

# ON THE SECOND DIFFERENTIAL COEFFICIENTS OF GIBBS' FUNCTION $\zeta$ . THE VAPOUR TENSIONS, FREEZING AND BOILING POINTS OF TERNARY MIXTURES

BY W. LASH MILLER

## *The Second Differential Coefficients of $\zeta$*

In his paper on «Equilibrium in Heterogeneous Systems» Professor Gibbs<sup>1</sup> introduces a function

$$\zeta = \varepsilon - t\eta + pv \quad (91)$$

and shews that

$$d\zeta = -\eta dt + v dp + \mu_1 dm_1 + \mu_2 dm_2 + \dots + \mu_n dm_n \quad (92)$$

As will be seen from its definition in (91),  $\zeta$  is a quantity whose value for any given system depends only on the values of the physical parameters  $\pi$  describing the state of that system for the time

<sup>1</sup> *Trans. Conn. Acad. III (1876-1878).*

The letters have the same meaning as in the work of Gibbs referred to,  $\varepsilon$  energy,  $t$  absolute temperature,  $p$  pressure,  $v$  volume,  $\eta$  entropy,  $m_i$  mass and  $\mu_i$  potential of the substance indicated by the suffix.  $\mu_i$  is defined by the equation  $\mu_i = (\partial\varepsilon/\partial m_i)_{\eta, v, m}$ . The small letters to the right of the differential coefficients (*e. g.*  $\eta$ ,  $v$ ,  $m$  in the last equation) indicate the quantities remaining constant during the differentiation;  $m$  (short for  $m_2, m_3 \dots m_n$ ) indicates all the quantities  $m_1 \dots m_n$  except that one ( $m_i$ ) mentioned in the differential coefficient.

The expressions for the potential  $\mu$  of a gas in Gibbs' work are deduced with the aid of the equation  $pv = at$ . In the present paper this equation has been replaced by the more convenient  $pv = nRt$ . Consequently in numerical applications of the equations in the text, the quantities of the various components must be expressed in (gramme molecules) not in grammes. This has been indicated by replacing the letters  $m_1, m_2$ , etc., by  $n_1, n_2 \dots$  wherever necessary. The numbers of the equations, *e. g.* (91) above, refer to Gibbs' paper *l. c.*

being, and is independent of the manner in which that state has been attained. The values of the second differential coefficients of  $\zeta$  must consequently be independent of the order of differentiation, or

$$\frac{d^2\zeta}{d\pi_1, d\pi_2} \pi = \frac{d^2\zeta}{d\pi_2, d\pi_1} \pi \quad \text{A}$$

From equation (92) there follows :

$$\frac{d\zeta}{dt} p, m = -\eta \quad \frac{d\zeta}{dp} t, m = v \quad \frac{d\zeta}{dm_1} t, p, m = \mu_1 \quad \text{etc., etc.}$$

Substituting these values in A there results a set of equations of the form

$$\begin{aligned} \frac{d\eta}{dp} t, m &= -\frac{dv}{dt} p, m & -\frac{d\eta}{dm_1} t, p, m &= \frac{d\mu_1}{dt} t, p, m. \\ \frac{dv}{dm_1} t, p, m &= \frac{d\mu_1}{dp} t, m & \frac{d\mu_1}{dm_2} t, p, m &= \frac{d\mu_2}{dm_1} t, p, m \end{aligned}$$

One of these, that connecting  $dv$  and  $d\mu_1$ , has been made use of by Gibbs<sup>1</sup>. The object of the present paper is to illustrate the importance, for the theory of ternary mixtures, of the last on the list, viz:—

$$\frac{d\mu_1}{dm_2} t, p, m = \frac{d\mu_2}{dm_1} t, p, m \quad \text{etc.} \quad \text{B}$$

NOTE. Although in equation B,  $p$  is represented as a constant, if the potentials  $\mu_1, \mu_2$  refer to components of a liquid or solid mixture they will not be affected by moderate<sup>2</sup> variations in  $p$ .

#### *The Interpretation of $\mu$ in Equation B*

An idea of the great number of special applications that may be made of equation B can best be gained from a review of the different methods by which the potentials  $\mu$  may be measured. Gibbs has shewn how  $\mu$  for a gas<sup>2</sup>, and  $\mu_1, \mu_2 \dots$  for the components of a gaseous mixture<sup>3</sup>, may be expressed as functions of the various physical coördinates which may be employed to describe the thermodynamical state of a gas. For a *liquid or solid phase* he has shewn the connection between the potentials of the various components and

<sup>1</sup>Gibbs. 1.c. equation 272, page 214.

