

# THE METHOD OF WILLARD GIBBS IN CHEMICAL THERMODYNAMICS<sup>1</sup>

W. LASH MILLER

*University of Toronto, Toronto, Canada*

## CONTENTS

INTRODUCTION . . . . .	294
MATHEMATICAL PROPERTIES OF THE PHYSICO-CHEMICAL FUNCTIONS . . . . .	297
1. Functions defined with reference to a phase . . . . .	297
Solutions . . . . .	297
Heterogeneous systems . . . . .	300
2. Functions defined with reference to a reaction; potential functions..	301
Relations between the derivatives of the physico-chemical functions . . . . .	304
Euler's theorem . . . . .	305
Value of second derivative independent of order of differentiation . . . . .	306
"Mathematical group" of second derivatives . . . . .	307
"Physical group" of second derivatives . . . . .	308
"Chemical group" of second derivatives . . . . .	310
Other derivatives . . . . .	310
The standard diagram . . . . .	310
Result of integration independent of the path . . . . .	311
THE FUNCTIONS OF THERMODYNAMICS . . . . .	312
The functions . . . . .	314
Derivatives of the thermodynamic functions . . . . .	316
Relations between the derivatives (Euler's theorem) . . . . .	317
Criteria of thermodynamic equilibrium . . . . .	318
Criterion of neutral equilibrium . . . . .	318
Criterion of neutral equilibrium in a heterogeneous system at constant temperature and pressures . . . . .	319
INSTANCES OF EQUILIBRIUM BETWEEN TWO PHASES IN A TWO-COMPONENT SYSTEM . . . . .	320
1. The pressures on the two phases are different . . . . .	320
Effect of pressure on the osmotic pressure . . . . .	321
2. The pressures on the two phases are the same . . . . .	322
Equation for the slopes of the equilibrium curves . . . . .	322
(2a) The general case . . . . .	322
(2b) $x' = 0$ . . . . .	324
Illustration 1 . . . . .	325
Simplifying assumptions . . . . .	329

---

<sup>1</sup> An essay prepared in connection with the dedication of the Sterling Chemistry Laboratory.

Fundamental Equations . . . . .	330
One-component liquids or solids . . . . .	331
One-component gases, "perfect gas" . . . . .	333
"Perfect" or "ideal" gaseous solutions . . . . .	333
"Perfect" liquid or solid solutions . . . . .	335
Osmotic pressures . . . . .	336
Solubilities . . . . .	336
Depression of the freezing-point . . . . .	337
Vapor tensions . . . . .	337
"Ideal" liquid or solid solutions . . . . .	337
Illustration 2. Duhem-Margules equation . . . . .	339
Abacus . . . . .	340

It is nearly fifty years since Willard Gibbs' first papers on thermodynamics were published,<sup>2</sup> and more than thirty years since the most important of them were translated into German. In his preface to the German edition,<sup>3</sup> Ostwald says: "The importance of these studies can best be characterized by the fact that a great part of the relations since discovered, which have led to so memorable an evolution in our knowledge of physical and chemical equilibria, are contained explicitly or implicitly in these papers . . . . of the treasures they contain, only a small part has yet been exploited." The treatise "On the equilibrium of heterogeneous substances" has been translated into French by Le Chatelier,<sup>4</sup> who compares the influence of Gibbs on the development of chemistry to that of Lavoisier himself; and only a few years ago a French translation<sup>5</sup> of the "Abstract"<sup>6</sup> appeared, provided with copious explanatory notes by Georges Matisse.

In these papers, so much appreciated abroad, Gibbs postulated the two laws of thermodynamics, invented what functions were necessary to put them into convenient mathematical form, and without further assumptions deduced from them the criteria of chemical equilibrium and shewed what experimental data were necessary in any given case for the solution of the problem presented. He also shewed how these data can be collected in the

<sup>2</sup> *Trans. Connecticut Acad.*, **2**, 309, 382 (1873); **3**, 108 (1876), 343 (1878).

<sup>3</sup> *Thermodynamische Studien*, Leipzig, 1892, Engelmann.

<sup>4</sup> *Équilibre des systèmes chimiques*, Paris, 1899, Gauthier-Villars.

<sup>5</sup> *L'équilibre des systèmes heterogenes, exposé abrégé*, Paris, 1919, Gauthier-Villars.

<sup>6</sup> *Am. Jour. Sci.*, (3) **16**, 441 (1878).

form of a "fundamental equation," so that by means of the criteria of equilibrium and one such equation for each phase all thermodynamic problems can be solved algebraically; the corresponding graphical method, in which the "fundamental equation" is replaced by a curve or surface has been developed in Holland by van Rijn van Alkemade,<sup>7</sup> Roozeboom<sup>8</sup> and Schreinemakers.

Until in 1906 "The Scientific Papers of J. Willard Gibbs" appeared,<sup>10</sup> his thermodynamical work was inaccessible in English; even yet there is no cheap edition of the treatise on the equilibrium of heterogeneous substances, and, so far as I am aware, no English-speaking university has prescribed it as a text. Courses of instruction and text-books dealing with "the phase rule" from a purely qualitative point of view are generally provided; "Le Chatelier's law," also qualitative, is taught. On the quantitative side, formulas for special cases of certain of the simpler equilibria—freezing-points, boiling-points, osmotic pressures, etc., of two-component systems—are a necessary ingredient of every text-book of physical chemistry; but these formulas are arrived at by a method very different from that of Gibbs. Molecular hypotheses, which however admirable in themselves have no place in a thermodynamic argument, are put in the foreground; special assumptions which greatly restrict the validity of the conclusions are made at the outset; the formulas that result are only those derivable from Gibbs' fundamental equation for "perfect" gaseous solutions adapted to liquids by neglecting their compressibility; how to handle the un-ideal chemicals met in daily practice is not shewn. Very few students after such training are aware that all the problems of chemical equilibrium can be solved if the necessary experimental data are available and none if they are not; fewer know what data must be secured; and fewer still could solve any but the specialized problems of the text-books even if the data were supplied.

<sup>7</sup> *Zeit. phys. Chem.*, **11**, 289 (1893).

<sup>8</sup> *Zeit. phys. Chem.*, **12**, 359 (1893).

<sup>10</sup> Edited by Bumstead and Van Name; London, 1906, Longmans, Green & Co., vol. I. Thermodynamics; vol. II, Dynamics, Vector analysis and multiple algebra, Electromagnetic theory of light, and Miscellaneous papers.

Eventually this will be changed by pressure from without, by demand for men capable of applying thermodynamic methods to the solution of technical problems. But why wait for pressure? If the trouble lies in inadequate mathematical preparation of the students, as has often been suggested, the remedy lies in our own hands. Already every serious student of chemistry attends "a course on the calculus;" these courses are offered at the request of the chemical staffs but it has been left to the mathematicians to decide on their content, and naturally enough the course provided is the standard elementary course, evolved for other groups of students and wholly unadapted to our special needs. Not from unwillingness to help, we may be sure; not because the chemist needs anything that their instructors cannot readily supply; but how can we expect our colleagues to anticipate our wants and make a change unless we tell them what we need?

The standard elementary course on the calculus deals almost exclusively with explicit functions of a single variable, and the drill consists of practice in differentiating them and in integrating complicated expressions carefully selected because reducible to a few canonical forms. Facility in this technique is of little service to the student of physical chemistry; in his own problems moreover he has to deal with functions of at least four independent variables, seldom presented in explicit form. Besides instruction in a few important mathematical properties of such functions, what our students need is drill in handling numbers as they come from the laboratory: construction of graphs and tables, use of interpolation formulas, practice in graphical and numerical differentiation and integration. This the standard course does not supply; but who will say that a course devised to meet our necessities need be longer or more difficult or less educative than the other? It could not fail to be more interesting to those for whom it was designed.

The present paper begins with an examination of the mathematical properties of the physico-chemical functions; these fix the nature of the mathematical training required by men who wish to use them. The functions of thermodynamics are then de-

finer; their mathematical relations are but a special case of what precedes. The rest of the paper is devoted to equilibria of a simple type, it aims to shew how these familiar problems fare when handled by the methods due to Gibbs: first the two laws, next the criteria of equilibrium under the conditions of the experiments, then the general solution free from special assumptions valid only for restricted groups, and Gibbs' way of condensing such assumptions in a "fundamental equation"; at the close an illustration of the use of an abacus to solve a well known problem. Electrochemical illustrations are omitted, the effects of gravity, capillarity, and states of strain in solids are ignored—though not by Gibbs—for what is needed at the present day is widespread knowledge of the means by which these problems fifty years ago were solved, and contrast between old and new is best brought out by simple instances.

#### MATHEMATICAL PROPERTIES OF THE PHYSICO-CHEMICAL FUNCTIONS

##### 1. *Functions defined with reference to a phase*<sup>11</sup>

*Solutions.* Tables of the physico-chemical properties of solutions (a table of the densities of sulphuric acid solutions may serve as example) are constructed by graphic interpolation from a limited number of experimental data; the fact that different computers obtain much the same tabulated values from the same experimental results shews that there is general agreement as to the nature of the curves to be drawn, that is, as to some of the mathematical properties of the functions they represent:

(i) The curve, and therefore the function, is presumed to be continuous.

(ii) It is "smooth," or free from kinks; i.e., the function is assumed to admit of but one derivative at each point.

(iii) It is "direct," i.e., as free as possible from the unwelcome waviness often met with in the graphs of simple power series

<sup>11</sup> A mass "uniform throughout not only in chemical composition but also in physical state". . . . "All bodies which differ only in quantity and form may be regarded as different examples of the same phase." *Trans. Conn. Acad.*, 3, 116, 152 (1876); *Sci. Papers*, 1, 63, 96.

drawn through the experimental points. Functions possessed of these qualities have received no group name from the mathematicians. Some at least of the qualities themselves have not always been taken for granted; Mendelejeff,<sup>12</sup> for instance preferred to graph the densities of sulphuric acid solutions by a series of lines joining at angles, and so later did Pickering and others; discussions<sup>13</sup> in which the latter took part make it clear that the form now generally adopted is the result of choice, not of necessity. The definition of Gibbs' "phases of variable composition" (or "solutions" as van't Hoff<sup>14</sup> renamed them) involves assumptions (i) to (iii); these assumptions are thus at the root of many applications of the phase rule—for instance its use in the identification of basic salts.<sup>15</sup>

(iv) In the case of sulphuric acid solutions, the density is represented as a one-valued function of the composition, although at 15°C. between 97 and 100 percent acid the composition is a two-valued function of the density; in all such tables indeed the physico-chemical property, no matter what, is represented as a one-valued function of the composition. Unanimity in this matter is the result of tacit agreement as to the meaning of the word "composition;" no chemist will admit that two solutions which at the same temperature and pressure have different densities, can have the same "composition". From Maumené's observations,<sup>16</sup> it seems possible that recently boiled solutions of sulphuric acid in water may differ in density as in other properties from those that have been kept, although their titre does not change on keeping; such solutions are excluded from the density table, if they were to be included a double entry table at least would be necessary, and the solutions would be spoken of as "containing" more than two components<sup>17</sup>—trioxide, acid, and water, for instance, or several hydrates perhaps, as in the case of solutions of phosphorus pentoxide.

<sup>12</sup> *Zeit. phys. Chem.*, **1**, 273 (1887).

<sup>13</sup> *British Association Reports, Leeds*, 1890; *Zeit. phys. Chem.*, **7**, 378 (1891).

<sup>14</sup> *Zeit. phys. Chem.*, **5**, 322 (1890).

<sup>15</sup> *Jour. Phys. Chem.*, **7**, 259 (1903).

<sup>16</sup> *Ber. d. d. chem. Ges.*, **8**, 1361 (1875).

<sup>17</sup> Wald: *Jour. Phys. Chem.*, **1**, 21 (1896); Trevor: *ibid.*, foot-note p. 22; Bancroft: *The Phase Rule*, Ithaca, 1897, Ch. 18.

(v) Instead of defining sulphuric acid solutions in terms of weight and percentage of acid, Gibbs would state the weights of acid<sup>18</sup> ( $x$ ) and of water ( $y$ ) they contained; much of the symmetry of his equations is due to this choice of variables, which carries with it important mathematical consequences. "Properties" of the solutions, like density independent of the weight, remain unchanged when *both*  $x$  and  $y$  are doubled or trebled, because such

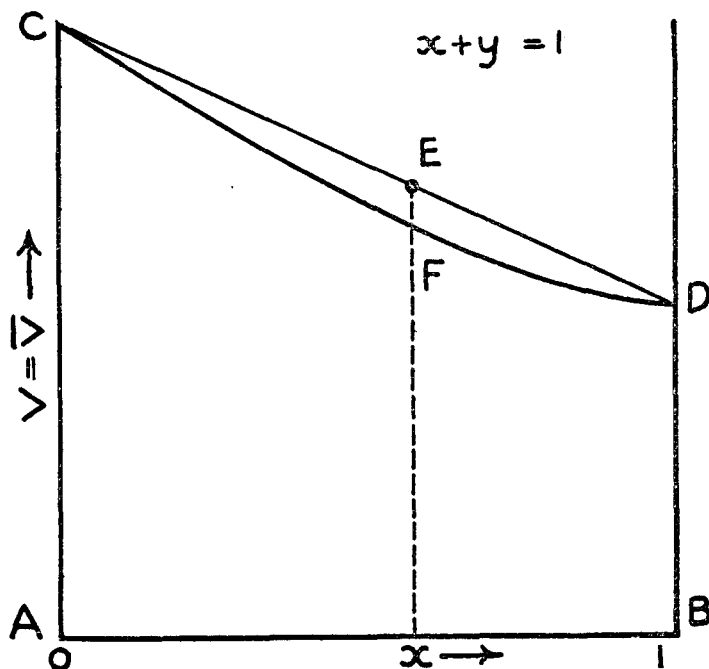


FIG. 1

a change leaves the "composition" unaltered; they are therefore "homogeneous in  $x$  and  $y$  and of degree zero"—while quantities like  $V$  (the number of cubic centimeters occupied by the solution) which under like circumstances would be doubled or trebled, are "homogeneous in  $x$  and  $y$  and of the first degree." Thus, because of the method of representation chosen by him, all the physico-chemical properties and quantities dealt with by Gibbs are homogeneous functions of two at least of the variables.

<sup>18</sup> Gibbs used  $m_1, m_2$ , instead of  $x, y$ .

What may be termed the "standard diagram," where  $x + y = 1$ , and the abscissas give values of  $x$  ranging from 0 to 1, combines the advantages of both methods of representation. In figure 1, the curve gives values of  $V$  and also of the specific volume<sup>19</sup>  $\bar{V} = V/(x + y)$  for sulphuric acid solutions at 15°C. and atmospheric pressure; if instead of values of  $V$  there be plotted values of Gibbs' function  $\zeta$ , figure 1 becomes the thermodynamic diagram of Roozeboom and van Ryn van Alkemade,<sup>20</sup> the introduction of which constitutes perhaps the most important contribution to the study of chemical equilibria since the publication of the papers of Gibbs.

*Heterogeneous systems.* The volume of one gram (or the "specific volume") of a system composed of  $x$  grams of acid and  $y$  grams of water *kept separate* is given by the ordinate  $xE$  drawn from the point  $x$  on  $AB$  to meet the straight line  $CED$ . Similarly the specific volumes of heterogeneous systems consisting of 20 and 50 per cent solutions in any proportions can be found by drawing a straight line to join the points on the curve  $CFD$  which have the abscissas  $0.2$  and  $0.5$  respectively. But though the specific volumes of such heterogeneous systems may readily be found by straight line construction from the graph of the specific volumes of the solutions, their densities or normalities could not similarly be obtained from graphs of the densities or normalities of the solutions on the standard diagram; it is therefore apparent that although a graph of the density gives exactly the same information as a graph of the specific volume, nevertheless for certain calculations the latter is the more convenient function. To emphasize the distinction, an "orthomeric" function may be defined to be one whose graph for a heterogeneous system on the standard diagram is a straight line.

