the temperatures. If condensation should take place, it would be easily observed, especially if the bulb were bent over, so that the mercury condensed could not run back into the stem. So long as condensation does not occur, it will be easy to give any desired (different) temperatures to the bulb and the top of the column of mercury in the stem. The temperature of the latter will determine the pressure of the vapor in the bulb. In this way, it would appear, we may obtain in the bulb vapor of mercury having pressures greater for the temperatures than those of saturated vapor.

form a solid figure unbounded in some directions, but bounded in others by this surface.\*

The lines traced upon the primitive surface by the rolling double tangent plane, which have been called the limit of absolute stability, do not end at the vertices of the triangle which represents a mixture of those states. For when the plane is tangent to the primitive surface in these three points, it can commence to roll upon the surface as a double tangent plane not only by leaving the surface at one of these points, but also by a rotation in the opposite direction. In the latter case, however, the lines traced upon the primitive surface by the points of contact, although a continuation of the lines previously described, do not form any part of the limit of absolute stability. And the parts of the envelopes of the rolling plane between these lines, although a continuation of the developable surfaces which have been described, and representing states of the body, of which some at least may be realized, are of minor interest, as they form no part of the

\* This description of the surface of dissipated energy is intended to apply to a substance capable of existing as solid, liquid, and vapor, and which presents no anomalies in its thermodynamic properties. But, whatever the form of the primitive surface may be, if we take the parts of it for every point of which the tangent plane does not cut the primitive surface, together with all the plane and developable derived surface, which can be formed in a manner analogous to those described in the preceding pages, by fixed and rolling tangent planes which do not cut the primitive surface,—such surfaces taken together will form a continuous sheet, which, if we reject the part, if any, for which  $p < 0$ , forms the surface of dissipated energy and has the geometrical properties mentioned above.

There will, however, be no such part in which  $p < 0$ , if there is any assignable temperature  $t'$  at which the substance has the properties of a perfect gas except when its volume is less than a certain quantity  $v'$ . For the equations of an isothermal line in the thermodynamic surface of a perfect gas are (see equations (B) and (E) on pages 321–322 of this volume.)

$$\begin{aligned} \epsilon &= C \\ \eta &= a \log v + C'. \end{aligned}$$

The isothermal of  $t'$  in the thermodynamic surface of the substance in question must therefore have the same equations in the part in which  $v$  exceeds the constant  $v'$ . Now if at any point in this surface  $p < 0$  and  $t > 0$  the equation of the tangent plane for that point will be

$$\epsilon = m\eta + nv + C'',$$

where  $m$  denotes the temperature and  $-n$  the pressure for the point of contact, so that  $m$  and  $n$  are both positive. Now it is evidently possible to give so large a value to  $v$  in the equations of the isothermal that the point thus determined shall fall below the tangent plane. Therefore, the tangent plane cuts the primitive surface, and the point of the thermodynamic surface for which  $p < 0$  cannot belong to the surfaces mentioned in the last paragraph as forming a continuous sheet.



surface of dissipated energy on the one hand, nor have the theoretical interest of the primitive surface on the other.

*Problems relating to the Surface of Dissipated Energy.*

The surface of dissipated energy has an important application to a certain class of problems which refer to the results which are theoretically possible with a given body or system of bodies in a given initial condition.

For example, let it be required to find the greatest amount of mechanical work which can be obtained from a given quantity of a certain substance in a given initial state, without increasing its total volume or allowing heat to pass to or from external bodies, except such as at the close of the processes are left in their initial condition. This has been called the *available energy* of the body. The initial state of the body is supposed to be such that the body can be made to pass from it to states of dissipated energy by reversible processes.