<sup>2</sup>Gibbs. 1.c. equations 259, 264, 268, pages 211 and 212.

<sup>3</sup>Gibbs. 1.c. page 215.

their *vapour tensions*<sup>1</sup> (partial pressures). The relation between the vapour tension (consequently  $\mu$ ) and the *freezing point* of a solution was worked out by Guldberg<sup>2</sup>; while Arrhenius employed the well known formula of Clausius to connect the vapour tension of a solution with its *boiling point*<sup>3</sup>. An ingenious speculation (on the value of the potentials when the quantity of one component is very small)<sup>4</sup> led Gibbs to the assumption of a relation between the potential and the *concentration* of a substance in dilute solution, which was afterwards shewn to hold for all substances whose vapours dissolve according to *Henry's law*<sup>5</sup>. From a paper by van 't Hoff may be deduced the corresponding relation for vapours which dissolve according to a modified (‘*potentized*’) *Henry's law*<sup>6</sup>, while Nernst's theory of distributive equilibrium<sup>7</sup> opens up the case where the vapour phase is replaced by a *second liquid*.

*Osmotic Pressure.* ( $\mathfrak{P}$ ) was brought into connection with vapour tension (and hence with  $\mu$ ) by van 't Hoff<sup>8</sup>; and the experimental confirmation of his equation  $\mathfrak{P}\mathfrak{V} = nRt$ , shews that the relation discerned by Gibbs holds for many substances which have never been gasified. Arrhenius lastly shewed how abnormal (molecular weights in solution) (on which the values of  $n$  in van 't Hoff's equation depend) may in many instances be predicted from measurements of the *electrical conductivity*<sup>9</sup> of the solution; as a result of the development of the Arrhenius-van 't Hoff theory, it is now possible in many cases to express the potential  $\mu$  of a dissolved substance as a function of its concentration in the solution, without any knowledge of its behaviour in the form of gas. The *electromotive force* of certain cells was connected with the potentials of the reacting sub-

<sup>1</sup>Gibbs. l.c. page 225.

<sup>2</sup>Guldberg. C.r. **70**, 1349.

<sup>3</sup>Arrhenius. Zeit. phys. Chem. **4**, 550 (1889).

<sup>4</sup>Gibbs. l.c. equation 216, page 196.

<sup>5</sup>Gibbs. l.c. page 226.

<sup>6</sup>Van 't Hoff. K. Svenska Vet. Akad. Handl. **21**, 21 (1887).

<sup>7</sup>Nernst. Theoretische Chemie.

<sup>8</sup>van 't Hoff. Études de dynamique chimique, p. 182 (1884).

<sup>9</sup>Arrhenius. Zeit. phys. Chem. **1**, 631 (1887).

stances by Gibbs<sup>1</sup> in the work referred to; and Nernst<sup>2</sup> by connecting E.M.F. with osmotic pressure has done much to make this relation better understood.

The object of this paragraph is to shew what a very large number of important relations may be deduced from equation A, by replacing the terms  $\mu_1, \mu_2, \text{etc.}$ , by their values in terms of the physical quantities enumerated. In the present paper only those applications will be considered in which the potential of one at least of the substances involved is expressed as a function of its *solubility* in the mixture under consideration.

*$\mu$  as a function of solubility*

In a solution saturated with a solid,  $S$ , the potential  $\mu_s$  of a given weight ( $n_s$  gramme molecules) of the substance  $S$  is equal to that of the same weight of the solid at the same temperature (and pressure). The potential  $\mu_s$  of the same weight of the same substance in a more dilute solution is less than  $\mu_s$  and assuming

$$\mathfrak{P}\mathfrak{V} = n_s R t$$

there follows

$$\mu_s = \mu_s + n_s R t \log \text{nat } \mathfrak{P}_s / \mathfrak{P}_s \quad (t \text{ const.})$$

in which  $\mathfrak{P}_s$  is the osmotic pressure of the salt in the dilute solution and  $\mathfrak{P}_s$  that in the saturated solution.

