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The Effect of Volume and Temperature on the Energy and Entropy of Pure Liquids[1]

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The change of the potential energy of a liquid with temperature has been considered in two steps, the change with temperature at constant volume and the change with volume at constant temperature. The assumption is made that the position and momentum variables are separable. These considerations show that the potential energy of non-polar liquids is more dependent upon the volume than upon the temperature. Similar results are obtained for that part of the entropy which may be associated with the position and orientation of the molecules in the liquid. The values of the change with volume of the parameter, a, defined by the equation $E = E_0 + a/V$, are markedly different for many liquids in the normal range of volume while those of the change with temperature are about the same order of magnitude. A study is made of this dependency on volume.

The differences in the change of the energy and entropy on mixing at constant volume at different temperatures and different total volumes have been shown by Wood and Gray[2] to be largely volume dependent and only slightly temperature dependent. A study is presented in the first part of this paper of these same effects for pure liquids. It is again found that the entropy associated with the position and orientation of the molecules, and also the potential energy are largely dependent on volume and are dependent on the temperature to a smaller extent. Since the volume appears to be such an important variable, a study of the dependence of the potential energy on volume and temperature for several pure liquids is presented in the second part of this paper. On an assumption equivalent to the assumption of corresponding states, it appears that a minimum of three constants is required to express the dependence with volume. The behavior of the entropy parallels that of the energy. However, because of insufficient data, exact information on the entropy cannot be obtained at the present time.

Part I

The change of energy and entropy with change of temperature and volume may be considered in two steps: that due to the change in volume at constant temperature, and that due to the change in temperature at constant volume. However, this latter change of state involves changes in the kinetic energy and internal modes of motion of the molecules in addition to changes in the potential energy and that part of the entropy which is associated with the position and orientation of the molecules in the liquid. This difficulty may be overcome in some respects by using the difference between the energy of the liquid at a given temperature and pressure and that of the substance in the ideal gas state at the same temperature. Then, if the assumptions are made that the translational, vibrational and internal rotational partition functions are independent of the state of aggregation at the same temperature and that they are separable from the partition function for the potential energy, this difference of energy may be interpreted as the potential energy of the liquid. Similarly the corresponding difference of entropy may be interpreted as a measure of the spatial and orientational entropy. These assumptions may be considered as defining the translational and potential energies of the molecules in the liquid phase. The first assumption is probably valid for many non-polar liquids but certainly will not be valid for many polar liquids.

The quantity E^* is defined as $E - E_0$, where E is the energy of the liquid at a given temperature and pressure and E_0 is the energy of the ideal gas at the same temperature. Also S^* is defined as $S - S_0$, where S is the entropy of the liquid at a given

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[1] The financial assistance of the Atomic Energy Commission and the National Science Foundation to this research is gratefully acknowledged.

[2] S. E. Wood and J. A. Gray, III, THIS JOURNAL, **74**, 3733 (1952).

temperature and pressure and S_0 is the entropy of the substance in the ideal gas state at the same temperature and some arbitrary pressure or volume. The effects of the temperature and the volume on E^* or S^* may be separated by considering the differential change in these functions for a differential change in temperature at constant pressure. The differential expression for E^* when both the temperature and volume are independent is

$$\mathrm{d}E^* = \left(\frac{\partial E^*}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial E^*}{\partial V}\right)_T \mathrm{d}V \tag{1}$$

When the condition of constant pressure is applied so that the volume is no longer independent, this equation becomes

$$(\mathrm{d}E^*)_P = \left[\left(\frac{\partial E^*}{\partial T}\right)_V + \left(\frac{\partial E^*}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P\right](dT)_P \tag{2}$$

Similarly, the equation for S^* is

$$(\mathrm{d}S^*)_P = \left[\left(\frac{\partial S^*}{\partial T}\right)_V + \left(\frac{\partial S^*}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P\right](\mathrm{d}T)_P \tag{3}$$