<sup>19</sup> The bar over a capital letter is used to indicate that the quantity represented by the unbarred letter is to be divided by the mass; thus barred capitals refer to unit mass (1 gram). Helm [*Grundzüge d. math. Chem.*, Leipzig, 1894, Engelmann; p. 41] used capitals and lower-case italics. Lewis and Randall use the bar and a subscript numeral to indicate the partial derivative with respect to the mass of one of the components, their unit of mass being the mol.; they use small capitals to indicate volume, etc., per mol, thus their  $v$  means  $M\bar{V}$  where  $M$  is the molecular-weight in grams.

<sup>20</sup> *Loc. cit.*



2. *Functions defined with reference to a reaction. Potential functions*

By the term "heat of a reaction" is meant the number of calories gained by the calorimeter when specified weights of the reagents all at the same temperature are brought together in a calorimeter, allowed to react, and the product of the reaction brought to the initial temperature of the reagents. Used in this connection, the word "reaction" has a special sense, as it implies equality of temperature between the initial and final states of the system. In what follows, temperature pressure and the masses of the components will be employed as "independent variables;"<sup>21</sup> it is therefore convenient that the word "reaction" without qualification should imply equality of pressure as well, so that it may be possible to speak of values of  $t$ ,  $p$ ,  $x$ , and  $y$  for a reaction.<sup>22</sup>

The number of calories gained by the (constant pressure) calorimeter during such a "reaction" may be represented by the symbol  $Q$ ; the properties of the function so defined must be established experimentally. It is found in the laboratory that  $Q$  for a given reaction is a one-valued function of  $t$ ,  $p$ ,  $x$  and  $y$  for the reaction, that it is independent of the temperature of the calorimeter (as distinct from that of the reaction), and that if both  $x$  and  $y$  be doubled (or trebled) while  $t$  and  $p$  remain unchanged,  $Q$  is also doubled (or trebled). Hence  $Q$  is homogeneous and of the first degree in  $x$  and  $y$ , and  $\bar{Q} = Q/(x + y)$ , gives the "heat of the reaction" for one gram.

The quantity  $Q$  moreover "admits of a potential" ( $\chi$ ); this means that the value of  $Q$  depends solely on the initial state ( $A$ ) and the final state ( $B$ ) of the system (both being at the same temperature and pressure), no matter through what intermediate states it may have passed during its change from  $A$  to  $B$ . This

<sup>21</sup> Gibbs prefers entropy, volume, and the masses of the components, for reasons given in a footnote to *Trans. Conn. Acad.*, 2, 382; *Sci. Papers*, 1, 34; for the beginner, however, entropy as independent variable is impossible.

<sup>22</sup> The masses of the components in grams are given by  $x$ ,  $y$ ,  $z$ , etc.;  $t$  gives the temperature on the thermodynamic scale; if the gram calorie be adopted as unit of heat, and the cubic centimeter as unit of volume,  $p$  gives the pressure in millimeters of mercury multiplied by 1.3596/42650; thus for one atmosphere  $p = 0.02423$ .

theorem is assumed every time the heat of a reaction is calculated by subtracting the heat of formation of the reagents from that of the products. The definition of the potential function is  $\chi_A - \chi_B = Q$ , where the value of  $\chi_A$  depends only on the temperature pressure weight and nature of the reagents and that of  $\chi_B$  on the products; thus  $\chi$  unlike  $Q$  is not defined with respect to a reaction, and from its definition it is apparent that  $\chi$  must be homogeneous in  $x$  and  $y$  and of the first degree; it is also, obviously, orthomeric.

The tabulated heats of formation (for one gram in each case) with signs changed, might be chosen as values of  $\bar{\chi} = \chi/(x + y)$ . This choice would be equivalent to setting  $\chi = 0$  for every chemical element at the temperature and pressure (usually 18°C. and one atmosphere) for which the heats of formation were given; and if the values of  $\chi$  so chosen were used to calculate the heat of any reaction in which one element was converted into another at this temperature and pressure, the result would be  $Q = 0$  in every case. Until such reactions are studied and the amounts of heat evolved determined, this is of no practical importance; and if it should be found necessary to allot an individual value of  $\bar{\chi}$  to each element, it would be easy to compute a new set of values of  $\bar{\chi}$  for the compounds; except for reactions between the elements, the values of  $Q$  obtained from one set would be the same of those from the other. (Another example of a potential function in general use is supplied by the tables of "individual electromotive forces;" in this case there exist at present two rival conventions as to the zero.)

The fact that in allotting numerical values to  $\chi$  convention as well as experiment plays a part, seems to awake an uneasy feeling in the minds of some; the number of possible reactions however so greatly exceeds the number of substances that tables of  $Q$  are out of the question. Others again feel that  $\chi$  is too "abstruse"; but for the purpose of calculating the results of physico-chemical experiments it is not necessary that there should be an "explanation" of the experimentally established fact that  $Q$  admits of a potential, it is sufficient that the fact itself be put in convenient mathematical form. By adopting this procedure,

not only can the argument be made clearer and more precise, but there is less danger that a sound conclusion might fall under suspicion should the day arrive for the irrelevant "explanation" to be abandoned.

Values of  $\bar{Q}$  for the reaction between sulphuric acid and water  
 $x$  grams acid +  $y$  grams water  $\rightarrow$  ( $x + y$ ) grams solution  
 are plotted (for 15°C and 1 atm.) in figure 2; at  $x = 0$  and at  $x = 1$

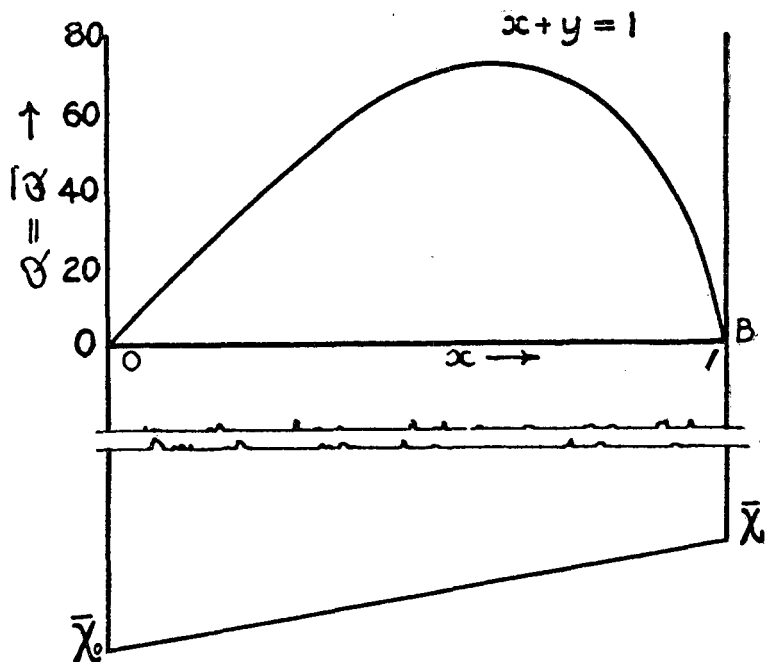


FIG. 2

$Q$  must obviously be zero, while  $\bar{\chi}$  will depend on temperature pressure and the choice of a zero. Writing  $\bar{\chi}_0$  and  $\bar{\chi}_1$  for the values of  $\bar{\chi}$  at  $x = 0$  and  $x = 1$  respectively, the values of  $\bar{\chi}$  for any heterogeneous system formed of  $x$  grams acid and  $y$  grams water will be given by  $x \cdot \bar{\chi}_1 + y \cdot \bar{\chi}_0$ , and  $Q = x \cdot \bar{\chi}_1 + y \cdot \bar{\chi}_0 - \bar{\chi}$ . Thus the curve drawn for  $Q$  could be used for  $\bar{\chi}$ , but while values of  $Q$  are found by measuring the distance from  $AB$  to the curve, values of  $\bar{\chi}$  must be found by measuring from the curve to a

straight line whose ordinates at  $x = 0$  and  $x = 1$  are  $\bar{\chi}_0$  and  $\bar{\chi}_1$  respectively.<sup>23</sup>

The "heat of dilution," or the number of calories gained by the calorimeter when one gram of water is added to a large quantity of solution is given by  $\partial Q/\partial y$ , (which may be written<sup>24</sup>  $q_y$ ); this differs by a constant from  $-\partial\chi/\partial y$  (or  $-\chi_y$ ); while  $\partial q_x/\partial y$  (or  $q_{xy}$ ) which measures the effect of concentration on the heat of dilution, is equal to  $-\chi_{xy}$ , the conventional constants disappearing in the second differentiation.

The physico-chemical properties of solutions, then, are represented by continuous one-valued functions of  $t$  (the temperature),  $p$  (the pressure),  $x$  and  $y$  (the weights of the components); they admit of but one derivative at each point, are homogeneous in  $x$  and  $y$ , and for choice are orthomeric. The mathematical properties of such functions, in particular the relations between their derivatives, are thus of special interest to chemists; while the "standard diagram" bears the same relation to the calculations of physical chemistry that the standard trigonometrical diagram—circle of unit radius, with lines named *sin*, *cos*, *tan*, etc., bears to those of the surveyor.

#### *Relations between the derivatives of the physico-chemical functions*

The notation for partial derivatives introduced by Gibbs is precise; he prints in small type to the right of the symbol the quantities held constant during the differentiation. Thus  $\frac{\partial V}{\partial x}{}_{t,p,y}$  is the

<sup>23</sup> By convention, a quantity measured *upwards* on the diagram is *positive*, one measured downwards is *negative*. If the (negative) heats of formation be adopted as values of  $\bar{\chi}$ , then  $\bar{\chi}_0 = -3820$  and  $\bar{\chi}_1 = -1973$ ; this part of figure 2 is not drawn to scale.

<sup>24</sup> Since  $t, p, x, y$ , have been adopted as independent variables,  $\partial Q/\partial y$  stands for  $dQ/dy$  ( $t, p, x, \text{const.}$ ). The symbol  $\partial Q/\partial y$  may be abbreviated to  $q_y$ , similarly  $\partial V/\partial x$  to  $v_x$ ,  $\partial V/\partial t$  to  $v_t$ , etc.; following this system, the symbol  $c_p$  is here used as an abbreviation for  $\partial C/\partial p$  (rate of change of heat capacity with pressure) and not with the customary meaning (specific heat at constant pressure, our  $\bar{C}$ ). Gibbs writes  $\mu_t$  for  $\partial\zeta/\partial m_1$  ( $t, p, m_2 \text{ const.}$ ); in the present paper  $\mu_x$  is written for  $\partial\zeta/\partial x$  ( $t, p, y, \text{const.}$ ), and similarly  $\mu_t$  for  $\partial\zeta/\partial t$  ( $p, x, y, \text{const.}$ ), etc. The symbol  $\partial\bar{V}/\partial x$  may conveniently be abbreviated to  $\bar{v}_x$ , but the use of this abbreviation should not mislead the beginner into thinking that  $\bar{v}_x = v_x/(x + y)$ .

derivative commonly written  $\partial V/\partial x$  and in this paper  $v_x$ ; another derivative to which because of its importance the special symbol  $DV/Dx$  may be assigned, is  $\frac{\partial V}{\partial x}$  *t, p, (x + v)*, it gives the slope of the  $V$  curve on the standard diagram. By means of the three equations  $dt = 0, dp = 0, d(x + y) = 0$  implied by the small letters in Gibbs' symbol,  $dt, dp$  and  $dy$  may be eliminated from the general expression for  $dV$ , viz:

$$dV = v_t \cdot dt + v_p \cdot dp + v_x \cdot dx + v_y \cdot dy \quad (1)^{25}$$

giving  $DV/Dx = -DV/Dy = v_x - v_y$ , and in general

$$D/Dx = -D/Dy = \partial/\partial x - \partial/\partial y$$

*Euler's theorem.* The fact that all physico-chemical functions are homogeneous in two of the variables ( $x$  and  $y$ ) and not in the other two ( $t$  and  $p$ ), leads to characteristic and important relations between their derivatives. Writing  $z_x$  for  $\partial Z/\partial x$  and  $z_y$  for  $\partial Z/\partial y$ , Euler's theorem asserts that if  $Z$  be a function homogeneous in  $x$  and  $y$  and of degree  $n$ , then

$$n \cdot Z = x \cdot z_x + y \cdot z_y \quad (2)$$

Since  $V$  is of the first degree this gives  $V = x \cdot v_x + y \cdot v_y$ , and as  $\bar{V}$  is of degree zero,  $0 = x \cdot \bar{v}_x + y \cdot \bar{v}_y$ ; when  $x = 0, v_y = V/y = \bar{V}$ , and  $\bar{v}_y = 0$ .

To arrive at these relations without appeal to Euler, a special case may be considered: If to a solution formed of acid and water, more acid and water be added *in the proportion in which they are already contained in the solution*, the composition of the solution will remain the same as before; and if temperature and pressure after the addition be made the same as before, there will be no change in the specific volume of the solution or in any other property that depends only on temperature pressure and composi-

<sup>25</sup> This equation implies only that  $V$  is a function of  $t, p, x$ , and  $y$ , and that it admits of a derivative; thus  $V$  and its derivatives may be replaced by  $\bar{V}$  and its derivatives. As  $V, v_t, v_p, v_x$  and  $v_y$  are one-valued functions of the independent variables, their values are fixed when definite values are chosen for  $t, p, x$ , and  $y$ ; but the three ratios between the four quantities  $dt, dp, dx$ , and  $dy$  may still be given any values desired.

tion; the volume of the solution on the other hand, and all other functions of the first degree, will be increased in the same proportion as that in which the amount of acid (and of water) in the solution was increased. In the language of the calculus, if  $dt = 0$ ,  $dp = 0$  and  $dx:dy = x:y$ , then  $d\bar{V} = 0$  and  $dV/V = dx/x$ ; substituting these values of  $dt$ ,  $dp$ ,  $dy$ , and  $dV$  (or  $d\bar{V}$ ) in Eq. (1), the equations sought result.

Equating the two expressions for  $dV$  given by Eq. (1) and Eq. (2), there follows the important relation:<sup>26</sup>

$$0 = -v_t \cdot dt - v_p \cdot dp + x \cdot dv_x + y \cdot dv_y \quad (3)$$

Gibbs' function  $\zeta$  is of the first degree; substituting  $\zeta$  for  $Z$  in (2) gives Gibbs' equation<sup>27</sup> 96, while (3) gives Gibbs' 97.

9	[11]	20
[4]	[-1]	[3]
5	[12]	17

FIG. 3

In order to apply Euler's theorem to  $v_t$ ,  $v_x$  etc., the degrees of these functions must be found: Since  $v_t$  is a special case of the fraction  $(V_2 - V_1)/(t_2 - t_1)$ , the difference between the volumes of two solutions divided by the difference between their temperatures, the degree of  $v_t$  will be the same as that of the fraction, viz; 1; while the degree of  $v_x$  is the same as that of  $(V_2 - V_1)/(x_2 - x_1)$  viz.: 0. Hence from (2):  $v_t = x \cdot \partial v_t / \partial x + y \cdot \partial v_t / \partial y$ , and  $0 = x \cdot \partial v_x / \partial x + y \cdot \partial v_x / \partial y$ . Similarly in other cases.

*Values of second derivatives independent of order of differentiation:* According to this theorem,  $\partial v_x / \partial t = \partial v_t / \partial x$  so that the

<sup>26</sup> As is obvious from its derivation, this equation implies not only that  $V$  is a function of  $t$ ,  $p$ ,  $x$ , and  $y$ , but also that it is homogeneous of the first degree in  $x$  and  $y$ ; thus  $V$  may not be replaced by  $\bar{V}$  in Eq. (4).