By differentiation,

$$d\mu_s = n_s R t d \log \text{nat } \frac{\mathfrak{P}_s}{\mathfrak{P}_s}$$

or, if  $\mathfrak{P}_s / \mathfrak{P}_s$  be set equal to  $C_s / C_s$  (the ratio of the concentrations<sup>3</sup> of  $S$  in the two solutions)

$$d\mu_s = n_s R t d \log \text{nat } C_s / C_s \quad \text{C.}$$

If then solutions of the substance  $S$  be prepared of equal concentrations in different solvents, the potential  $\mu_s$  will be greatest for that solution which is nearest saturated; or the greater the solubility of

<sup>1</sup>Gibbs. l.c. page 501.

<sup>2</sup>Nernst. Zeit. phys. Chem. 4, 129 (1889).

<sup>3</sup>This is allowable only when the molecular weight of  $S$  is approximately the same in the two solutions.

$S$  in any solvent the less the potential  $\mu_s$  for any given concentration. If to a solution of  $S$  in a liquid mixture of  $A$  and  $B$  there be added an additional quantity of  $A$ , the potential  $\mu_s$  will be *increased* if less  $S$  can dissolve in the mixture after addition of  $A$  than before, and *vice versa*. It is not sufficient that  $S$  should be less soluble in  $A$  than in  $B$ , or in mixtures containing a large percentage of  $A$  than in those with a less; *the total quantity of  $S$  that can dissolve must be lessened by addition of  $A$  to the solvent*. This is one of the most important (qualitative) conclusions from equation C.

#### *Solubility and Electromotive Force*

The relation expressed in equation C may be made use of in calculating the E.M.F. of cells of the type

metal  $M$  / salt  $MX$  in water / salt  $MX$  in dil. alcohol / metal  $M$ .

If the aqueous and alcoholic solutions of  $MX$  be of the same concentration, the current will pass within the cell from the water to the alcohol (assuming  $MX$  less soluble in alcohol than in water) and the electromotive force will be

$$E.M.F. = \frac{v}{u+v} \frac{n_i}{n_e} 0.0002 t \log \frac{C_W}{C_A}$$

where  $C_W$  and  $C_A$  are the concentrations of saturated solutions of  $MX$  in water and in the dilute alcohol respectively. (The substitution of  $C$  for  $\mathfrak{D}$  is allowable only when the molecular weight of  $MX$  is the same in both solutions, and where  $MX$  is not very soluble in either).

#### *The Freezing Points of Ternary Mixtures*

The subject has been treated of in the May number of this Journal by Mr. D. McIntosh<sup>1</sup>. He finds:—

“When we have two non-miscible substances  $A$  and  $C$  and a third substance  $B$  with which the other two are miscible<sup>2</sup>, we can distinguish two cases.

(i) The component  $A$  can exist as solid phase under the conditions of the experiment. Under these circumstances addition of  $C$  to the liquid phase containing  $A$  and  $B$  will raise the temperature at

<sup>1</sup>D. McIntosh. Solubility and Freezing Point. This Journal I, 474 (1897).

<sup>2</sup>NOTE. The letters  $A$ ,  $B$  and  $C$  will be used in this sense throughout the remainder of this paper.

which  $A$  can exist as solid phase [illustrated by experiments with benzene ( $A$ ), alcohol ( $B$ ) and water ( $C$ )].

(ii) The component  $B$  can exist as solid phase under the conditions of the experiment. Under these circumstances addition of  $C$  to the liquid phase will lower the temperature at which  $B$  can exist as solid phase [illustrated by the experiments of Abegg<sup>1</sup> and others on the freezing points of solutions of salts in aqueous alcohol, *etc.*]]

The connection between these propositions and the requirements of equation B may be seen from the following considerations. As the substance  $C$  is soluble in  $B$  but not in  $A$ , it is fair to assume that its solubility in mixtures of  $A$  and  $B$  will decrease with rise in the proportion of  $A$  in the mixture. If the decrease in solubility should be so rapid that (as is the case with the mixtures of benzene, alcohol and water) addition of  $A$  precipitates  $C$  from its saturated solution in a mixture of  $A$  and  $B$ , then, by equation C

$$\frac{d\mu_c}{dm_c} \text{ at } t, p, m \text{ is positive}$$

and consequently (by equation B)

$$\frac{d\mu_a}{dm_c} \text{ at } t, p, m \text{ is positive}$$

or, on addition of  $C$  the potential of  $A$ , and consequently its vapour tension and the temperature at which it is in equilibrium with solid  $A$ , will rise. McIntosh's second case, as quoted above, is the converse of the first.