The first term within the brackets of each equation is the differential change in E^* and S^*, respectively, for a unit differential change of the temperature at constant volume while the second term is the differential change in these functions for the differential change of the volume necessary to keep the pressure constant for the same change of temperature. These quantities have been evaluated by use of the familiar relations

$$\left(\frac{\partial E^*}{\partial T}\right)_V = C_V(\mathrm{l}) - C_V(\mathrm{g}) \tag{4}$$

$$\left(\frac{\partial S^*}{\partial T}\right)_V = \frac{C_V(\mathrm{l}) - C_V(\mathrm{g})}{T} \tag{5}$$

$$\left(\frac{\partial E^*}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P = \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right]\left(\frac{\partial V}{\partial T}\right)_P \tag{6}$$

and

$$\left(\frac{\partial S^*}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P = \left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_P - \frac{R}{T} \tag{7}$$

In equation 6, P is negligible in respect to $T(\partial P/\partial T)_V$ and has been omitted in the calculations. Then the only difference between eq. 4 and 5 is the factor $1/T$ and, between eq. 6 and 7, is the term R and the factor $1/T$. For purposes of calculation $(\partial P/\partial T)_V$ has been expressed as $-(\partial V/\partial T)_P/(\partial V/\partial P)_T$.

Table I gives the results of calculations for five non-polar substances and two polar ones. All values are molar quantities expressed in cal. per mole deg. except those in the last column. (This column will be discussed in a later section of this paper.) The states of the liquids are all at 25° and one atmosphere pressure, and those of the ideal gases are also at 25°; the arbitrary pressure of the ideal gas necessary to define the state for the entropy does not enter into the calculations. The first and second columns of numbers give the molar heat capacities at constant pressure of the liquid and the ideal gas, respectively. The third column gives the difference between the heat capacities at constant volume of the two phases. The fourth column gives $-T(\partial V/\partial T)_P{}^2/(\partial V/\partial P)_T$ for the liquid phase. For these calculations, the values of $(\partial V/\partial T)_P$ and the molar volumes of benzene, cyclohexane, carbon tetrachloride and 2,2,4-trimethylpentane (isoöctane) have been taken from the work of Wood and his co-workers,[2-4] for water from the equation of Tilton and Taylor,[5] and for methanol and heptane from the International Critical Tables.[6] The values of $(\partial V/\partial P)_T$ have been calculated by means of the Tait equation for benzene,[7] carbon tetrachloride,[8] and water.[8] Coefficients of the Tait equation were determined from compressibility data for cyclohexane,[9] methanol[10] and isoöctane.[11] The coefficient of compressibility of n-heptane was estimated from those given in the International Critical Tables.[12] A comparison of the third and fourth columns shows that the effect of the volume change is much greater than that of the temperature for the non-polar liquids while the opposite is true for water and methanol. Of course the assumptions made in this paper are not valid for these two substances. The results for the non-polar substances may be explained qualitatively in terms of a cell model. It may be assumed that, at constant volume, each molecule is confined in a cell of fixed volume determined by its nearest neighbors. The molecule is thus in an essentially constant potential field and an increase in temperature could have only a limited effect. However, on increasing the volume, the potential field within this cell would be changed, and if the molecule tended to be oriented in respect to its neighbors, this orientation could also be changed.

Table I

	$C_p(\mathrm{l})$	$\bar{C}_p(\mathrm{g})$	$\bar{C}_V(\mathrm{l}) - \bar{C}_V(\mathrm{g})$	$-T(\partial V/\partial T)_P{}^2/(\partial V/\partial P)_T$	$(\partial a/\partial T)_V$
Cyclohexane	37.4[a]	25.4[f]	4.7	9.3	510
Benzene	32.5[b]	19.5[f]	4.9	10.1	440
Carbon tetrachloride	31.5[c]	20.0[c]	3.4	10.1	330
n-Heptane	53.7[d]	40.8[f]	2.2	12.7	320
Methanol	19.5[c]	10.7[g]	7.2	3.6	290
Water	18.0[c]	8.0[f]	11.8	0.2	210
2,2,4-Trimethylpentane	56.2[e]	46.6[f]	1.0	10.6	170

[a] R. A. Ruehrwein and H. M. Huffman, This Journal, **65**, 1620 (1943). [b] G. D. Oliver, M. Eaton and H. M. Huffman, *ibid.*, **70**, 1502 (1948). [c] "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards, Washington, D. C., Circular 500. [d] N. S. Osborne and D. C. Ginnings, *J. Research Natl. Bur. Standards*, **39**, 453 (1947). [e] J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier Publishing Co., Inc., New York, N. Y., 1950. [f] "Selected Values of Properties of Hydrocarbons," National Bureau of Standards, Washington, D. C., Circular C461. [g] W. Weltner, Jr., and K. S. Pitzer, This Journal, **73**, 2606 (1951).