<sup>27</sup> The numbers are those of the equations in the paper "On the equilibrium of heterogeneous substances."

compact symbol  $v_{ix}$  may be used in place of either of them. The theorem is a special case of a general relation existing between the differences of any four numbers; in figure 3 the four numbers are written at the corners of a rectangle, and their differences (left from right, bottom from top) are given in brackets between them; the differences between these differences (taken in the same order) must be identical, no matter what the numbers may be. This understood, the proof of the theorem resolves itself into a reading lesson in the symbols of the calculus (fig. 4); and it is obvious that unless  $Z$  be a one-valued function of the variables the

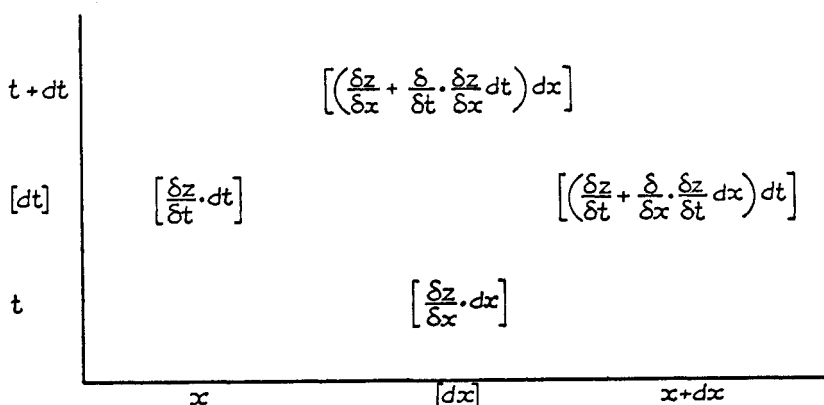


FIG. 4\*

theorem will not apply. Clausius found it necessary to emphasize this point when dealing with the quantity  $\mathbf{W}$  in the introduction to his celebrated treatise.<sup>28</sup>

*The "mathematical group" of second derivatives:* There are in all sixteen second derivatives of  $V$  of the type  $\frac{\partial v_{ix}}{\partial t}$ ,  $\frac{\partial v_{ix}}{\partial p}$ , etc., in which all four independent variables appear either in the denominator or as small letters to the right; these are the derivatives for which in works on mathematics the symbols  $\partial^2 V / \partial t^2$ ,  $\partial^2 V / \partial t \cdot \partial p$  etc. are employed, and in this paper the symbols  $v_{it}$ ,

<sup>28</sup> R. Clausius, *Mechanische Wärmetheorie*, 3 ed., Braunschweig, 1887, Vieweg.—*Mathematische Einleitung*.

\* In making this cut, the symbol  $\delta$  was inadvertently used instead of  $\partial$ .

$v_{tp}$ , etc.; for want of a better name they may be called the "mathematical group." By means of the two theorems stated above, ten of them can be expressed in terms of the other six. In Table I,  $v_{tt}$ ,  $v_{tp}$ ,  $v_{tx}$ ,  $v_{pp}$ ,  $v_{px}$ ,  $v_{xx}$  are chosen as the six; \* indicates that the reduction was effected by means of Euler's theorem for

TABLE I  
Mathematical group

DENOMINATORS	NUMERATORS			
	$\partial v_t$	$\partial v_p$	$\partial v_x$	$\partial v_y$
$\partial t$	$v_{tt}$	$v_{tp} \S$	$v_{tx} \S$	$(v_t - x \cdot v_{tx})/y \S$
$\partial p$	$v_{tp}$	$v_{pp}$	$v_{px} \S$	$(v_p - x \cdot v_{px})/y \S$
$\partial x$	$v_{tx}$	$v_{px}$	$v_{xx}$	$-x \cdot v_{xx}/y \S$
$\partial y$	$(v_t - x \cdot v_{tx})/y \dagger$	$(v_p - x \cdot v_{px})/y \dagger$	$-x \cdot v_{xx}/y^*$	$x^2 \cdot v_{xx}/y^{2*}$

TABLE II  
Physical group

DENOMINATORS	NUMERATORS							
	$\partial v_t$		$\partial v_p$		$\partial t$		$\partial p$	
$\partial v_t$	—	—	1 · (t) R 7	2 · (p) R 8	3 · (v <sub>p</sub> ) R 13	4 · (p) R 14	5 · (v <sub>p</sub> ) R 19	6 · (v <sub>t</sub> ) R 20
$\partial v_p$	7 · (t) s/t	8 · (p) r/s	—	—	9 · (v <sub>t</sub> ) R 15	10 · (v <sub>p</sub> ) R 16	11 · (v <sub>t</sub> ) R 21	12 · (t) R 22
$\partial t$	13 · (v <sub>p</sub> ) (rt - s <sup>2</sup> )/t	14 · (p) r	15 · (v <sub>t</sub> ) (s <sup>2</sup> - rt)/s	16 · (p) s	—	—	17 · (v <sub>t</sub> ) R 23	18 · (v <sub>p</sub> ) R 24
$\partial p$	19 · (v <sub>p</sub> ) (s <sup>2</sup> - rt)/s	20 · (t) s	21 · (v <sub>t</sub> ) (rt - s <sup>2</sup> )/r	22 · (t) t	23 · (v <sub>t</sub> ) - s/r	24 · (v <sub>p</sub> ) - t/s	—	—

$$r = v_{tt} \quad s = v_{tp} \quad t = v_{pp}$$

functions of degree zero, † by Euler's theorem for functions of the first degree, § by the "order of differentiation" theorem.

The "physical group" of second derivatives: There are twenty-four second derivatives of  $V$  for which both  $x$  and  $y$  are constant and in whose symbols neither  $v_x$  nor  $v_y$  appear; such are  $\frac{\partial v_t}{\partial t} \text{ }^{pxv}$ .

$\frac{\partial v_t}{\partial v_p} \text{ }^{pxv}$ , etc. These may be called the "physical group," as they



arise in the discussion of experiments where the compositions of the substances involved were not changed. Twelve of them are reciprocals (*R*) of the other twelve, and all can be expressed in terms of three, viz.,  $v_{tt}$ ,  $v_{tp}$ ,  $v_{pp}$ . To save space in Table II, the customary abbreviations  $\mathbf{r} = v_{tt}$ ,  $\mathbf{s} = v_{tp}$ ,  $\mathbf{t} = v_{pp}$  have been used, while the third quantity held constant during differentiation is printed in brackets.

If  $V$  be replaced by  $\zeta$  (and consequently  $v_t$  by  $-\eta$ ,  $v_p$  by  $V$ ,  $v_{tt}$  by  $-C/t$ ,  $v_{tp}$  by  $v_t$ , and  $v_{pp}$  by  $v_p$ , see page 317), Table II

TABLE III  
Chemical group

DENOMINATORS	NUMERATORS							
	$\partial v_x$		$\partial v_y$		$\partial x$		$\partial y$	
$\partial v_x$	—	—	1·(x) R 7	2·(y) R 8	3·(v <sub>y</sub> ) R 13	4·(y) R 14	5·(v <sub>y</sub> ) R 19	6·(v <sub>x</sub> ) R 20
$\partial v_y$	7·(x) — y/x	8·(y) — y/x	—	—	9·(v <sub>x</sub> ) R 15	10·(v <sub>y</sub> ) R 16	11·(v <sub>x</sub> ) R 21	12·(x) R 22
$\partial x$	13·(v <sub>y</sub> ) 0	14·(y) — y $\mathbf{s}/x$	15·(v <sub>x</sub> ) 0	16·(y) $\mathbf{s}$	—	—	17·(v <sub>x</sub> ) R 23	18·(v <sub>y</sub> ) R 24
$\partial y$	19·(v <sub>y</sub> ) 0	20·(x) $\mathbf{s}$	21·(v <sub>x</sub> ) 0	22·(x) — x $\mathbf{s}/y$	23·(v <sub>x</sub> ) — x/y	24·(v <sub>y</sub> ) — x/y	—	—

$$\frac{Dv_x}{D_x} = -\frac{Dv_x}{D_y} = -\frac{x+y}{x} \mathbf{s}; \quad \frac{Dv_y}{D_x} = -\frac{Dv_y}{D_y} = \frac{x+y}{y} \mathbf{s}; \quad \mathbf{s} = v_{xy}$$

includes Clerk Maxwell's relations between the eight thermoelastic coefficients;<sup>29</sup> and as moreover the two specific heats (at constant pressure and at constant volume) can also be expressed in terms of the second derivatives of  $\zeta$  (see page 317), all the mathematical relations existing between the thermal coefficients are comprised in Table II, only three of them are independent. As an illustration of these relations: the assumptions that liquids and solids are incompressible ( $v_p = 0$ ), and that their thermal expansions are negligible ( $v_t = 0$ ), carry as consequences

<sup>29</sup> See *E. Ariès, Chimie physique élémentaire*, Paris, 1914, Hermann. Ch. 1.

that their specific heats (at constant pressure) must be independent of the pressure, and that their Joule-Thomson heats must be zero; the wholly different assumptions as to the compressibilities and thermal expansions of gases made by the equation  $pV = mat$  carry these very same consequences.

*The "chemical group" of second derivatives.* If in the symbols of the twenty-four members of the "physical group" the letter  $x$  be substituted for  $t$  and  $y$  for  $p$ , wherever these letters occur, there will result a list of the twenty-four members of the "chemical group;" and by similar transliteration the relations obtained in Table II can be made available. But while  $v_{tt}$ ,  $v_{tp}$ , and  $v_{pp}$  are independent,  $v_{xx}$ ,  $v_{xy}$ , and  $v_{yy}$  are not; they are related by the two equations  $0 = x \cdot v_{xx} + y \cdot v_{xy}$  and  $0 = x \cdot v_{xy} + y \cdot v_{yy}$  (Euler's theorem). Of the three,  $v_{xy}$ , the most symmetrical, has been retained; and Table III gives expressions for the other twenty-three in terms of  $v_{xy}$ .

*Other derivatives.* Numerous other groups of the second derivatives of  $V$  might be constructed, but these three are the most important. The derivatives of  $\bar{V}$  might be classified similarly; but all of them can be expressed in terms of the derivatives of  $V$  by means of the equation of definition  $V = (x + y) \cdot \bar{V}$ .

*The standard diagram.* In figure 5,  $BH$  gives  $V = \bar{V}$  for  $x = 0.8$ , and  $GF$  is the tangent to the  $V = \bar{V}$  curve  $LHK$  at  $x = 0.8$ ; for the eighty per cent solution at the temperature and pressure of the diagram, therefore,  $DV/Dx$  is negative, and its numerical value is given by the length  $NF$  measured on the scale of ordinates. By means of two relations already obtained, viz.,  $V = x \cdot v_x + y \cdot v_y$ , and  $DV/Dx = v_x - v_y$ , it may be shown that  $v_x$  is given by  $CF$  and  $v_y$  by  $AG$  both positive; while similarly  $\bar{v}_x$  (negative) and  $\bar{v}_y$  (positive) are given by  $HE$  and  $HM$  respectively.

If instead of  $V$ , Gibbs' function  $\zeta$  had been plotted, the lengths  $CF$  and  $AG$  would give  $\partial\zeta/\partial x$  and  $\partial\zeta/\partial y$  respectively (or  $\mu_x$  and  $\mu_y$  in Gibbs' notation). Much of the usefulness of van Rijn's thermodynamic diagram depends on the advantage he has taken of this construction.



ferences are given in brackets in the figure, and the demonstration of the theorem is reduced to a reading lesson in the symbols of the calculus. When functions of four variables are involved, it is not necessary that the other two should be held constant during the integration; they might vary with the first two according to any law, for instance,  $x + y$  might be constant for the diagram. What is essential is, that  $Z$  should be a one-valued function of the variables, like  $V$ , or any of the potential functions; quantities like  $Q$  or  $W$ , whose values are not uniquely determined by the initial and final states of the system, are excluded.

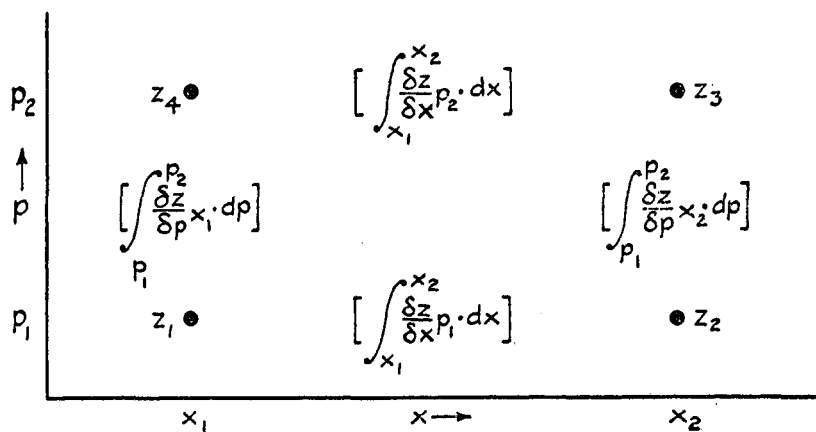


FIG. 6\*

## THE FUNCTIONS OF THERMODYNAMICS

The calculations of chemical thermodynamics deal with (1) chemical changes in a system, (2) the quantity  $Q$ , viz., the number of calories <sup>30</sup> gained<sup>31</sup> by a heat reservoir, e.g., a calorimeter, when these changes occur, and (3) the number of gram-centimetres gained by a weight or weights while the system changes and the

<sup>30</sup> The conceptions "quantity of heat" and "temperature" are admirably discussed by E. Mach in his *Principien der Wärmelehre*, Leipzig, 1900, Barth.

<sup>31</sup> The "chemical convention" is here adhered to; according to the "thermodynamic convention" the symbol should be defined to give the number of calories lost by the reservoir.

\*In making this cut, the symbol  $\delta$  was inadvertently used instead of  $\partial$ .

reservoir gains the  $Q$  calories. To simplify the formulas, the quantity  $W$  is defined to be the quotient of the number of gram-centimetres divided by the factor 42650, and the unit of pressure is so chosen that for a pressure of one millimetre of mercury,  $p = 1.3596/42650$ . The experimental work is supposed to be carried out under such conditions that, except the reservoir and the weights, no bodies not included in the "system" are affected by changes occurring in it; to simplify the definitions, only one heat reservoir is assumed; if in practice more should be involved, all but one must be restored to their original condition before the operation is considered to be complete. Temperatures are those of the thermodynamic scale,<sup>32</sup> invented<sup>33</sup> to simplify the formulas.

All that is known of these two quantities  $Q$  and  $W$  has been ascertained by experiment; what is needed for the present purpose is stated in the following two laws:

I. In the first place, neither  $Q$  nor  $W$ , depends solely on the initial and final states of the system, i.e., neither of them admits of a potential; the sum of the two, however, does; and Gibbs' symbol for this potential function,<sup>34</sup> viz.:  $\epsilon$ , may be defined by the equation

$$\epsilon_A - \epsilon_B = Q + W \quad (\text{I})$$

where  $\epsilon_A$  is the value of  $\epsilon$  for the system in the (initial) state  $A$ , and  $\epsilon_B$  in the (final) state  $B$ . This definition imposes no restriction as to the temperature of the heat reservoir, and is valid whether  $A$  and  $B$  be uniform in temperature pressure and composition throughout or the reverse, whether the change be reversible or non-reversible, and whether it be a "reaction" in the narrow sense defined above, a change of temperatures or of pressures or a combination of all three. Since experience shows that both  $Q$  and  $W$  are doubled or trebled when the masses of all the components are doubled or trebled while in every other respect the change  $A \rightarrow B$  remains the same as before, it follows that  $\epsilon$  must be homogeneous and of the first degree in the variables defining the masses of the components.