If the body is in a state represented by any point of the surface of dissipated energy, of course no work can be obtained from it under the given conditions. But even if the body is in a state of thermodynamic equilibrium, and therefore in one represented by a point in the thermodynamic surface, if this point is not in the surface of dissipated energy, because the equilibrium of the body is unstable in regard to discontinuous changes, a certain amount of energy will be available under the conditions for the production of work. Or, if the body is solid, even if it is uniform in state throughout, its pressure (or tension) may have different values in different directions, and in this way it may have a certain available energy. Or, if different parts of the body are in different states, this will in general be a source of available energy. Lastly, we need not exclude the case in which the body has sensible motion and its *vis viva* constitutes available energy. In any case, we must find the initial volume, entropy, and energy of the body, which will be equal to the sums of the initial volumes, entropies, and energies of its parts. ('Energy' is here used to include the *vis viva* of sensible motions). These values of  $v$ ,  $n$ , and  $\epsilon$  will determine the position of a certain point which we will speak of as representing the initial state.

Now the condition that no heat shall be allowed to pass to external bodies, requires that the final entropy of the body shall not be less than the initial, for it could only be made less by violating this condition. The problem, therefore, may be reduced to this,—to find the amount by which the energy of the body may be diminished

without increasing its volume or diminishing its entropy. This quantity will be represented geometrically by the distance of the point representing the initial state from the surface of dissipated energy measured parallel to the axis of  $\epsilon$ .

Let us consider a different problem. A certain initial state of the body is given as before. No work is allowed to be done upon or by external bodies. Heat is allowed to pass to and from them only on condition that the algebraic sum of all heat which thus passes shall be 0. From both these conditions any bodies may be excepted, which shall be left at the close of the processes in their initial state. Moreover, it is not allowed to increase the volume of the body. It is required to find the greatest amount by which it is possible under these conditions to diminish the entropy of an external system. This will be, evidently, the amount by which the entropy of the body can be increased without changing the energy of the body or increasing its volume, which is represented geometrically by the distance of the point representing the initial state from the surface of dissipated energy, measured parallel to the axis of  $\eta$ . This might be called the capacity for entropy of the body in the given state.\*

Thirdly. A certain initial condition of the body is given as before. No work is allowed to be done upon or by external bodies, nor any heat to pass to or from them; from which conditions bodies may be excepted, as before, in which no permanent changes are produced. It is required to find the amount by which the volume of the body

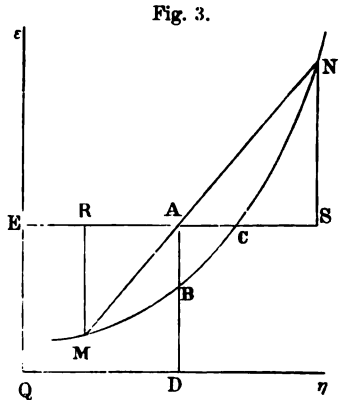
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\* It may be worth while to call attention to the analogy and the difference between this problem and the preceding. In the first case, the question is virtually, how great a weight does the state of the given body enable us to raise a given distance, no other permanent change being produced in external bodies. In the second case, the question is virtually, what amount of heat does the state of the given body enable us to take from an external body at a fixed temperature, and impart to another at a higher fixed temperature. In order that the numerical values of the available energy and of the capacity for entropy should be identical with the answers to these questions, it would be necessary in the first case, if the weight is measured in units of force, that the given distance, measured vertically, should be the unit of length, and in the second case, that the difference of the reciprocals of the fixed temperatures should be unity. If we prefer to take the freezing and boiling points as the fixed temperatures, as  $\frac{1}{273} - \frac{1}{373} = 0.00098$ , the capacity for entropy of the body in any given condition would be 0.00098 times the amount of heat which it would enable us to raise from the freezing to the boiling point (i. e., to take from a body of which the temperature remains fixed at the freezing point, and impart to another of which the temperature remains fixed at the boiling point).