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(3) S. E. Wood and A. E. Austin, This Journal, **67**, 480 (1945).

(4) S. E. Wood and O. Sandus, *J. Phys. Chem.*, **60**, 801 (1956).

(5) L. W. Tilton and J. K. Taylor, *J. Research Natl. Bur. Standards*, **18**, 205 (1937).

(6) "International Critical Tables," Vol. III, McGraw-Hill Book Co., Inc., New York, N. Y., p. 27.

(7) R. E. Gibson and J. F. Kincaid, This Journal, **60**, 511 ((1938).

(8) R. E. Gibson and O. H. Loeffler, *ibid.*, **63**, 898 (1941).

(9) "Tables Annuelles de Constants et Donneés Numeriques," Vol. VI, p. 16 (1923-1924).

(10) Reference 6, p. 41.

(11) W. A. Felsing and G. M. Watson, This Journal, **65**, 780 (1943).

(12) Reference 6, p. 37.

Part II

Since the potential energy is so dependent upon the volume, an examination of this dependence is important, both for its own intrinsic value and for its possible application to solutions. For a van der Waals liquid, the potential energy for one mole is given as $a/\bar{V}^0$ where a is a constant. Past work has shown that this relation is not adequate. Moreover, for a van der Waals liquid, $(\partial E/\partial V)_T$ equals $\Delta E/V$, where ΔE is the energy of evaporation. For actual liquids, these quantities are not equal but, at least, are of the same order of magnitude for most non-polar liquids. In order to overcome these difficulties, the form $k/(\bar{V}^0)^n$ has been used by many authors.[13-16] In this relation k has been taken as a constant and n as independent of the volume. Under these circumstances n is the ratio of $(\partial E/\partial V)_T$ and $\Delta E/V$, and has values ranging from 0.33 for mercury to 1.09 for n-heptane.[13] Studies have been made of the dependence of $(\partial E/\partial V)_T$ and, hence, n on the temperature,[17,18] but little attention has been paid to their dependence on volume. The relation $k/(\bar{V}^0)^n$, appears to be adequate for small ranges of volume but cannot be adequate for large ranges, particularly down to small volumes where the effect of the repulsive forces becomes important, unless k or n or both are functions of the volume. This is so because this relation cannot give a minimum in the potential energy curve when both k and n are independent of the volume.

Further consideration of the dependence of the potential energy on the volume is certainly necessary, especially when large ranges of volume are considered. Some advance can be made by expressing the potential energy in terms of the integral of the product of the potential energy between pairs of molecules and the distribution function. Thus, the energy of one mole of a liquid may be expressed by the equation[19-21]

$$\bar{E} = \bar{E}_0 + a/\bar{V}^0 \tag{8}$$

where

$$a = \int \text{-----} \int \bar{\epsilon}\bar{g}d\tau \tag{9}$$

In these equations $\bar{E}_0$ is the energy of one mole of an ideal gas at the same temperature as the liquid and includes the translational, vibrational and rotational energies of the molecules; $\bar{V}^0$ is the molar volume of the liquid; $\bar{\epsilon}$ is the potential energy, including the contribution due to the repulsive forces as well as that due to the attractive forces, between two molecules averaged over the position and orientation of all the other molecules and is a function of the distance and angular coördinates necessary to give the position and orientation of one molecule of the pair relative to the other; $\bar{g}$ is the combined radial and orientational distribution function averaged over the position and orientation of all the other molecules; and $d\tau$ expresses the product of all the differentials of the necessary distance and angular coördinates. This equation will not be applicable to substances whose vibrational and internal rotational energies are different in the gas and liquid phases. If a were independent of the temperature and volume, eq. 8 would represent a van der Waals liquid. But from its definition, eq. 9, a cannot be constant and must be considered a function of both the volume and the temperature.