<sup>32</sup> Called also "absolute scale" or "Kelvin scale," *deg. K.*

<sup>33</sup> W. Thomson: *Trans. Roy. Soc. Edin.*, **21**, 123 (1854).

<sup>34</sup> Introduced by Clausius, who used the symbol  $U$ . *Pogg. Ann.*, **79**, 384 (1850).

II. In the second place, if the change in the chemical system and also all operations necessary to ensure that only one reservoir is affected, be "reversible" in the technical sense in which that word is used in thermodynamical reasoning,<sup>35</sup> then for any given change  $A \rightarrow B$ , and a heat reservoir of temperature  $t_r$ , the number of calories gained by the reservoir is a minimum (and consequently, by I, the number of gram-centimeters gained by the weights a maximum); and the quotient of this minimum number of calories divided by the temperature of the reservoir admits of a potential<sup>36</sup>  $\eta$ :

$$\eta_A - \eta_B = \frac{\text{minimum number of calories}}{\text{temperature of reservoir}} \quad (\text{II})$$

Like  $\epsilon$ , and for a similar reason,  $\eta$  must be homogeneous and of the first degree in  $x$  and  $y$ .

These two functions  $\epsilon$  and  $\eta$  are sufficient; but, as in trigonometry, a large number of convenient though unnecessary functions<sup>37</sup> have been introduced:

1.  $Q, \chi$ : In the special case that the change  $A \rightarrow B$  consists of a "reaction" carried out by bringing the reagents together in :

<sup>35</sup> Illustrated by Clausius *Mechanische Wärmetheorie*, 3 ed., Braunschweig, Vieweg (1887) Vol. I, Abschnitt III.

<sup>36</sup> Due to Clausius, who used the symbol  $S$ . *Pogg. Ann.*, **93**, 500 (1854).

<sup>37</sup> Massieu's "characteristic functions"  $\psi = (t\eta - \epsilon)/t$  and  $\psi' = (t\eta - \epsilon - pV)/t$ , [*C. r.*, **69**, 858, 1087 (1869)] antedate Gibbs' work and are quoted by him; they correspond to Gibbs'  $-\psi/t$  and  $-\zeta/t$  respectively. Planck gave Massieu's  $\psi'$  the symbol  $\Phi$  [*Wied. Ann.*, **32**, 462 (1887)], van Laar gave it the symbol  $\Psi$  and called it "Planck's potential."

G. N. Lewis' "fugacity" may be defined by the equation  $\mu_x = at \cdot \log f_x/a + \bar{E}_1 + t(\bar{C}_1 - \bar{H}_1 - \bar{C}_1 \cdot \log t)$  where  $f_x$  (written  $f_1$  by Lewis) is the fugacity of the component whose mass in the phase is denoted by  $x$  and the symbols  $\bar{E}_1$ ,  $\bar{H}_1$ ,  $\bar{C}_1$ , and  $a$  have the meanings assigned them in the paragraph on perfect gaseous solutions (page 334 below), regardless of the state of aggregation or the degree of "perfection" of the phase to which  $\mu_x$  refers; thus for a perfect gas,  $f = p$ .

Lewis' "(absolute) activity"  $\xi$  is defined by  $\xi_1 = f_1/Rt$ , where  $R$  is the gas constant [*Proc. Am. Acad.*, **43**, 259 (1907)]. His "(relative) activity  $a$ ," or "activity" *tout court*, is the quotient of  $f_1$  by the value of the fugacity of the same component in an arbitrarily selected "standard state;" i.e., in a phase which is to be chosen from case to case with the object of simplifying the equations, and which may differ in concentration (or even in composition) and in pressure, but not in temperature, from that to which  $f_1$  refers. Thus, in the standard state itself,  $a_1 = 1$ .

constant pressure calorimeter (as distinguished from a calorimetric bomb)  $\mathbf{W} = p(V_B - V_A)$ , and  $Q$  is written for  $\mathbf{Q}$ . From I it follows that  $\epsilon_A - \epsilon_B = Q + p(V_B - V_A)$ , and from this, that  $\mathbf{Q}$  admits of a potential ( $\chi$ ), and that  $\chi = \epsilon + pV$ . (G 89).<sup>38</sup>

2.  $\mathcal{Q}, t\eta; \mathcal{W}, \psi$ : In the special case that the change is reversible and a "reaction," and that the temperature  $t_r$  of the reservoir is the same as that of the reaction, viz:  $t$ ,  $\mathbf{Q}$  may be replaced by  $\mathcal{Q}$  and  $\mathbf{W}$  by  $\mathcal{W}$ . From II,  $\mathcal{Q} = t(\eta_A - \eta_B)$ ; and from this and I,  $\mathcal{W} = \epsilon_A - \epsilon_B - t(\eta_A - \eta_B)$ , whence the conclusion that  $\mathcal{W}$  admits of a potential ( $\psi$ ), and that  $\psi = \epsilon - t\eta$  (G 87).

3.  $\mathcal{L}, \zeta$ : The quantity  $\mathcal{L} = \mathcal{W} - p(V_B - V_A)$ , if multiplied by 42650, gives the amount by which the number of gram centimeters gained by the weights when the reaction is carried out reversibly exceeds the number gained when the reaction is carried out in a constant-pressure calorimeter, viz:  $p(V_B - V_A)$ . It likewise gives the number of gram-centimeters calculable from electrochemical equivalents and the voltage of a reversible cell, without regard to any change of volume caused by the electrochemical process. From its definition it follows that  $\mathcal{L}$  admits of a potential ( $\zeta$ ) and that  $\zeta = \epsilon - t\eta + pV$  (G 91).

Names<sup>39</sup> have been given to some of these functions:  $\epsilon$  for instance is "the energy of the system,"  $\eta$  "the entropy of the system,"  $\mathcal{W}$  "the free energy of the reaction" and  $\psi$  "the free

<sup>38</sup> Equation 89 of Gibbs' paper "On the equilibrium of heterogeneous substances." *Trans. Conn. Acad.*, 3, 108 (1876); *Sci. Papers*, 1, 55.

<sup>39</sup> W. Thomson called  $\epsilon$  "the mechanical energy of a body in a given state" [*Trans. Roy Soc. Edin.*, 30, 475 (1851)]. Kirchoff used the term "Wirkungsfunktion" for  $-\epsilon$  [*Pogg. Ann.*, 103, 177 (1858)], and Zeuner "innere Wärme" [*Grundzüge d. mech Wärmetheorie* (1860)]. Clausius [*loc. cit.*] gave the name "entropy" to  $\eta$ . Gibbs called  $\psi$  "the force function of the system for constant temperature," and, earlier, the "available energy"; for other senses in which the words entropy and available energy have been used, see a note by Gibbs [*Trans. Conn. Acad.*, 2, 401 (1873)]. Helmholtz gave  $\psi$  the name "free energy" [*Math. u. nat. Mitt. d. Berlin. Akad.*, 1, 7 (1882)], and Duhem called it "inner thermodynamic potential" [*Le Potentiel thermodynamique*, Paris, 1886]. The name "thermodynamic potential at constant pressure" for  $\zeta$  is due to Duhem [*Traité élém. de méch. chimique*, Paris, 1897; Hermann]. The name "potential" was given by Gibbs to  $\mu_x$ ; Helm suggested "chemical intensity" [*Lehre v. d. Energie*, Leipzig, 1887; Felix; *Die Energetik*, Leipzig, 1898; Veit]. The product of  $\mu_x$  into the molecular-weight of the component is called by G. N. Lewis "the partial molal free energy" of the component.

energy of the system,"  $\mathcal{Q}$  "the bound energy of the reaction,"  $\zeta$  "the thermodynamic potential at constant pressure," and  $\partial\zeta/\partial x$  (or  $\mu_x$ ) the "potential" of the component whose mass in the phase is given by  $x$ . These names however are often used rather loosely,<sup>40</sup> and moreover are apt to suggest to the beginner something other than the exact meaning of the functions whose names they were intended to be;<sup>41</sup> all misunderstanding is avoided if such names as epsilon, eta, zeta, etc., are employed.<sup>42</sup>

### *Derivatives of the thermodynamic functions*

*With respect to  $t$ .* If a substance of uniform temperature pressure and composition be contained in a cylinder closed at the top by a frictionless piston the weight of which fixes the pressure on the substance, and if without changing  $p, x$ , or  $y$  the temperature of the substance be brought from  $t$  to  $t + dt$  by immersing the

<sup>40</sup> In Lewis and Randall's *Thermodynamics and the free energy of chemical substances* [New York, 1923, McGraw-Hill Book Co.], which appeared after the above was written, the symbol  $F$  and the name "free energy" are used for Gibbs' function  $\zeta$  instead of for  $\psi$ .

<sup>41</sup> The "free energy" of a reaction, for instance, may be greater than the "total energy" of the same reaction—a relation that would never be suggested by the nomenclature.

<sup>42</sup> In place of  $\epsilon, \eta, \psi, \chi, \zeta$ , respectively, Massieu in 1869 [*loc. cit.*] used  $U, S, -t\psi, U', -t\psi$ , and in 1877 [*Jour. de phys.*, (i) **6**, 16]  $U, S, -H, U', -H'$ . Helm [*Die Energetik*] used  $E, F, S, G, H$ . Van Laar [*Lehrb. d. math. Chem.*, Leipzig, 1901, Barth] used  $E, S, \Phi, X, Z$ . Duhem [*Thermodynamique et Chimie*, Paris, 1902, Hermann] used  $U, S, \mathcal{F}, U + PV, \Phi$ . Ariès [*Chimie physique élément.*, Paris, 1914, Hermann] used  $U, S, I, J, K$ . Planck in his *Vorl. u. Thermodynamik* [Leipzig, 1897, Veit] used  $U, S, F, U + pV, \Phi$ ; in the English version [*Treatise on Thermodynamics*, translated by Ogg, London, 1903, Longmans, Green & Co.]  $U, \Phi, F, U + pV, -t\psi$ ; in the first and second of his four papers *ü. d. Vermehrung d. Entropie* [*Wied. Ann.*, **30**, 562; **31**, 189 (1887)] he used  $-W$  for  $\zeta$ , in the third and fourth [*Wied. Ann.*, **32**, 462 (1887); **44**, 385 (1891)] he used  $-t\Phi$ . Lewis and Randall use  $E, S, A, H, F$ .

There is no generally accepted mark (such as the bar in the present paper) to distinguish homogeneous functions of the first degree from those which refer to unit mass. In many papers, unless the equations happen to prove familiar, one must pore over the text to ascertain whether the symbols refer to the whole mass, to one gram, or to one mol; some writers give two of the meanings to the same symbol in the course of a single article, and even where it is clear that the quantities refer to "one mol", there is often no definition of the "molecular-weight" to be used—no definition, that is, in terms of quantities measurable in the laboratory—though without such information, the formulas themselves, no matter how laboriously deduced, are pretty useless.



cylinder in a bath of temperature  $t + dt$ , the only weight to move will be that of the piston and  $\mathbf{W} = p \cdot v_t \cdot dt$ , while  $\mathbf{Q}$  would be recorded as  $-C \cdot dt$ ,  $C$  being named the "heat capacity at constant pressure" of the substance. (The heat capacity of the cylinder itself is supposed negligible.) Substituting these values for  $\mathbf{Q}$  and  $\mathbf{W}$  in Eq. I, and writing  $-\partial\epsilon/\partial t \cdot dt$  for  $\epsilon$  (at  $t$ )  $-\epsilon$  (at  $t + dt$ ), there follows  $\partial\epsilon/\partial t = C - p \cdot v_t$ .

If on cooling again to  $t$ , the substance regains all its former properties, (and it is only in such a case that the heat absorbed would be recorded as the "heat capacity"), the operation described above is thermodynamically reversible, and it follows from II that  $-\partial\eta/\partial t \cdot dt = \mathbf{Q}/t$ , whence  $\partial\eta/\partial t = C/t$ .

The derivatives of the other functions can be found from their definitions, they are:  $\partial\psi/\partial t = -\eta - p \cdot v_t$ ;  $\partial\chi/\partial t = C$ ;  $\partial\zeta/\partial t = -\eta$ ,  $\partial\mu_x/\partial t = -\eta_x$ .

*With respect to  $p$ .* Again, if the pressure on the cylinder be increased from  $p$  to  $p + dp$ , while  $t$ ,  $x$ , and  $y$  remain unchanged,  $\mathbf{W} = p \cdot v_p \cdot dp$  and  $\mathbf{Q} = -t \cdot \partial\eta/\partial p \cdot dp$ , so that  $\partial\epsilon/\partial p = t \cdot \partial\eta/\partial p - p \cdot v_p$ . But from the definition of  $\zeta$ ,  $\partial\epsilon/\partial p = t \cdot \partial\eta/\partial p - p \cdot v_p - V + \partial\zeta/\partial p$ ; therefore  $\partial\zeta/\partial p = V$ ,  $\partial\eta/\partial p = -v_t$ ,  $\partial\epsilon/\partial p = -t \cdot v_t - p \cdot v_p$ ; and from their definitions,  $\partial\psi/\partial p = -p \cdot v_p$ ,  $\partial\chi/\partial p = V - t \cdot v_t$ ,  $\partial\mu_x/\partial p = v_x$ .

*Relations between the derivatives (Euler's theorem).* Since from its definition  $\zeta = \epsilon - t\eta + pV$ ,  $\zeta$  like  $\epsilon$ ,  $\eta$ , and  $V$  must be homogeneous and of the first degree in the variables  $x$ ,  $y$  etc. that denote the masses of the components; it follows at once from Euler's theorem that  $\zeta = x \cdot \mu_x + y \cdot \mu_y + \dots$  (G 96) and that  $0 = \eta \cdot dt - v \cdot dp + x \cdot d\mu_x + y \cdot d\mu_y + \dots$  (G 97). Substituting the value of  $\zeta$  from (G 96) in (G 91), differentiating, and striking out the four terms whose sum is zero, (G 97), there follows an expression for  $d\epsilon$  (G 12), and similarly for the others. The definitions of the thermodynamic functions, the relations between them following from (G 96), and the expressions for their derivatives obtainable by means of (G 97) are collected here for convenience of reference; when there are more than two components, additional terms such as  $z \cdot \mu_z$  or  $\mu_z \cdot dz$  must be added.

$$\begin{aligned}
 (\text{G } 93) \quad & \epsilon = t\eta - pV + x\mu_x + y\mu_y \\
 (\text{G } 89) \quad & \chi = \epsilon + pV = t\eta + x\mu_x + y\mu_y \quad (\text{G } 95) \\
 (\text{G } 87) \quad & \psi = \epsilon - t\eta = -pV + x\mu_x + y\mu_y \quad (\text{G } 94) \\
 (\text{G } 91) \quad & \zeta = \epsilon - t\eta + pV = x\mu_x + y\mu_y \quad (\text{G } 96) \\
 (\text{G } 12) \quad & d\epsilon = t \cdot d\eta - p \cdot dV + \mu_x \cdot dx + \mu_y \cdot dy \\
 (\text{G } 90) \quad & d\chi = t \cdot d\eta + V \cdot dp + \mu_x \cdot dx + \mu_y \cdot dy \\
 (\text{G } 88) \quad & d\psi = -\eta \cdot dt - p \cdot dV + \mu_x \cdot dx + \mu_y \cdot dy \\
 (\text{G } 92) \quad & d\zeta = -\eta \cdot dt + V \cdot dp + \mu_x \cdot dx + \mu_y \cdot dy \\
 (\text{G } 97) \quad & 0 = \eta \cdot dt - V \cdot dp + x \cdot d\mu_x + y \cdot d\mu_y
 \end{aligned}$$

*Criteria of thermodynamic equilibrium*

The criteria of equilibrium are implicitly contained in the two laws of thermodynamics as stated above; Gibbs has put them into mathematical forms convenient for dealing with the results of measurements carried out under a number of different experimental conditions. For the present purpose it will be sufficient to establish the criterion of neutral equilibrium in a heterogeneous system with respect to changes which do not affect the temperature or the pressures of the phases involved.