The relations of these quantities to one another and to the surface of dissipated energy are illustrated by figure 3, which represents a plane perpendicular to the axis

can be diminished, using for that purpose, according to the conditions, only the force derived from the body itself. The conditions

of  $v$  and passing through the point A, which represents the initial state of the body. MN is the section of the surface of dissipated energy.  $Q\epsilon$  and  $Q\eta$  are sections of the planes  $\eta = 0$  and  $\epsilon = 0$ , and therefore parallel to the axes of  $\epsilon$  and  $\eta$  respectively. AD and AE are the energy and entropy of the body in its initial state, AB and AC, its available energy and its capacity for entropy respectively. It will be observed that when either the available energy or the capacity for entropy of the body is 0, the other has the same value. Except in this case, either quantity may be varied without affecting the other. For, on account of the curvature of the surface of dissipated energy, it is evidently possible to change the position of the point representing the initial state of the body so as to vary its distance from the surface measured parallel to one axis without varying that measured parallel to the other.



As the different senses in which the word *entropy* has been used by different writers is liable to cause misunderstanding, it may not be out of place to add a few words on the terminology of this subject. If Professor Clausius had defined *entropy* so that its value should be determined by the equation

$$dS = - \frac{dQ}{T},$$

instead of his equation (*Mechanische Wärmetheorie*, Abhand. ix, § 14; *Pogg. Ann.*, July, 1865)

$$dS = \frac{dQ}{T},$$

where  $S$  denotes the entropy and  $T$  the temperature of a body and  $dQ$  the element of heat imparted to it, that which is here called *capacity for entropy* would naturally be called *available entropy*, a term the more convenient on account of its analogy with the term *available energy*. Such a difference in the definition of *entropy* would involve no difference in the form of the thermodynamic surface, nor in any of our geometrical constructions, if only we suppose the direction in which entropy is measured to be reversed. It would only make it necessary to substitute  $-\eta$  for  $\eta$  in our equations, and to make the corresponding change in the verbal enunciation of propositions. Professor Tait has proposed to use the word entropy "in the opposite sense to that in which Clausius has employed it," (*Thermodynamics*, § 48. See also § 178), which appears to mean that he would determine its value by the first of the above equations. He nevertheless appears subsequently to use the word to denote available energy (§ 182, 2d theorem). Professor Maxwell uses the word entropy as synonymous with available energy, with the erroneous statement that Clausius uses the word to denote the part of the energy which is not available, (*Theory of Heat*, pp. 186 and 188). The term entropy, however, as used by Clausius does not denote a quantity of the same kind (i. e., one which can be measured by the same unit) as energy, as is evident from his equation, cited above, in which  $Q$  (heat) denotes a quantity measured by the unit

require that the energy of the body shall not be altered nor its entropy diminished. Hence the quantity sought is represented by the distance of the point representing the initial state from the surface of dissipated energy, measured parallel to the axis of volume.

Fourthly. An initial condition of the body is given as before. Its volume is not allowed to be increased. No work is allowed to be done upon or by external bodies, nor any heat to pass to or from them, except a certain body of given constant temperature  $t'$ . From the latter conditions may be excepted as before bodies in which no permanent changes are produced. It is required to find the greatest amount of heat which can be imparted to the body of constant temperature, and also the greatest amount of heat which can be taken from it, under the supposed conditions. If through the point of the initial state a straight line be drawn in the plane perpendicular to the axis of  $v$ , so that the tangent of the angle which it makes with the direction of the axis of  $\eta$  shall be equal to the given temperature  $t'$ , it may easily be shown that the vertical projections of the two segments of this line made by the point of the initial state and the surface of dissipated energy represent the two quantities required.\*

These problems may be modified so as to make them approach more nearly the economical problems which actually present themselves, if we suppose the body to be surrounded by a medium of constant pressure and temperature, and let the body and the medium together take the place of the body in the preceding problems. The results would be as follows:

If we suppose a plane representing the constant pressure and temperature of the medium to be tangent to the surface of dissipated energy of the body, the distance of the point representing the initial state of the body from this plane measured parallel to the axis of  $\epsilon$  will represent the available energy of the body and medium, the distance of the point to the plane measured parallel to the axis of  $\eta$  will represent the capacity for entropy of the body and medium, the distance of the point to the plane measured parallel to the axis of  $v$  will represent the magnitude of the greatest vacuum which can be produced in the body or medium (all the power used being derived from

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of energy, and as the unit in which  $T$  (temperature) is measured is arbitrary,  $S$  and  $Q$  are evidently measured by different units. It may be added that entropy as defined by Clausius is synonymous with the thermodynamic function as defined by Rankine.