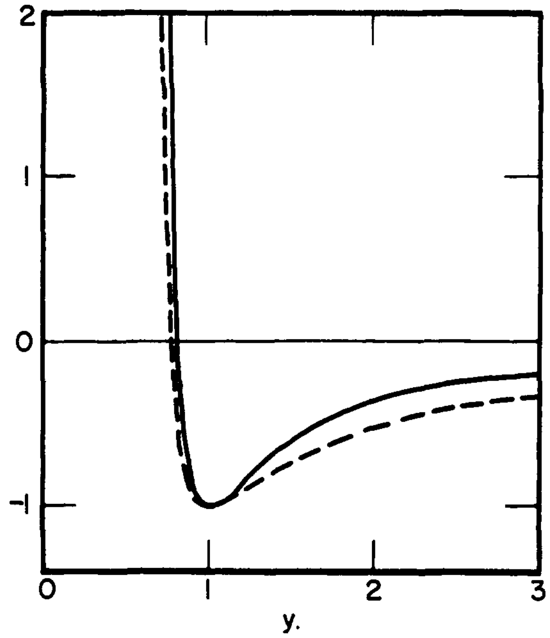

Fig. 1.—The potential energy as a function of the volume.

The Effect of Volume.—The differentiation of eq. 8 with respect to the volume at constant temperature gives

$$\left(\frac{\partial \bar{E}}{\partial \bar{V}^0}\right)_T = \frac{1}{\bar{V}^0}\left(\frac{\partial a}{\partial \bar{V}^0}\right)_T - \frac{a}{(\bar{V}^0)^2} \tag{10}$$

and substitution of eq. 8 into eq. 10 yields

$$\left(\frac{\partial \bar{E}}{\partial \bar{V}^0}\right)_T = \frac{\Delta \bar{E}}{\bar{V}^0} + \frac{1}{\bar{V}^0}\left(\frac{\partial a}{\partial \bar{V}^0}\right)_T \tag{11}$$

where $\Delta\bar{E} = \bar{E}_0 - \bar{E}$ and is the change of energy on going from one mole of liquid in a given state to one mole of an ideal gas at the same temperature. Thus, the difference of $(\partial\bar{E}/\partial\bar{V}^0)_T$ and $\Delta\bar{E}/\bar{V}^0$ depends upon the variation of a with volume. Buff and Brout have recently obtained an expression for this quantity in terms of radial distribution functions.[22]

Table II gives values of both $\bar{V}^0(\partial\bar{E}/\partial\bar{V}^0)_T$ and $\Delta\bar{E}$ and their difference, $(\partial a/\partial\bar{V}^0)_T$, for some representative liquids. The values of $(\partial\bar{E}/\partial\bar{V}^0)_T$ for bromobenzene, chlorobenzene and water have been calculated at 25° and one atmosphere pressure by means of the Tait equation and the data of Gibson and Loeffler.[8,23] Vapor pressure data and

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(13) J. H. Hildebrand and R. L. Scott, "The Solubility of Nonelectrolytes," Reinhold Publ. Corp., New York, N. Y., 1950, pp. 94–101.

(14) H. S. Frank, *J. Chem. Phys.*, **11**, 493 (1945).

(15) S. W. Benson, *ibid.*, **15**, 367 (1947).

(16) R. Dunlap, *ibid.*, **21**, 1293 (1953).

(17) H. Benninga and R. L. Scott, *ibid.*, **23**, 1911 (1955).

(18) L. A. K. Staveley, W. I. Tupman and K. R. Hart, *Trans. Faraday Soc.*, **51**, 323 (1955).

(19) (a) G. Scatchard, *Chem. Revs.*, **8**, 321 (1931); (b) *Trans. Faraday Soc.*, **33**, 160 (1937).

(20) J. H. Hildebrand and S. E. Wood, *J. Chem. Phys.*, **1**, 817 (1933).

(21) (a) J. G. Kirkwood, *ibid.*, **3**, 300 (1935); (b) J. G. Kirkwood, E. K. Maun and B. J. Alder, *ibid.*, **18**, 1040 (1950).

(22) F. P. Buff and R. Brout, *ibid.*, **23**, 458 (1955).

(23) R. E. Gibson and O. H. Loeffler, *ibid.*, **43**, 207 (1939).