At the present time, in papers on chemical thermodynamics, the word "equilibrium" used without qualification is generally intended to be synonymous with "neutral equilibrium." A system in "stable equilibrium" may be compared to a balance having a 10 pound weight on one pan and 1 pound on the other; if the weights on both pans were the same, the balance would be in "neutral equilibrium." Gibbs wished to include both cases, hence the inequality sign in many of his formulas.

*Criterion of neutral equilibrium.* According to the two laws of thermodynamics, for a given change  $A \rightarrow B$  in the system and a given temperature  $t_r$  of the heat reservoir,  $\mathbf{W}$  will have its maximum value, viz.,  $\epsilon_A - \epsilon_B - t_r(\eta_A - \eta_B)$ , if the change be carried out reversibly. If under specified experimental conditions  $\mathbf{W}$  would be less than this maximum, it follows that under these conditions the change may occur but will not be reversible; if the conditions are such that  $\mathbf{W}$  for the change if it should occur would be greater than this maximum, it follows that under these

conditions the change will not occur, i.e., that the system will be in stable equilibrium with respect to the change in question; and finally, that the change  $A \rightarrow B$  will be reversible, i.e., that the system will be in neutral equilibrium with respect to this change, if, and only if, under the specified experimental conditions,

$$\mathbf{W} = \epsilon_A - \epsilon_B - t_r (\eta_A - \eta_B).$$

*Criterion of neutral equilibrium in a heterogeneous system at constant temperature and pressures.*<sup>43</sup> (a) If the system be made up of a number of phases each with its own temperature, pressure, weight and composition, then the volume of the system  $V = V' + V'' + \dots$ , accents being used to indicate the phase to which the symbol refers; similarly  $\epsilon = \epsilon' + \epsilon'' \dots$ ,  $\eta = \eta' + \eta'' + \dots$ , etc. (b) If the phases are all at the same temperature  $t$ , and (c)\* if the change  $A \rightarrow B$  does not involve change in the temperature  $t$  or (d) in the pressures  $p'$ ,  $p''$ , of the phases (which need not all be at the same pressure); and (e) if experimental conditions are such that the only weights to move are those that fix the pressures on the various phases, then  $\mathbf{W} = p' (V'_B - V'_A) + p'' (V''_B - V''_A) + \dots$ , and the criterion of neutral equilibrium with respect to the change in question becomes  $p' (V'_B - V'_A) + p'' (V''_B - V''_A) + \dots = \epsilon'_A - \epsilon'_B + \epsilon''_A - \epsilon''_B + \dots - t(\eta'_A - \eta'_B) - t(\eta''_A - \eta''_B) - \dots$ , that is,  $0 = \zeta'_A - \zeta'_B + \zeta''_A - \zeta''_B + \dots$ , or  $(\delta\zeta)_{t,p} = 0$  (G 117).

The experimental conditions specified above obtain in practically all the cases of chemical equilibrium discussed in elementary text-books of physical chemistry.

From the theorem just established it follows that the value of  $\bar{\zeta}$  for any heterogeneous system formed of two solutions which are miscible in all proportions (solutions of alcohol and water for instance) must be greater than the value of  $\bar{\zeta}$  for the homogeneous solution of the same temperature pressure and composition; in

<sup>43</sup> Neglecting the influence of gravity, electricity, distortion of solids, and capillary tensions, and therefore neglecting any quantities of heat or work that may be involved in the separation of two phases that are in contact.

\* To ensure this, the system may be immersed in a thermostat of temperature  $t$ ;  $t_r = t$ .

other words, that the  $\zeta$  curve for such solutions on the standard diagram must be a festoon, like the  $V$  curve of figure 1. Hence for all such solutions the potential ( $\mu_x$ , or  $\mu_y$ ) of each component must increase with the concentration of that component in the solution, and  $\mu_{xy}$  must be negative for all of them (page 311); while in the case of two liquids of limited miscibility, like ether and water,  $\mu_{xy}$  will be negative for all the solutions that can be prepared.

#### INSTANCES OF EQUILIBRIUM BETWEEN TWO PHASES IN A TWO-COMPONENT SYSTEM

##### 1. *The pressures on the two phases are different*

If the cell containing the sugar solution in an osmotic apparatus be closed by a piston weighted so as to maintain the pressure  $p''$  on the solution, the "change  $A \rightarrow B$ " will consist in the passage of  $dy$  grams of water through the semi-permeable membrane into the solution while  $t$   $p'$   $p''$  and  $x''$  remain constant; and the condition of neutral equilibrium,  $d\zeta' + d\zeta'' = 0$  becomes  $\mu_y' dy - \mu_y'' dy = 0$ , or  $\mu_y' = \mu_y''$ , that is (since  $\partial\mu_y/\partial p = v_y$ )

$$0 = \mu_y'' - \mu_y' = \int_{p'}^{p''} v_y \cdot dp + \int_0^{x''} \mu_{xy} \cdot dx$$

(values of  $v_y$  for  $x = x''$ ,  $y = y''$ ; values of  $\mu_{xy}$  for  $p = p'$ ,  $y = y''$ ; see fig. 6).

Writing  $P_x = p'' - p'$  (at equilibrium) for "the osmotic pressure of the sugar", the same relation may be put in the form

$$v_y \cdot \partial P_x / \partial x = -\mu_{xy} \tag{4}$$

(values of  $v_y$  and of  $\mu_{xy}$  for  $x = x''$ ,  $y = y''$ ,  $p = P_x + p'$ ).

If a membrane could be found permeable for sugar (alcohol would be a better example) and impermeable for water, the "osmotic pressure of the water" could be measured, and as above,  $v_x \cdot \partial P_y / \partial y = -\mu_{xy}$  (values of  $v_x$  and  $\mu_{xy}$  for  $x = x''$ ,  $y = y''$ ,  $p = P_y + p'$ ).

At first sight there does not seem much gained by merely expressing a quantity (osmotic pressure) which it might be desired

to determine, in terms of the equally unknown and moreover unfamiliar functions  $\mu_y$  and  $\mu_{xy}$ . It is not necessary, however, to know the values of  $\mu_{xy}$  in order to make use of the equation; the slopes of other equilibrium curves will be expressed in terms of the same function, and by eliminating it, relations between osmotic pressures, freezing-points, boiling-points, etc., may be obtained which lead to the so-called "indirect methods of determining the osmotic pressure." Conversely, osmotic pressure determinations, if available, can be used to predict the outcome of other experiments involving the same solution. As an example of the method,  $\mu_{xy}$  may be eliminated between the expressions obtained above for the slopes of the two osmotic pressure curves; neglecting the effect of pressure on  $v_x$ ,  $v_y$  and  $\mu_{xy}$  ( $\mu_{pxy} = v_{xy}$ ) there results:  $v_y \cdot \partial P_x / \partial x = v_x \cdot \partial P_y / \partial y$ , so that if one were known a close approximation to the other could be found by determining the densities of the solutions. In the second place, expressions for  $\mu_{xy}$  in terms of temperature pressure and concentration have been established which though valid only when certain conditions are fulfilled, yet in these special cases enable the osmotic pressures to be computed; examples are given in the paragraphs headed "fundamental equations". In the third place, though  $\mu_y$  and  $\mu_{xy}$  may be unfamiliar, yet  $\partial \mu_y / \partial p = v_y$  is not, and by means of this last relation it is easy to shew that "the effect of pressure on the osmotic pressure" may be calculated from the densities of the solutions.

*Effect of pressure on the osmotic pressure.* When equilibrium is attained in an osmotic apparatus, let the pressure on the solvent be increased by  $dp'$  while temperature and the concentration of the solution remain as before; and let  $dp''$  be the consequent increase in the pressure of the solution when equilibrium is again attained. Because of these changes in the pressures, both  $\mu_y'$  and  $\mu_y''$  will be changed; but at the new equilibrium the new values will be equal, as the old were. Hence  $\mu_y' \cdot dp' = \mu_y'' \cdot dp''$ , or  $dp''/dp' = v_y'/v_y''$ ; but, by definition,  $dP_x = dp'' - dp'$ , therefore  $dP_x/dp' = (\bar{V}' - v_y'')/v_y''$ .

2. *The pressures on the two phases are the same*

Here the "change  $A \rightarrow B$ " consists in the passage of  $dx$  grams of one component and  $dy$  grams of the other from one phase to the other, and the condition of equilibrium  $0 = d\zeta' + d\zeta''$  becomes  $0 = \mu'_x \cdot dx + \mu'_y \cdot dy - \mu''_x \cdot dx - \mu''_y \cdot dy$ .

(a) In the general case, where  $dx$  and  $dy$  are independent, this is equivalent to the two equations  $\mu'_x = \mu''_x$  and  $\mu'_y = \mu''_y$

(b) If one of the phases (that denoted by a single accent) contains but one component, then  $x' = 0$ ,  $dx = 0$  and the condition of equilibrium is  $\mu'_y = \mu''_y$ .

(c) If the composition of one of the phases (that denoted by a single accent) be fixed, so that  $y' = k \cdot x'$ , then  $dy = k \cdot dx$ ,  $\mu'_x$  and  $\mu'_y$  have no meaning (just as  $v'_x$  and  $v'_y$  have no meaning), and the criterion of equilibrium becomes:  $\bar{\zeta}' = (\mu''_x + k \cdot \mu''_y) / (1 + k)$ . By suitable choice of components, however, this case may be avoided; if, for instance, in the discussion of equilibrium between Glauber's salt and its solution in water, anhydrous sodium sulphate ( $y$ ) and water ( $x$ ) be chosen as components, Glauber's salt will contain the two components in fixed proportions and  $dy = 142/180 \cdot dx$ ; but if Glauber's salt itself ( $y$ ) and water ( $x$ ) be chosen as components, then  $x' = 0$ , as in case (b).

*Equation for the slopes of the equilibrium curves*

(2a) *The general case.* If two phases (e.g. an aqueous solution of alcohol and its vapour) be in equilibrium at  $t$  and  $p$ , and again at  $t + dt$  and  $p + dp$  (the values of  $x'$ ,  $y'$ ,  $x''$  and  $y''$  being in general slightly different in the two cases) the value of  $\mu'_x$ , in the second case will differ from that in the first by  $d\mu'_x$ , and the value of  $\mu''_x$  in the second case will differ from that in the first by  $d\mu''_x$ ; but since in both cases the two phases were in equilibrium,  $d\mu'_x = d\mu''_x$  and the accents may be omitted. Similarly  $d\mu'_y = d\mu''_y = d\mu_y$ .

Now the four variations  $dt$ ,  $dp$ ,  $d\mu_x$  and  $d\mu_y$  are not independent, but are connected by the two equations (G 97)

$$0 = \eta' dt - v' dp + x' d\mu_x + y' d\mu_y$$

$$\text{and } 0 = \eta'' dt - v'' dp + x'' d\mu_x + y'' d\mu_y$$

$$\text{whence } 0 = \left(\frac{\eta'}{y'} - \frac{\eta''}{y''}\right)dt - \left(\frac{V'}{y'} - \frac{V''}{y''}\right)dp + \left(\frac{x'}{y'} - \frac{x''}{y''}\right)d\mu_x \quad (5)$$

on the assumption, of course, that neither  $y'$  nor  $y''$  is zero.

If  $x' = x'' = 0$  (e.g. pure water and its vapour), the last term disappears and Eq.(5) is reduced to Clausius' equation. If either  $x'$  or  $x''$  be not zero, the term in  $d\mu_x$  could be eliminated if a third equation of the type (G 97) were available, i.e., if there were equilibrium between three phases instead of two in the two-component system. Generalized, this is Gibbs' "phase rule."

In still another case the third term would disappear, viz.: if for certain values of  $t$ ,  $p$ , and  $x''$  (but not for all of them as in one-component systems) the composition of the two phases should be the same, and therefore  $x'/y' - x''/y'' = 0$ . In such a case, if under the experimental conditions  $dt = 0$  (vapour tension measurements), then by Eq. (5),  $(V'/y' - V''/y'') \cdot dp$  must be zero; and if  $V'/y'$  and  $V''/y''$  are known to be different, then  $dp$  must be zero, i.e.,  $p$  must be a maximum or a minimum. Similarly when  $dp = 0$  (boiling-point determinations). As Gibbs puts it: "It follows that for constant temperature the pressure is in general a maximum or a minimum when the composition of the two phases is identical; in like manner the temperature of the two phases is in general a maximum or a minimum for constant pressure when the composition of the two phases is identical."<sup>44</sup> This result is often spoken of as "Konowalow's law;" familiar examples are furnished by the aqueous solutions of hydrochloric or acetic acid.

Without loss in generality, by merely algebraic transformation, Eq. (5) may be put in another form viz.:

$$0 = (\eta'_{y'} - \eta''_{y'})dt - (v'_{y'} - v''_{y'})dp - \mu'_{xy}(dx' - x'/y' \cdot dy') + \mu''_{xy}(dx'' - x''/y'' \cdot dy'') \quad (6)$$

[From Eq. (1):  $d\mu_x = \mu_{tx}dt + \mu_{px}dp + \mu_{xx}dx + \mu_{xy}dy$ ; from derivs. of the thc. fnc.:  $\mu_{tx} = -\eta_x$ ,  $\mu_{px} = v_x$ ; from Euler's th'm.:  $v = xv_x + yv_y$ ,  $\eta = x\eta_x + y\eta_y$ ,  $0 = x\mu_{xx} + y\mu_{xy}$ ]

in which further  $(\eta'_{y'} - \eta''_{y'})$  may be replaced by  $(\chi'_{y'} - \chi''_{y'})/t$

[from  $\chi'_{y'} = t\eta'_{y'} + \mu'_{y'}$  and  $\chi''_{y'} = t\eta''_{y'} + \mu''_{y'}$ , since  $\mu'_{y'} = \mu''_{y'}$ ]

<sup>44</sup> *Trans. Conn. Acad.*, **3**, 156 (1876); *Scientific Papers*, **1**, 99.

This equation in its various forms is all that the laws of thermodynamics have to say about equilibria of the class considered;  $\chi'_y - \chi''_y$  gives the number of calories gained by the (constant pressure) calorimeter when one gram of the component whose weight in the two phases is given by  $y'$  and  $y''$  respectively is transferred from phase ('') to phase ('');  $v'_y - v''_y$  can be obtained from density determinations;  $\mu'_{xy}$  and  $\mu''_{xy}$  must be determined experimentally or guessed, and as the equation for the general case involves both of them, it does not lead to direct methods for their determination such as are furnished by (2b). The problem dealt with as "illustration 2" belongs to this group.

(2b)  $x' = 0$ . If  $x' = 0$ , the last equation of the preceding section becomes

$$0 = (\bar{\chi}' - \chi_y'')/t \cdot dt - (\bar{V}' - v_y'')dp + \mu''_{xy}(dx'' - x''/y'' \cdot dy'') \quad (7)$$

If the experimental work be carried out at constant temperature, the first term on the right becomes zero; if at constant pressure, the second term becomes zero. Some examples are:

(i)  $dt = 0$ :  $G'L''$  vapour tensions of salt solutions, etc.,<sup>45</sup> ( $y$  water).  $G'L'$  measurements of "the effect of pressure on the vapour tension of mercury etc." in which mercury ( $y$ ) is shaken with nitrogen under various pressures and the vapours analysed.  $G'S''$  vapour tensions of zeolites or of reversible colloids ( $y$  water).  $G''S'$  dissociation of phosphorus pentachloride or of ammonium chloride ( $y$ ) in presence of excess of chlorine or ammonia respectively.  $L''S'$  effect of pressure on the solubility of salts ( $y$ ) etc.