In order to throw further light on this *second case* it is convenient to introduce another of Gibbs' equations.

$$0 = -vdp + \eta dt + m_1 d\mu_1 + m_2 d\mu_2 + \dots + m_n d\mu_n \quad (97^2)$$

which for liquid mixtures of three components, kept at constant temperature and fairly constant pressure, becomes

$$0 = m_a d\mu_a + m_b d\mu_b + m_c d\mu_c \quad D$$

It has just been shewn that addition of  $C$ , which involves an increase

<sup>1</sup>Abegg. Zeit. phys. Chem. **15**, 260 (1894).

<sup>2</sup>Gibbs. l.c. page 143.

in  $\mu_c$  (see equation C), increases the value of  $\mu_a$  as well. To satisfy equation (97) the value of  $\mu_b$  must diminish, and it will readily be seen that the less soluble  $C$  is in  $A$  (consequently the greater the change in  $\mu_a$  on addition of  $C$ ), the greater will be the diminution in the value of  $\mu_b$ . The experimental evidence on this point has been collected by McIntosh who finds that:—

«Addition of  $C$  will lower the temperature at which  $B$  can exist as solid phase, and this lowering will be more than it would be if  $A$  and  $C$  were miscible to some extent».

«The freezing point is lowered if the substance added be non-miscible with the component which does not appear as solid phase, and this lowering is greater than if the substances were added to the pure solvent».

The considerations advanced in this paragraph and in that on  $(\mu$  as a function of solubility) may serve further to connect the two apparently isolated facts (*i*) that the solubility of a mixture of two solids in a common solvent is usually not the sum of their individual solubilities, and (*ii*) that the depression in the freezing point of a solvent produced by dissolving in it a mixture of two substances is in general not equal to the sum of the separate depressions, even when the dissolved substances seem incapable of acting chemically on each other.

#### *The Vapour Tensions of Ternary Mixtures*

If  $\mu_a$  be expressed in terms of  $p_a$  (the partial pressure of  $A$  in the vapour given off by the mixture), and  $\mu_c$  as in equation C, equation B takes the form

$$n_a \frac{d \log \text{nat } p_a}{dn_c} {}_{t, p, n} = n_c \frac{d}{dn_a} \log \text{nat } \frac{C_c}{C_c} {}_{t, p, m} \quad \text{E}$$

Similarly with  $p_b$ , etc.

More or less empirical formulae to represent the alterations in the composition of the vapour (distillate) on addition of  $C$  may be deduced by combining equation E with the expressions found by Bodländer<sup>1</sup> and by Bancroft<sup>2</sup> and his pupils for the solubility of salts

<sup>1</sup>Bodländer. Zeit. phys. Chem. **7**, 308 (1891).

<sup>2</sup>Bancroft. This Journal **1**, 34 (1896).

in aqueous alcohol, *etc.* On the other hand, from measurements of the partial pressures of the vapours given off by mixtures of *A* and *B*, and of the alterations in them produced by addition of *C*, the molecular weight of the latter in the solution (hence  $n_c$  in equation E) may be determined<sup>1</sup>; and then, by means of equation E, the form of the solubility isotherms for *C* in mixtures of *A* and *B*.

#### *The Boiling Points of Ternary Mixtures*

If only *one* of the components be sensibly volatile at the temperatures of the experiment, the problem is very simple. If *A* be volatile, addition of *C* will increase the vapour tension or lower the boiling point of the mixture. If *B* be volatile the reverse is true.

If on the other hand both *A* and *B* have a noticeable vapour tension, while *C* has not, (for example alcohol (*A*), water (*B*), salt (*C*)), the change in the total vapour tension of the mixture on adding *C* is the algebraical sum of the changes in the partial pressures of *A* and *B*. In the case selected for illustration, addition of salt increases the vapour tension of the alcohol and diminishes that of the water. Whether the *total* tension will be increased or the reverse (*i. e.* whether the boiling point of the mixture will be lowered or raised by addition of *C*) depends on two circumstances.