Table II

Values of $\bar{V}^0(\partial\bar{E}/\partial\bar{V}^0)_T$, $\Delta\bar{E}$, and $(\partial a/\partial\bar{V}^0)$ in Cal. per Mole

Substance	$\bar{V}^0(\partial\bar{E}/\partial\bar{V}^0)_T$	$\Delta\bar{E}$	$(\partial a/\partial\bar{V}^0)_T$
n-Heptane	8,900	8,140	760
Silicon tetrachloride	7,140	6,560	580
Carbon tetrachloride	7,790	7,250	540
Benzene	7,920	7,500	420
Silicon tetrabromide	10,200	9,800	400
Tin tetrachloride	9,310	8,970	340
Bromobenzene	10,210	9,970	240
Chlorobenzene	9,400	9,200	200
Titanium tetrachloride	9,190	9,030	160
Chloroform	7,140	7,030	110
Ethyl ether	6,300	6,210	90
Carbon disulfide	5,390	6,050	−660
Acetone	5,850	6,570	−720
Methanol	2,840	8,140	− 5,640
Mercury	4,660	14,250	− 9,590
Water	720	11,390	−10,670

densities given in the International Critical Tables have been used to calculate $\Delta\bar{E}$ for these same substances. The Berthelot equation was used to correct for gas imperfections. The values for all the other compounds have been taken from Hildebrand and Scott.[13]

The outstanding feature of the values of $(\partial a/\partial\bar{V}^0)_T$ is the extremely wide range. The application of the equation to water and methanol is not strictly valid. Still, the omission of these two substances would make little difference in the over-all range of values.

Further progress can be made by considering the curve of $(\partial\bar{E}/\partial\bar{V}^0)_T$ as a function of volume and comparing the relative position of the observed values of $(\partial\bar{E}/\partial\bar{V}^0)_T$ for various substances on this curve with the values of $(\partial a/\partial\bar{V}^0)_T$.[24] Figure 2 shows a generalized curve of $(\partial\bar{E}/\partial\bar{V}^0)_T$ as a function of the volume; the coördinates will be discussed later. The observed values of $(\partial\bar{E}/\partial\bar{V}^0)_T$ for *n*-heptane, benzene and carbon tetrachloride lie to the right of the maximum and their values of $(\partial a/\partial\bar{V}^0)_T$ are relatively large and positive. The observed values of $(\partial\bar{E}/\partial\bar{V}^0)_T$ of ethyl ether and carbon disulfide lie on or near and also to the left of the maximum and the value of $(\partial a/\partial\bar{V}^0)_T$ for ethyl ether is small and positive, and for carbon disulfide it is negative. For mercury the values of $(\partial\bar{E}/\partial\bar{V}^0)_T$ lie on the very steep portion of the curve to the left of the maximum and its value of $(\partial a/\partial\bar{V}^0)_T$ is large and negative. It, therefore, seems that for liquids which are sufficiently compressed the value of $(\partial a/\partial\bar{V}^0)_T$ is negative, and that for liquids which are sufficiently expanded the value of $(\partial a/\partial\bar{V}^0)_T$ is positive.

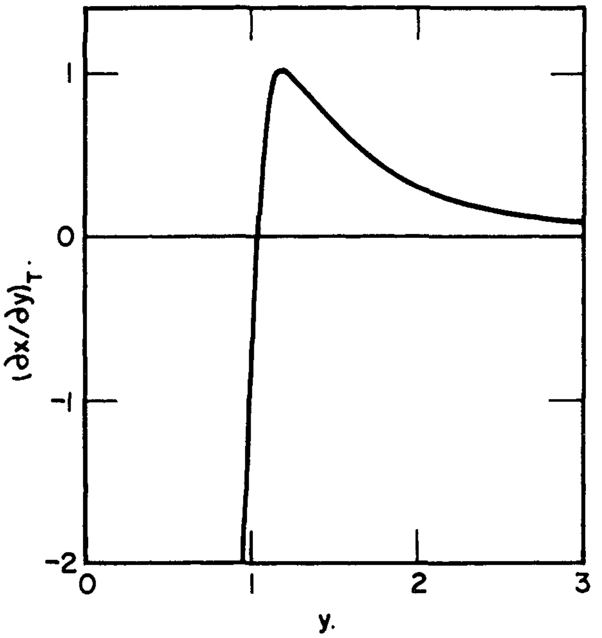

Fig. 2.—The change of energy with volume as a function of the volume.