(ii)  $dp = 0$ :  $G'L''$  boiling points of salt solutions etc. ( $y$  water).  $G''L'$  dew points ( $y$  water).  $L''S'$  solubility determinations ( $x$  water), determinations of the freezing points of solutions ( $y$  water).  $S'S''$  equilibrium between graphite ( $y$ ) and martensite, etc.

Quantitative relations between the slopes of the various equilibrium curves may be obtained from Eq. (7) by eliminating  $\mu''_{xy}$  as illustrated in (1); or values of  $\mu''_{xy}$  may be determined from the results of one set of equilibrium measurements and used to

<sup>45</sup>  $G'L'$  stands for "examples of equilibrium between a gaseous phase for which  $x = 0$ , and a liquid phase containing both components", and so on.



predict the results of another, as in "illustration 1" below; or values of  $\mu''_{xy}$  may be given in the form of a "fundamental equation" and substituted in Eq. (7)

An important qualitative conclusion can be drawn from Eq. (7) by means of the theorem already established (page 320) as to the sign of  $\mu_{xy}$ : If  $dx + dy = 0$ , (standard diagram), the last term of Eq. (7) after dividing through by  $dx''$ , becomes  $(x'' + y'')/y'' \cdot \mu''_{xy} = D\mu''_y/Dx''$ , and will be *negative* for stable solutions. Hence if  $dt = 0$ , the sign of  $Dp/Dx$  will be opposite to that of  $\bar{V}' - v''_y$ , and if  $dp = 0$ , the sign of  $Dt/Dx$  will be the same as that of  $\bar{\chi}' - \chi''_y$ . This is commonly known as "Le Chatelier's law."

#### Illustration 1

The problem is: Given the freezing-point curve  $fe$  and the solubility curve  $em$ , (fig. 7) to find the osmotic pressures of the solutions at the arbitrary temperature  $\theta$ . The method suggested is: Compute values of  $\mu''_{xy}$  for points on the curves; correct them for temperature and so obtain values of  $\mu_{xy}$  at  $t = \theta$ ; and finally use the expression connecting  $\partial P_x/\partial x$  with  $\mu_{xy}$  to find the osmotic pressures. For the solubility curve this is probably the best method of procedure; for the freezing point curve it might be better to work with  $\mu_y$  instead of  $\mu_{xy}$ , and so avoid the practical difficulties involved in determining the slopes of the freezing-point curve. Whichever method be adopted, the argument begins with no assumptions but the laws of thermodynamics and the experimental data furnished by the curves; its development leaves no doubt as to what other experimental data must be secured. To shorten the equations, it is assumed that the specific heat of the solid and those of the solutions are independent of the temperature throughout the range of the computation, but it will be shown at the close how this restriction can be removed. Doubly accented symbols refer to the saturated or freezing solutions, singly accented to the solids, unaccented to the solutions at  $t = \theta$ .

(a) First the values of  $\mu''_{xy}$  for one gram of the solutions of the freezing-point curve may be computed by means of

$$(\bar{\chi}' - \chi''_y)/T \cdot DT/Dx = -\mu''_{xy}/(1 - x'') \quad (8)$$

[obtained from (7) by substituting  $T$  for  $t$  to avoid confusion, setting  $dp = 0$  to agree with experimental conditions and  $x'' + y'' = 1$  to suit the diagram, remembering that  $x \cdot \mu_{xx} + y \cdot \mu_{xy} = 0$ , and dividing through by  $dx$ .] Since in (7),  $x' = 0$ ,  $x''$  gives the weight of salt and  $y''$  that of water in the solution;  $DT/Dx$  gives the slope of the curve  $fe$  measured with reference to the scales of  $t$  and of  $x$ . One value of  $\bar{\chi}' - \chi''_y$  must be supplied, that at  $x = 0$  viz.  $-80$  cal. (the latent heat of one

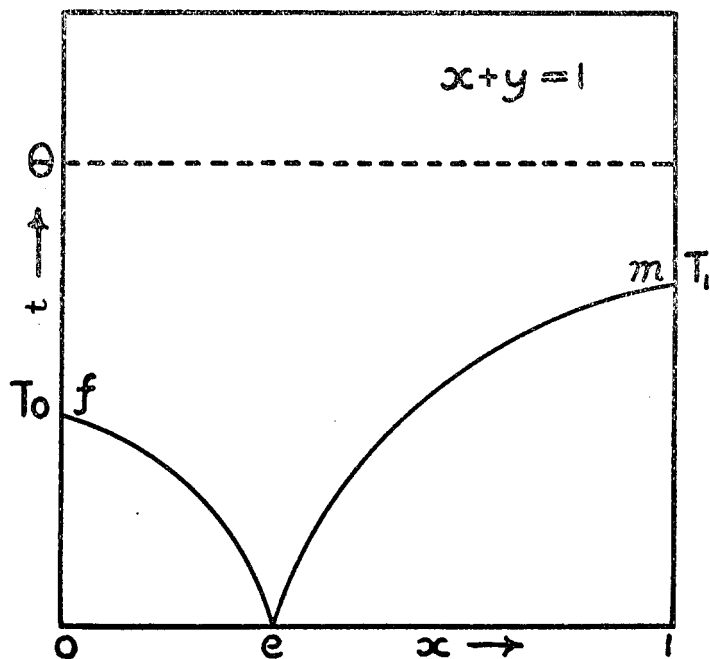


FIG. 7

gram of ice) will serve; since  $\bar{\chi}'_t = \bar{C}'$ , and  $\chi''_{ty} = c''_y$ , knowledge of the specific heats of ice and of the solutions of the curve together with  $\chi''_{xy}$ , (i.e. the effect of concentration on the heat of dilution of the solutions) enables the value of  $\bar{\chi}' - \chi''_y$  to be calculated for all other points on  $fe$ .

(b) The value of  $\mu_{xy}$  for any solution (at  $t = \theta$ ) may be obtained from  $\mu''_{xy}$  for the same solution (at  $t = T$ , the pressure being the same in both cases) by means of

$$\mu_{xy} = \theta \cdot \mu''_{xy}/T + (\theta - T)(c_{xy} - \chi''_{xy}/T) - \theta \cdot c_{xy} \cdot \log(\theta/T) \quad (9)^{46}$$

[from  $\chi = \theta\eta + \zeta$ ;  $\chi'' = T\eta'' + \zeta''$ ;  $\chi_t = \chi''_t = C$ ; and  $\eta_t = C/t$ ]

No additional experimental data are required for the computation.

(c) In like manner from the curve *em* the rest of the values of  $\mu_{xy}$  (at  $t = \theta$ ) may be obtained. [The letters  $x''$  and  $y''$  in (7) must be interchanged to avoid confusion, giving  $(\bar{\chi}' - \chi''_x)/T \cdot DT/Dx = \mu''_{xy}/x''$ ]

As the value of  $\mu''_{xy}$  at the eutectic point *e* has already been found from the freezing-point curve, a value of  $\bar{\chi}' - \chi''_x$  may be calculated for that point from Eq. (8), and it is not mathematically necessary to bring in a new experiment; the specific heat of the solid, however, and those of the solutions along *em*, must be determined.

(d) The values of  $P_x$  (the osmotic pressure of the salt, if one is dealing with solutions of a salt in water) may now be computed from  $v''_y \cdot \partial P_x / \partial x = -\mu''_{xy}$  (Eq. 4); a form more convenient for the present purpose is  $v''_y \cdot DP_x / Dx = -(x'' + y'') \mu''_{xy} / y''$ , or (since in figure 7,  $x + y = 1$ )  $v''_y \cdot DP_x / Dx = -\mu''_{xy} / (1 - x'')$ . This is equivalent to

$$0 = \int_{p'}^{P_x + p'} v_y \cdot dp + \int_0^x \mu_{xy} \cdot dx / (1 - x) \quad (\text{see Fig. 6})$$

in which the values of  $\mu_{xy}$  are those at  $t = \theta$  and  $p = p'$  already obtained, and the values of  $v_y$  are those for the solution whose osmotic pressure is sought. The numerical value of the second integral (using as upper limit the value of  $x$  for the solution whose osmotic pressure is sought) may be computed by integrating graphically, numerically, or by use of an interpolation formula as may be most convenient; if  $v_y$  be known as a function of  $p$  (from density and compressibility determinations) the first integral can be expressed as a known function of  $P_x$ ; and by the methods of algebra, or by graphical methods, that value of  $P_x$  can be found which reduces the sum of the two integrals to zero.

Thus if the thermal and density data are available, the osmotic pressures at any arbitrarily selected temperature  $\theta$  can be cal-

<sup>46</sup> The abbreviation "log" is used for "log. nat." throughout.

culated from the freezing-point and solubility curves without more labour than is involved in most technical computations, and without introducing molecular hypotheses of any kind, or any other assumptions that might detract from the generality or reliability of the results.

The operations involved in the computation of osmotic pressures from the freezing-point curve are summarized in Eq. (10), where  $x + y = 1$  and  $\bar{p}$  is written as abbreviation for  $\bar{\chi}' - \chi''_y$ .

$$\int v_y \cdot dP_x = \int \left\{ \frac{\theta \bar{p}}{T^2} \cdot \frac{DT}{Dx} - \frac{\theta - T}{1 - x} (c_{xy} - \chi''_{xy}/T) + \frac{\theta}{1 - x} c_{xy} \cdot \log \frac{\theta}{T} \right\} dx \quad (10)$$

The formula for computing  $P_x$  from the solubility curve may be obtained from Eq. (10) by multiplying the term  $\theta \bar{p}/T^2 \cdot DT/Dx$  by  $-x/y$ , leaving all the rest unchanged. If in these two equations  $x$  be replaced by  $y$  and  $y$  by  $x$  wherever they occur (in subscripts, factors and differentials) formulas are obtained for computing  $P_y$ , the "osmotic pressure of the water;" in the expression derived from Eq. (10),  $DT/Dy = -DT/Dx$  is the slope of the solubility curve (fig. 7) with changed sign, in the other that of the freezing-point curve.

Eq. (10), and all similar formulas, may be modified in three different ways:

1. It may be freed from the only special assumption made (viz.: that the specific heats are independent of the temperature) and thus be made as general as the laws of thermodynamics themselves, by replacing  $(\theta - T) \cdot c_{xy}$  by  $\int_T^\theta c_{xy} \cdot dt$ , and  $c_{xy} \cdot \log(\theta/T)$  by  $\int_T^\theta c_{xy}/t \cdot dt$ , etc.

2. It may be very much simplified by omitting all terms that, in most cases at all events, contribute but little to the final result. To avoid the risk of using such a simplified formula in cases where it is inapplicable, the assumptions made in simplifying it should be listed.

3. It may be modified by introducing general (though not universal) laws discovered in the laboratory; such laws are often expressed in the language of some molecular or atomic theory, but so long as the relations asserted to exist between the experimental quantities are clearly stated and reasonably accurate, the form of words chosen to express them is immaterial.

To give a few examples.  $V$  might be expressed in terms of  $p$  and  $t$  by van der Waals' equation, or by Dieterici's; specific heats might be expressed as functions of the temperature by means of some one of the equations recently proposed; in formulas which include a heat of vaporization, this might be expressed in terms of the boiling-point temperature by means of Trouton's law in its original or improved form; Thomsen's generalization connecting heat of solution with contraction might be introduced, or relations derived from the law of corresponding states, from the "law of maximum work" or from the "third law of thermodynamics;" even such quantities as refractive index, electrical conductivity etc. have been correlated with the thermodynamical data. What the resulting formulas may lose in accuracy they gain in interest by relating quantities drawn from widely different branches of chemistry.

By way of example, certain simplifying assumptions will be introduced into the calculations of the "illustration."

#### *Simplifying assumptions*

The assumptions made in a given case need hold only over a limited range viz., that covered by the computation in question; their applicability outside of the range in question is obviously a matter of indifference. Those most commonly made are:

1. *Specific heats independent of temperature*:— $c_t = 0$ . Customary when the range of temperature is not great.

2. *Heat capacities of solutions a linear function of their composition*:— $c_{xy} = 0$ , i.e.  $c_x$  and  $c_y$  independent of  $x$ ; hence  $\mu_{xy} = \theta \cdot \mu''_{xy}/T - (\theta - T) \cdot \chi''_{xy}/T$ , see Eq. 9. Assumptions 1 and 2 together make  $\bar{\chi}' - \chi''_y$  a linear function of  $T$ , since  $\chi_{ty} = c_y$ . In the case of sulphuric acid solutions the specific heats agree with the linear formula within about 10 per cent.

3. *Heat of solution constant for all points on the solubility and freezing-point curves (a special case of Kopp's law):*—This involves neglecting the difference between the specific heats of ice and water; it is a dangerous assumption, justified only when the range of  $T$  is not great, or when the heat of solution is (arithmetically) large.

4. *No heat of dilution:*— $\chi_{xy} = 0$  and  $c_{xy} = 0$  (since  $\chi_t = C$ ); this involves all the consequences of (2), and in addition that  $\mu_{xy} = \theta/T \cdot \mu''_{xy}$  (Eq. 9), i.e., that  $\mu_{xy}$  is proportional to  $t$ , and therefore that the osmotic pressure of any given solution is proportional to the temperature, except in so far as temperature may affect the compressibility and the specific volume of the solution.

5. *Liquids and solids incompressible:*— $v_p = 0$ ; commonly assumed for experiments at ordinary temperatures and pressures.

6. *No contraction on dilution:*— $v_{xy} = 0$ , i.e.  $v_y$  independent of  $x$ . Even for sulphuric acid solutions containing up to 75 per cent acid, this would introduce an error in  $v_y$  of less than 10 per cent.

If all four assumptions be made (Number 2 is included in Number 4 and Number 6 is not needed) Eq. (10) becomes  $v_y \int dP_x = \theta \bar{p} \int 1/T^2 \cdot DT/Dx \cdot dx$ , and the osmotic pressure of the salt in millimeters of mercury at  $t = \theta$  for solutions from  $x = 0$  to  $x = e$  (where  $x + y = 1$ ) is given by  $31360\theta \cdot \bar{p}/v_y \cdot (1/T_0 - 1/T)$ , where  $\bar{p} = -80$  is the latent heat of 1 gram of ice,  $T_0 = 273.1$  is the melting-point of ice, and  $T$  is the temperature at which the solution is in equilibrium with ice. If  $P_x$  be replaced by  $P_y$ , and the word "ice" in the definitions of  $\bar{p}$ ,  $T_0$  and  $T$  by "salt," the "osmotic pressure of the water" may be calculated for solutions from  $x = e$  to  $x = 1$ ; the other two equations derived from Eq. (10) are not reducible to such a simple form.

#### *Fundamental equations*

Eq. (6) gives the slopes of the equilibrium curves in terms of  $\chi_y$ ,  $v_y$  and  $\mu_{xy}$ , and if each of these quantities were known for both phases in terms of  $t$ ,  $p$ ,  $x$  and  $y$ , the solution would be complete. An equation for each phase expressing  $\mu_y$  in terms of  $t$ ,  $p$ ,  $x$ ,  $y$  and known constants would contain more information than is required for this purpose, while similar expressions for  $\zeta$  if

available would permit numerical solution of all thermodynamic problems, since from them by the relations of page 317 expressions for  $\epsilon$  and  $\eta$  and consequently for all the thermodynamic functions could be derived. [ $\eta = -\partial\zeta/\partial t$ ;  $\epsilon = \zeta - t \cdot \partial\zeta/\partial t - p \cdot \partial\zeta/\partial p$ ]. Such an expression is called by Gibbs a "fundamental equation."