(i) *The form of the curve of solubility of C in mixtures of A and B.* If alterations in the proportions of *A* and *B* in the mixture has but little effect on the solubility of *C*, the addition of *C* will bring about little or no increase, or even a diminution in the vapour tension of *A*; it is only when the quantity of *C* that can dissolve in a given mixture of *A* and *B* is lessened by addition of *A* that the vapour tension of *A* will be increased by addition of *C*. When *C* is equally soluble in all mixtures of *A* and *B*, the composition of the vapour will be unaffected by addition of *C*; cases of this nature were selected by Nernst and Roloff<sup>2</sup> for the determination of molecular weights in mixed solvents by means of the ebullioscope.

(ii) *The relation between the proportion of A to B in the Solution and in the vapour given off by it.* This may be illustrated by

<sup>1</sup>By means of Gibbs' equation (97). See also Nernst, *Zeit. phys. Chem.* **11**, 1, (1893.)

<sup>2</sup>Roloff, *Zeit. phys. Chem.* **11**, 7 (1893).



the case of mixtures of propyl alcohol (*A*), water (*B*), and salt (*C*)—the vapour given off by 75 percent propyl alcohol has the same composition as the boiling liquid, while if the liquid contain more alcohol the vapour contains less and *vice versa*.

By substituting for  $\mu_a$  and  $\mu_b$  their values in terms of the vapour tensions  $p_a$  and  $p_b$  of the alcohol and the water in the mixture, equation D becomes

$$-n_b R d \log \text{nat } p_b = n_a R d \log \text{nat } p_a + m_c d \mu_c$$

whence

$$-\frac{\partial p_b}{\partial p_a} = \frac{p_b}{p_a} \cdot \frac{n_a}{n_b} \quad \text{F}$$

and for 75 percent alcohol, (where  $p_b : p_a = n_b : n_a$ )

$$-\partial p_b = \partial p_a$$

From this it follows that the total diminution in the vapour tension of 75 percent propyl alcohol on addition of salt, will be numerically equal to the diminution that would have been produced in the tension of the water vapour alone if the tension of the alcohol had not been affected by the addition of the salt. The conditions under which the boiling point of a mixture of alcohol and water is unaffected by addition of salt, may be obtained by combining equations C and F and introducing the condition

$$dp_a + dp_b = 0$$

My attention was first attracted to the subject of this paper by a measurement made in this laboratory in 1893 by Mr. F. B. Kenrick, who observed that the boiling point of aqueous alcohol was lowered by the addition of potassium chlorid, and found that, as suspected, the percentage of alcohol in the distillate was increased by the addition of the salt. Measurements made last autumn together with Mr. T. R. Rosebrugh, by means of an apparatus similar to that employed by Lehfeldt<sup>1</sup> gave the following results :

<sup>1</sup>Phil Mag. 1895.

Solution *i*. consisted of 46.27 percent alcohol.

Its vapour tension at  $54^{\circ}.6 - 54^{\circ}.9$  C was 232 *mm.* Hg.

The vapour consisted of 82.18 percent alcohol.

Solution *ii*. consisted of 330.4 grammes of 46.27 percent alcohol in which were dissolved 28.1756 grammes of sodium chlorid.

Its vapour tension at  $54^{\circ}.7$  C was 244 *mm.* Hg.

The vapour consisted of 85.85 percent alcohol.

From these data there follows :

Solution *i*. Tension of the alcohol 190.6 *mm.*, of the water 41.4 *mm.*

Solution *ii*.     "     "     "     209.5     "     "     "     34.5     "

Difference           + 18.9 *mm*                   — 6.9 *mm.*

The boiling point of solution *ii* determined in a Beckmann's apparatus was  $0.9^{\circ}$  C lower than that of solution *i*. (Bar. 759 *mm.* B.pt. about  $82^{\circ}$  C).

Owing to the great influence which slight errors in determining the composition of the vapour exert on the value obtained for the molecular weight of the salt, the work was laid aside until a more accurate means of arriving at the composition of the vapour could be devised. At present, Mr. Rosebrugh and myself are engaged with a much improved apparatus, in determining the partial pressures of the vapours given off at different temperatures by aqueous alcohol of different strengths ; we hope also to obtain material with which to test the relations discussed above.

*The Chemical Laboratory of the University of Toronto,  
May, 1897.*