\* Thus, in figure 3, if the straight line  $MAN$  be drawn so that  $\tan NAC = t'$ ,  $MR$  will be the greatest amount of heat which can be given to the body of constant temperature and  $NS$  will be the greatest amount which can be taken from it.

the body and medium); if a line be drawn through the point in a plane perpendicular to the axis of  $v$ , the vertical projection of the segment of this line made by the point and the tangent plane will represent the greatest amount of heat which can be given to or taken from another body at a constant temperature equal to the tangent of the inclination of the line to the horizon. (It represents the greatest amount which can be given to the body of constant temperature, if this temperature is greater than that of the medium; in the reverse case, it represents the greatest amount which can be withdrawn from that body). In all these cases, the point of contact between the plane and the surface of dissipated energy represents the final state of the given body.

If a plane representing the pressure and temperature of the medium be drawn through the point representing any given initial state of the body, the part of this plane which falls within the surface of dissipated energy will represent in respect to volume, entropy, and energy all the states into which the body can be brought by reversible processes, without producing permanent changes in external bodies (except in the medium), and the solid figure included between this plane figure and the surface of dissipated energy will represent all the states into which the body can be brought by any kind of processes, without producing permanent changes in external bodies (except in the medium).\*

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\* The body under discussion has been supposed throughout this paper to be homogeneous in substance. But if we imagine any material system whatever, and suppose the position of a point to be determined for every possible state of the system, by making the co-ordinates of the point equal to the total volume, entropy, and energy of the system, the points thus determined will evidently form a solid figure bounded in certain directions by the surface representing the states of dissipated energy. In these states, the temperature is necessarily uniform throughout the system; the pressure may vary (e. g., in the case of a very large mass like a planet), but it will always be possible to maintain the equilibrium of the system (in a state of dissipated energy) by a uniform normal pressure applied to its surface. This pressure and the uniform temperature of the system will be represented by the inclination of the surface of dissipated energy according to the rule on page 383. And in regard to such problems as have been discussed in the last five pages of this paper, this surface will possess, relatively to the system which it represents, properties entirely similar to those of the surface of dissipated energy of a homogeneous body.

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## ERRATA.

- Page 1, line 13, for "Flordia," read Florida.
- " 11, " 35, " "immargination," read emargination.
- " 16, " 26, " "spistome," read epistome.
- " 31, " 18, " "*Podophthalmia*," read *Podophthalmia*.
- " 35, " 9, " "*Eucrete*," read *Eucrate*.
- " 35, last line but one, for "margin," read margins.
- " 106, line 4, from foot, for "Norton Street," read Blake Street.
- " 108, " 11, " "twenty rods," read twenty-one rods.
- " 118, " 11, for "styiferus," read styliferus.
- " 138, " 11, " "immargination," read emargination.
- " 139, " 11, " "immarginate," read emarginate.
- " 153, first line of foot note, for "is marked 3," read is marked 3<sup>e</sup>.
- " 162, above "*Euryplax*," insert CARCINOPLACIDÆ.
- " 188, line 8, for "spinosus," read spinosum.
- " 197, " 31, " "palpaster," read polpaster.
- " 343, in title of paper, for "1873," read 1872.
- " 343, under No. 5, for "varible," read variable.
- " 346, No. 24, line 7, for "Montague," read Montagne.
- " 348, No. 44, for "Euteromorpha," read Enteromorpha.