If the object were to solve as accurately as possible an individual problem like that of "illustration 1", little would be gained by assembling the data in a fundamental equation; on the other hand the use of fundamental equations in which are incorporated general laws or simplifying assumptions not only leads to a gain in algebraic compactness, but, by gathering the assumptions into named groups, it tends to emphasize the restrictions under which the results obtained are valid. The following are some of the simplest forms:

1. *One-component liquids or solids.* Applicable to substances such as  $L'$  and  $S'$  (page 324) whose composition is not changed during the experiment. For moderate ranges of temperature and pressure well below the critical values it may be assumed that liquids and solids are incompressible ( $\bar{v}_p = 0$ ), that their specific heats are independent of the temperature ( $\bar{c}_t = 0$ ), and that their coefficients of thermal expansion are negligible ( $\bar{v}_t = 0$ , whence  $\bar{c}_p = 0$ , since  $\bar{c}_p = \bar{\chi}_{tp} = -t\bar{v}_{tt}$ ). Substituting these values in the expressions for the derivatives of  $\epsilon$  and  $\eta$  (pg 317) and integrating<sup>47</sup> there follow  $\bar{\epsilon} = \bar{E} + \bar{C}t$ , and  $\bar{\eta} = \bar{H} + \bar{C} \cdot \log t$ ; whence<sup>48</sup>  $\bar{\zeta} = \mu = \bar{E} + t(\bar{C} - \bar{H} - \bar{C} \log t) + p\bar{V}$ . The specific heat  $\bar{C}$  may be determined directly;  $\bar{E} = \bar{\chi} - \bar{C}t - p\bar{V}$  may be computed from the heat of formation, its value obviously depending on the zeros chosen for  $\chi$ ; while a numerical value of  $\bar{H}$  can be determined only if the zeros for  $\eta$  have been fixed and some reversible method for bringing the substance into this zero state has been discovered and measured. To find the *slopes* of the equilibrium curves, however, the values of  $\bar{H}$  need not be known here or even in the funda-

<sup>47</sup> Gibbs wrote  $E$  and  $H$ ; but as these quantities refer to 1 gram, the bar has been written over them.

<sup>48</sup> *Trans. Conn. Acad.*, **3**, 213 (1876), footnote, Eq. (A); *Sci. Papers*, **1**, 153.

mental equations for solutions, since the quantities occurring in Eq. (6) (viz.,  $\chi_y v_y$  and  $\mu_{xy}$ ) do not involve  $\bar{H}$ .

Setting  $t = 0$  in the above expression for  $\bar{\epsilon}$ ,  $\bar{E}$  appears as the value of  $\bar{\epsilon}$  for the liquid or solid at the "absolute zero". To take this seriously however would be a misuse of the formula, which is valid only for the limited range of temperature over which the specific heats may be regarded as approximately constant; if the range is to be extended, the assumption  $c_i = 0$  must be replaced by  $\bar{C} = f(t)$ , leading to  $\bar{\xi} = \bar{E} + \int f(t) \cdot dt - t \cdot \bar{H} + p\bar{V} - t \cdot \int f(t) \cdot dt/t$ , the lower limits of the integrations being those for which  $\bar{E}$  and  $\bar{H}$  were defined. Similarly for work running to very high pressures, the assumptions  $\bar{v}_p = 0$  and  $\bar{v}_p = 0$  might have to be abandoned. In the case of crystallized solids, an expression has been evolved<sup>49</sup> representing  $\bar{C}$  as a function of  $t$  which contains but two arbitrary constants for each substance, and is in such good agreement with the data at present available that it has been seriously proposed to choose the zero of the thermodynamic temperature scale as the temperature for which  $\bar{E}$  and  $\bar{H}$  may be defined; as is customary, the value zero would be allotted to  $\bar{E}$  and to  $\bar{H}$  for the chemical elements under the standard conditions so chosen. If it be assumed that the Thomsen-Berthelot "law of maximum work" [viz.:  $\mathcal{L} = Q$ , whence  $\eta_A - \eta_B = 0$  for two states of the system at the same temperature and pressure] is valid for crystalline solids at the thermodynamic zero, it follows that  $\bar{H} = 0$  for all substances in the crystalline modification in which they are stable at zero. The "law of maximum work" in its generality was successfully combatted by Duhem<sup>50</sup> and others; it holds very well for most reactions between solids at ordinary temperatures, and it *may* hold absolutely for crystalline solids at the thermodynamic zero; but if like most other generalizations it should prove to have exceptions, the title "third law of thermodynamics" is likely to prove embarrassing.

<sup>49</sup> Lewis and Gibson: *Jour. Am. Chem. Soc.*, **39**, 2565 (1917).

<sup>50</sup> P. Duhem: *Thermochimie à propos d'un livre récent de M. Marcelin Berthelot*, Paris, 1897, Hermann; *Introduction à la mécanique chimique*, Gand, 1895, Hoste.



2. *One component gases, "perfect gas."* Following the same procedure, the assumptions  $c_t = 0$  and  $pV = mat$  ( $m$  the mass of the gas,  $a$  a specific constant)<sup>51</sup> lead to:

$$\begin{aligned}\bar{\xi} = \mu &= \bar{E} + t(\bar{C} - \bar{H} - (\bar{C} - a) \log t + a \log m/V) \quad (\text{G. 264}) \\ &= \bar{E} + t(\bar{C} - \bar{H} - \bar{C} \log t + a \log p/a) \quad (\text{G. 268})\end{aligned}$$

This expression may be used to find  $\mu_y$  for solutions with one volatile component (type  $G'L''$ ,  $G'S''$ ) from measurements of their vapor tensions, in the many cases where the vapor conforms to the assumptions made in deriving the equation.

The value of  $\bar{\chi}$  for the gas (and therefore the value of  $\bar{E}$ , since  $\bar{\chi} = \bar{E} + \bar{C}t$ ) can be found if the specific heats and  $\bar{\chi}''$  for the same substance in the solid or liquid form be known, by measuring  $\bar{\chi} - \bar{\chi}''$  (the latent heat of vaporization of the solid) at some known temperature; if in addition  $\bar{H}''$  for the solid be known,  $\bar{H}$  for the gas can be calculated, since at any temperature and pressure at which the two are in equilibrium  $\bar{\xi} = \bar{\xi}''$ . Thus the generalizations used to find  $\bar{E}$  and  $\bar{H}$  for crystalline solids can be used to help find  $\bar{E}$  and  $\bar{H}$  for gases as well; and the need for even a single equilibrium measurement would be escaped if van der Waals' law of corresponding states could be trusted to furnish the vapor-tension curve, the chemical formula to suggest the critical constants, and Trouton's law to supply the latent heat. Attempts are being made to improve the generalizations in question with this object in view, and are meeting with some success.

A fundamental equation valid over a wider range of pressures has been deduced by van Laar<sup>52</sup> from van der Waals' equation connecting temperature pressure and volume.

3. *"Perfect" or "ideal" gaseous solutions.* When oxygen ( $x$  grams) and nitrogen ( $y$  grams) unite to form a gaseous solution, no heat is evolved and there is no contraction or expansion, hence

<sup>51</sup> From  $pv = mat$  and  $pv = nRt$ ,  $R = ma/n$ , useful in transliterating. When the gas is an element or a chemical compound,  $m/n$  is its molecular-weight; so, in that case, Gibbs'  $a = R/(\text{molecular-weight})$ .

<sup>52</sup> J. J. van Laar: *Die Thermodynamik in der Chemie*, Amsterdam and Leipzig, 1893, Engelmann.

$\chi = x \cdot \bar{\chi}_1 + y \cdot \bar{\chi}_2$  and  $V = x \cdot \bar{V}_1 + y \cdot \bar{V}_2$  [Symbols with the subscript 1 refer to pure oxygen, with subscript 2 to pure nitrogen, with no subscript to the solution]. Experimental study of equilibria of the types  $G''L'$  and  $G''S'$  shows that  $\mu_x$  for oxygen as a component of the solution has the same value as  $\mu$  for pure oxygen at the same temperature if in both cases the weight of oxygen per cubic centimeter of the gas be the same. Since both oxygen and nitrogen are approximately "perfect gases" as defined above, the above relations lead to  $\mu_x = \bar{E}_1 + t \{ \bar{C}_1 - \bar{H}_1 - \bar{C}_1 \log t + a \cdot \log xp/(ax + by) \}$  and a similar expression<sup>53</sup> for  $\mu_y$ ; since  $\zeta = x \cdot \mu_x + y \cdot \mu_y$ , the fundamental equation for perfect gaseous solutions (G. 293) is found. [ $a$  and  $b$  are the constants for oxygen and nitrogen respectively in the equation  $p\bar{V}/t = \text{const}$ ;  $a = 1.98/32$  and  $b = 1.98/28$ ]. From the expression for  $\mu_x$  or  $\mu_y$ ,  $\mu_{xy} = -abt/(ax + by)$ , for use in Eq. (6). The quantity  $axp/(ax + by)$  is often represented by the symbol  $\pi_1$ , and spoken of as the "partial pressure" of the oxygen, similarly  $bpy/(ax + by) = \pi_2$  is the "partial pressure" of the nitrogen, the sum of the two gives  $p$ , the pressure of the gas; the quantity  $ax/(ax + by)$  is sometimes called the "mol-fraction" of the oxygen.

In cases where the potentials of the components of a gas at ordinary temperatures and pressures prove to be in fair agreement with the above expressions for  $\mu_x$  and  $\mu_y$ , the gas is said to be a "perfect" or "ideal" gaseous solution of the components; where there is no such agreement, the components are said to have "reacted chemically"—this is the only definition we have for this term, and the nomenclature is somewhat indefinite, for if the want of agreement is not very great it is sometimes ascribed to "deviation from the laws of perfect gases." Whenever two gases mix without evolution of heat or change of volume it is customary to assume that they form a "perfect gaseous solution," just as in determining the vapor density of a new organic compound it is customary to assume that its vapor obeys Boyle's law, closely

<sup>53</sup> The above expression for  $\mu_x$  corresponds in form to Gibbs' Eq. 293; the fraction may be made symmetrical by writing  $-a \cdot \log a + a \cdot \log axp/(ax + by)$  instead of  $a \cdot \log xp/(ax + by)$ .

enough at all events for the purpose in hand. By means of this assumption it is possible to calculate values of  $\mu_x$  and  $\mu_y$  for solid or liquid solutions of two volatile components from the results of experimental study of equilibria of the types  $G''L''$  or  $G''S''$ .

4. "Perfect" liquid or solid solutions. Making the same simple assumptions as for one-component liquids or solids, and assuming further that there is no heat of dilution and that the specific volume is a linear function of  $x/(x+y)$ , there follows:  $\mu_x = \bar{E}_1 + t\{\bar{C}_1 - \bar{H}_1 - \bar{C}_1 \log t + f(x, y)\} + p\bar{V}_1$ . If this equation holds over a range of concentrations that includes  $x/(x+y) = 1$ , the values of  $\bar{E}_1$ ,  $\bar{C}_1$ ,  $\bar{H}_1$  and  $\bar{V}_1$  are obviously those of the pure component in the same state of aggregation as the solution; otherwise they must be regarded as constants to be determined by experiments with the solutions. An expression for  $f(x, y)$  may be found experimentally by the study of suitable equilibria; if it should prove possible to express  $f(x, y)$  in the form  $\alpha \cdot \log \alpha x / (\alpha x + \beta y)$ , where over a moderate range  $\alpha$  and  $\beta$  are independent of temperature pressure and composition, the solution may be said to be "perfect"<sup>54</sup> for the given range; thus, for "perfect" solutions,  $\mu_{xy} = -\alpha\beta t / (\alpha x + \beta y)$ .

The formulas given in elementary text-books of physical chemistry for the solubility curve, and for the osmotic pressures, freezing-points, vapor-tensions, etc. of solutions, may be derived from Eqs. (4) or (7), i.e. from the two laws of thermodynamics, by means of this fundamental equation.

*The essence of this method of dealing with the matter is, that the problems are put before the student with the assurance that they can always be solved if certain specified experimental data are available, and the simple formulas are presented merely as particular solutions valid only when certain of these data have negligibly small or otherwise special values.*<sup>55</sup> All molecular "explanations" are omitted in this method of deducing the formulas, because they are irrelevant to the argument; it is their place to explain why the

<sup>54</sup> The term "perfect solutions" is often used to denote the group here distinguished as *dilute* perfect solutions.

<sup>55</sup> This view has been emphasized by G. W. Morey, *Jour. Franklin Inst.* 194 425 (1922); see his closing sentence.

data necessary for the calculation have the values observed in the laboratory; but if the data themselves be available, whether "explained" or not, the problems can be solved.

*Osmotic pressures.* Replacing  $\mu_{xy}$  in Eq. (4) by its value from the fundamental equation, there follows  $v_y \cdot \partial P_x / \partial x = \alpha \beta t / (\alpha x + \beta y)$ ; which on integration [ $v_p = 0$ ;  $P_x = 0$  when  $x = 0$ ] gives  $v_y P_x = \beta t \cdot \log(\alpha x + \beta y) / \beta y$ . If the solutions be dilute, i.e. if  $\alpha x$  be small in comparison with  $\beta y$ , two<sup>56</sup> simplifications can be introduced:—in the first place the logarithm can be replaced by  $\alpha x / \beta y$  [since when  $h$  is small,  $\log(1+h) = h$  approx.], and in the second place  $V$  may be substituted for  $y \cdot v_y$  [Euler's theorem]. Making these substitutions, there results  $P_x \cdot V = \alpha x t$ , which if transliterated [ $\alpha = 1.98 i / M_x$ , where  $M_x$ , is the "molecular weight" of the dissolved substance and  $i$  is van't Hoff's constant; 31360  $P_x = \text{osm. press. in mm. mercury}$ ] will be recognized as the formula of van't Hoff.

*Solubilities.*—Replacing  $\mu_{xy}$  in Eq. (7) by its value from the fundamental equation, there results

$$(\bar{\chi}' - \chi_y'') / t^2 \cdot dt = \alpha \beta / (\alpha x + \beta y) \cdot (dx - x / y \cdot dy)$$

which holds both for solubility curve and for freezing-point curve;  $y$  gives the weight in the solution of the component common to both phases, and  $\bar{\chi}' - \chi_y''$  gives the number of calories gained by the (constant pressure) calorimeter when one gram of that component is transferred from the solid to the solution.

In the case of the solubility curve,  $x$  gives the weight of solvent in the solution. Integrating with  $x$  constant, there results

$$\bar{\rho}_1 \left( \frac{1}{t_1} - \frac{1}{t_2} \right) + \left( \bar{C}' - c''_y \right) \left( \frac{t_1 - t_2}{t_2} + \log \frac{t_2}{t_1} \right) = \beta \cdot \log \frac{y_1(\alpha x + \beta y_2)}{y_2(\alpha x + \beta y_1)}$$

where  $\bar{\rho}_1$  is the value of  $\bar{\chi}' - \chi_y''$  when  $t = t_1$ . Neglecting the second term on the left, neglecting  $\beta y$  in comparison with

<sup>56</sup> In van't Hoff's second paper [*Zeit. phys. Chem.* 1, 483 (1887)] both substitutions are made; in his first paper [*K. Sven. Vet. Handlingar* 21, 3 (1886)] a formula was obtained which involved the first only. See Bancroft; *Jour. Phys. Chem.* 10, 318 (1906). The (more accurate) quantity  $y \cdot v_y$  is often called "the volume of the water in the solution", it can be replaced by  $V$  "the volume of the solution" only when  $x \cdot v_x$  is negligible.

$\alpha x$ , and transliterating, this gives van't Hoff's formula for the solubility curve.

*Depression of the freezing-point.* Here  $y$  gives the weight of solvent in the solution. Integrating the general expression of the preceding paragraph, with  $y$  constant, the terms on the left will be the same as for the solubility curve, while the term on the right becomes  $\beta \cdot \log(\alpha x_1 + \beta y) / (\alpha x_2 + \beta y)$  which if  $\alpha x_2$  be small in comparison with  $\beta y$  (dilute solutions) and  $x_1 = 0$ , is very closely equal to  $-\alpha x_2 / y$ . For dilute solutions, moreover, the second term on the left will be negligible, since  $t_2 - t_1$  will be small. By making these substitutions and transliterating, van't Hoff's expression for the depression of the freezing-point may be obtained.

*Vapor-tensions.* If only one component ( $y$ ) be volatile ( $G'L'', G'S''$ ) and if it be assumed that  $G'$  is a "perfect" gas, and  $L''$  (or  $S''$ ) a "perfect" solution, expressions for the effect of temperature or of pressure on the solubility of the gas, or for the effect of temperature or of concentration on the vapor-tension of the solution can be obtained by methods similar to those of the preceding paragraphs. If  $\beta = b$ , the graph of the vapor-tensions  $\pi_2$  on a diagram for which  $t$  is constant and the abscissas give the values of  $\alpha x / (\alpha x + by)$ , will be straight line; by choice of a suitable value for  $\alpha/b$  it is always possible to bring any three selected points of the curve into alignment, and if when this is done the curve as a whole is fairly straight, the formulas for "perfect" solutions may be counted on to give reasonably close results.

If both components be volatile, and both phases "perfect", then from the fundamental equations, neglecting the specific volume of the liquid in comparison with that of the gas,  $a \cdot \log \pi_1 = \alpha \cdot \log \alpha x / (\alpha x + \beta y) + f(t)$ ; whence, for any given temperature,  $\pi_1$  raised to the power  $a/\alpha$  is proportional to  $\alpha x / (\alpha x + \beta y)$  and similarly  $\pi_2$  raised to the power  $b/\beta$  is proportional to  $\beta y / (\alpha x + \beta y)$ .

5. "*Ideal*" liquid or solid solutions.<sup>57</sup> It is only in the special case where  $\alpha = a$  and  $\beta = b$  that  $\pi_1$  and  $\pi_2$  (and consequently also their sum, the vapor tension of the solution) can be repre-

<sup>57</sup> E. W. Washburn: *Introduction to the principles of physical chemistry*, New York, 1915, McGraw-Hill Book Co., p. 145.

sented by straight lines on a diagram whose abscissas give  $ax / (ax + by)$  or indeed  $Ax / (Ax + By)$  where  $A$  and  $B$  are any constants. This special group of "perfect" solutions has received the name "ideal" solutions; for them the values of  $\alpha$  and  $\beta$  can be calculated from the vapor densities of the components. Where one or both of the components are non-volatile, however, the distinction loses its sharpness; if by the choice of suitable values for  $\alpha$  or  $\beta$  or both of them, experimentally determined freezing-points, solubilities, etc., can be brought into fair accord with the formulas for "perfect" solutions, then the solution experimented with is "perfect;" if in addition the values of  $1.98/\alpha$  and  $1.98/\beta$  are approximately equal to the "molecular weights" of the components as deduced from the ordinary chemical formulas or from some molecular theory, then the solution is "ideal."

For all "ideal" solutions, as may be seen from the fundamental equation, not only is  $\mu_x$  a one-valued function of  $t$ ,  $p$ , and the "mol fraction"  $ax/(ax + by)$ , but the mol fraction<sup>58</sup> is also a one-valued function of  $\mu_x$ ; and for many purposes the numerical value of the former is as useful as that of the latter. Since concentration is supposed to be a "concrete" conception, while potential is "abstruse" there is a tendency to force as many solutions as possible into the "ideal" group, and to express an experimentally determined potential in terms of a fictitious "concentration" arrived at by assuming the solution to "contain" as many polymers, addition-compounds, etc., as may be necessary to make the mol-fraction take the value desired. As a result, the term "concentration" has lost precision; and it is sometimes difficult to decide whether a given equation expresses an experimentally determined relation between the freezing-point (for instance) of a solution and its analytically determined composition, or on the other hand merely presents an alternative method of recording the freezing-point, without saying anything at all about the analytical composition of the solution frozen.

<sup>58</sup> Planck calls  $ax/(ax + by)$  "concentration;" with G. N. Lewis this word means  $ax/RV$ , he calls  $ax/(ax + by)$  "mol-fraction," and  $ax/by$  "mol ratio." The name "numerical concentration" is sometimes given to  $ax/(ax + by)$ .

Perhaps this method of recording thermodynamic data would be less uncritically employed, if it were generally recognized that it is not possible to employ it universally. To assume that in every case identity of potential means identity of "concentration," would be to assert that the concentration of each constituent, no matter what or how many might be assumed, must have the same value in the upper as in the lower layer when ether and water are shaken together; but this would be to say, that the analytical composition of the two layers must be the same.

*Illustration 2. Duhem-Margules equation*

In experiments to determine the vapor-tensions of aqueous solutions of alcohol, the composition of the liquid is varied while the temperature is held constant, the pressures are those at which the two phases are in equilibrium, and the variations in the potentials of the two components of the liquid [unaccented symbols] are related by

$$x \cdot d\mu_x + y \cdot d\mu_y = V \cdot dp \quad (\text{G 97, } dt = 0)$$

If it be assumed that the vapor is a "perfect gaseous solution" of the two components, it follows from the fundamental equation that (for the vapor)  $d\mu'_x = at \cdot d \log \pi_1$ ; since the two phases are in equilibrium, this expression may be substituted for  $d\mu_x$ , and  $bt \cdot d \log \pi_2$  for  $d\mu_y$  in (G 97) above. If moreover the vapor-tension measurements were made at temperatures well below the critical temperatures, as is the case with those published for aqueous alcohol, the term  $V \cdot dp$  is negligible in comparison with the other two and may be omitted. Making these substitutions, there results:

$$ax \cdot d \log \pi_1 + by \cdot d \log \pi_2 = 0 \quad (11)$$

which is often spoken of as the "Duhem<sup>59</sup>-Margules equation". [ $a = 1.98/46$ ;  $b = 1.98/18$ ;  $\pi_1 + \pi_2 = \pi$  the vapor-tension of the solution.]

<sup>59</sup> Duhem: *Ann. de l'École norm. sup.* (3), 4, 9 (1887); *Zeit. phys. Chem.*, 35, 483 (1900).

By means of this equation, if the values of  $\pi_1$  are known those of  $\pi_2$  can be calculated; but as the experiments necessary for a direct determination of  $\pi_1$  (viz., measurement of the vapor-tension and analysis of the vapor) also give values of  $\pi_2$ , the computation could serve only as a check on the experimental results and on the assumption that the vapor is a perfect gaseous solution of the components.

Writing Eq. (11) in the form

$$\frac{ax}{ax + by} \cdot d \log \frac{\pi_1}{\pi} + \left(1 - \frac{ax}{ax + by}\right) \cdot d \log \left(1 - \frac{\pi_1}{\pi}\right) + d \log \pi = 0$$

it appears as a differential equation from which, if  $\pi$  were known as a function of the composition of the solutions,  $\pi_1$  and therefore the composition of the vapor, might be found. The equation, however, is not linear; and the only solution hitherto suggested, that of Margules,<sup>60</sup> assumes  $\pi$  to be given as a function of the concentration by an interpolation formula of very special form. Until methods have been devised for finding the values of the coefficients in this formula from the experimental data, this solution in its generality is unworkable; although Margules has shown that, by introducing simplifying assumptions, approximate results may in some cases be obtained. Marshall<sup>61</sup> and Bose's<sup>62</sup> method of computation by approximation, on the other hand, has proved satisfactory in practice.

It is possible to arrive at a numerical solution of the equation by means of an abacus constructed of rods suitably ruled once for all with straight lines. If the logarithms of the vapor tensions  $\pi$  be plotted against  $ax/(ax + by)$  as abscissas, and the rods be moved parallel to the ordinate axis until their pointed ends touch the  $\log \pi$  curve, a number of curves can be traced by eye across the rods, to which the segments of the straight lines are tangent. Each of these curves presents a particular solution of the differential equation for the given experimental values of  $\pi$ ; but only

<sup>60</sup> *Wien. Akad. Ber.*, **104**, II A, 1243 (1895).

<sup>61</sup> *Jour. Chem. Soc.*, **89**, 1350 (1906).

<sup>62</sup> *Physik. Ztschr.*, **8**, 353 (1907); *Zeit. phys. Chem.*, **65**, 480 (1909).



one of them fulfils the boundary conditions that  $\pi_1 = 0$ , at  $x = 0$  and  $\pi_2 = 0$  at  $y = 0$ ; the slope of this curve at any point, i.e. for any composition of the liquid, gives the ratio  $\pi_1/\pi_2$ , and therefore the composition of the vapor. In order to decide which curve to follow, some assumption may be made as to the partial pressures for the dilute solutions, or a single analysis of the vapor may be made in the laboratory; this would serve to identify the curve and the compositions of the other vapors could then be read off.

To rule the rods, the ends are made to touch a straight line parallel to the axis of abscissas whose ordinate may be taken as zero; straight lines are then drawn from a point on the right whose abscissa is 1.0 and whose ordinate is  $\log h$ , to a point on the left whose abscissa is zero and whose ordinate is  $\log(1 - h)$ ,  $h$  being given in turn all values from 0.1 to 0.9. The graph so obtained (Fig. 8) is the solution of Clairaut's equation. The slope of each line is proportional to  $\log h/(1 - h)$ ; and where the abscissa  $ax/(ax + by) = n$ , its ordinate is  $n \cdot \log h + (1 - n) \cdot \log(1 - h)$  when the rod is being ruled, or  $n \cdot \log h \pi + (1 - n) \cdot \log(1 - h)\pi$  after the rod has been moved up until its point touches the  $\log \pi$  curve (Fig. 9). For the curve that fulfils the boundary conditions the ordinates are  $n \cdot \log \pi_1 + (1 - n) \cdot \log \pi_2$ , so that this curve if provided with a base line and a suitable scale of ordinates would be the  $\zeta$  curve for the solutions at the temperature of the vapor-tension measurements; its slope is  $\log(\pi_1/\pi_2)$ , and if the straight lines are ruled for equal intervals of  $h$ , every fifth line thicker, the "mol-fraction" of the vapor can be read off without difficulty.

Figures 8, 9, 10 give an idea of the limitations of the method and of the accuracy obtainable; the abacus from which they are photographed was constructed by Professor Burt-Gerrans from fifty quarter-inch-square brass rods, about 75 cm. long, finished black and ruled in white; the scale of ordinates is 200 cm. between  $h = 1.0$  and  $h = 0.1$  Wrewsky's values of  $\log \pi$  for aqueous solutions of alcohol at 39.76°C.<sup>63</sup> were plotted, the rods adjusted to the curve, and a photostat made of the useful part with linear dimensions three-quarters of those of the abacus.

<sup>63</sup> Thirty-one experimental points; *Zeit. phys. Chem.*, **81**, 17 (1913).

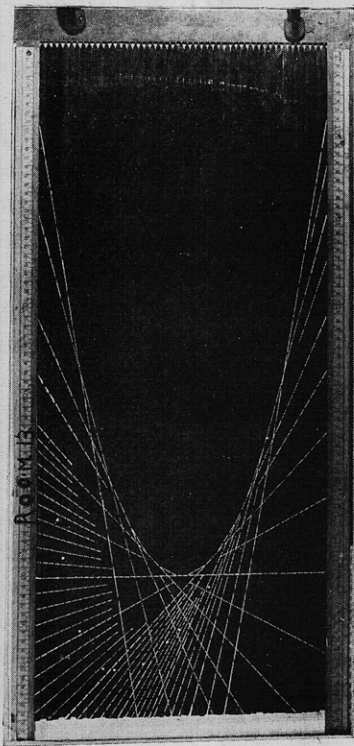


FIG. 8

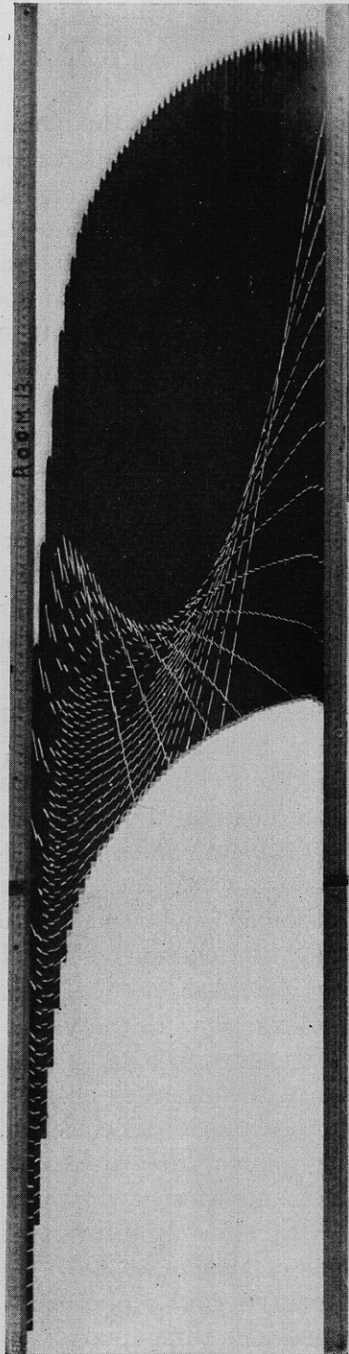


FIG. 9

Wrewsky's analysis of the vapor given off by the liquid containing 27 mol-percent alcohol (viz: 60.5 mol-percent alcohol in the vapor) was used to identify the curve, which was then drawn with ink on the photostat, rod by rod, its slope being determined by interpolation between the slopes of the lines of the abacus; this is slow work, but there is no uncertainty as to the proper position of the curve. Figure 10 shows part of the curve so drawn, viz. that from 15 to 39 mol-percent alcohol in the liquid

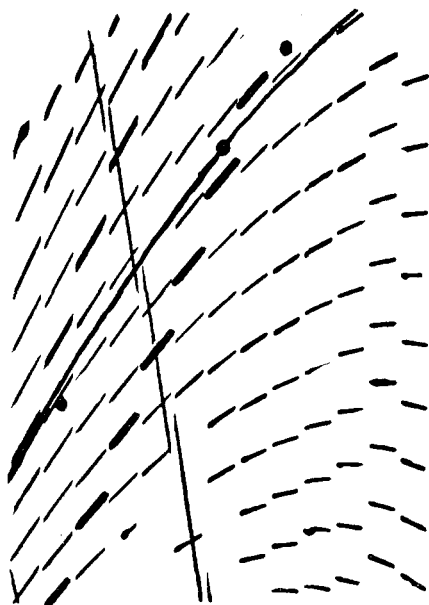


FIG. 10

(13 rods); the diagonals corresponding to 60 mol-percent alcohol in the vapor are thicker than the others, the diagonals immediately below them correspond to 61 percent and so on. The three dots give Wrewsky's results with liquids containing 23, 27 and 37 percent alcohol.

For liquids containing from 17 to 70 mol-percent of alcohol, the compositions of the vapors read from the curve agree with the experimental values within less than 1 mol-percent of alcohol; for 9 percent liquid the curve gives 46 percent in the vapor and

Wrewsky found 48.3; for 7 percent liquid the curve gives 41 percent and experiment 45.5 percent. The segments of the ruled lines which bound the curve are spaced at intervals of one mol-percent alcohol in the vapor for liquids containing up to 55 mol-percent alcohol; from 57 to 63 percent the interval is 3 percent; from 65 to 69 percent, 5 percent; above 71 percent, 10 percent. Obviously, close results are obtainable only when the composition of the vapor is not too near that of the liquid; but as the discrepancies between calculated and observed partial pressures<sup>64</sup> occur just where the spacing is widest, they can not be ascribed to errors in drawing the curve.

<sup>64</sup> Recognized by Wrewsky: *Zeit. phys. Chem.*, **83**, 583 (1913); he seems willing to ascribe them to experimental errors (*loc. cit.*, p. 584).