The law of corresponding states has been applied to liquids by Pitzer[25] and Guggenheim[26] and according to this law, a would be the same function of the volume for all liquids. Therefore, the assumption is made here that, for all liquids to which eq. 8 and 9 are applicable, $(\partial a/\partial\bar{V}^0)_T$ shall be negative for sufficiently small volumes and its value shall increase, pass through zero, and become positive as the volume is increased at constant temperature. An unequivocal expression of a as a function of the volume cannot be given at the present time, but it is certainly possible to gain some concept of this function. A term arising from the repulsive forces must be included as well as a term related to the attractive forces. As a first attempt, the repulsive term may be assumed to be proportional to some inverse power of the volume and the attractive term may be represented by a constant similar to a van der Waals liquid, so that $a = [C_1/(\bar{V}^0)^p] - C_2$. However, with this equation, $(\partial a/\partial V)_T$ is always negative. Another term must be added which will give positive values to $(\partial a/\partial V)_T$ at large volumes. Then a may be written to a simple approximation as

$$a = [C_1/(\bar{V}^0)^p] - C_2 - C_3/\bar{V}^0 \qquad (12)$$

The coefficients C_1, C_2, and C_3 are functions of the temperature, but at constant temperature are characteristic of each substance.

It is advantageous to convert this equation to dimensionless variables in order to obtain the desired concept of the dependence of a on the volume without evaluating the coefficients. Three properties of the curve of $\bar{E} - \bar{E}_0$ as a function of $\bar{V}^0$ (Fig. 1) have been used to make this conversion. These are the energy at the minimum of the curve, $\bar{E}_m$, the molar volume at the minimum, $\bar{V}^0_m$, and the molar volume at the point of inflection, $\bar{V}^*$. The three equations used then are eq. 8 at the minimum and the two equations (1) $(\partial\bar{E}/\partial\bar{V}^0)_T = 0$ at the minimum and (2) $(\partial^2\bar{E}/\partial\bar{V}^{02})_T = 0$ at the point of inflection. The results can be expressed in terms of dimensionless variables defined as $x = (\bar{E} - \bar{E}_0)/(\bar{E}_0 - \bar{E}_m)$, $y = \bar{V}^0/\bar{V}^0_m$, and $z = \bar{V}^*/\bar{V}^0_m$. With these substitutions

$$x = \frac{1}{y}\left(\frac{\alpha}{y^p} - \beta - \frac{\gamma}{y}\right) \qquad (13)$$

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(24) For details, see ref. 13, p. 100.

(25) K. S. Pitzer, *J. Chem. Phys.*, **7**, 583 (1939).

(26) E. A. Guggenheim, *ibid.*, **13**, 253 (1945).

where

$$\alpha = \frac{z^{p-1}(1 - 2z/3)}{pz^{p-1} - (p - 1)z^p/3 - (p + 1)(p + 2)/6} \quad (14)$$

$$\beta = \frac{(p + 1)z^{p-1}\,[1 - (p + 2)/3z^{p-1}]}{pz^{p-1} - (p - 1)z^p/3 - (p + 1)(p + 2)/6} \quad (15)$$

$$\gamma = \frac{(p + 1)(p + 2)/6 - (p + 1)z^p/3}{pz^{p-1} - (p - 1)z^p/3 - (p + 1)(p + 2)/6} \quad (16)$$

For illustrative calculations, p has been chosen as 9. The point of inflection where C_3 equals zero then occurs at z equal to 1.21. When eq. 12 is used, z can have values only between 1.18 and 1.21, in order to keep α, β and γ or C_1, C_2, and C_3 positive as originally defined. The effect of the third constant is then to steepen the walls of the minimum of the potential energy. This effect is consistent with the work of Pitzer[27] in which he finds that a third parameter, which steepens the potential well, is necessary to express the intermolecular potentials of molecules. Equation 13 is illustrated in Fig. 1 by the solid curve for which z is equal to 1.18. The dotted curve is the equivalent curve where C_3 equals zero. Figure 2 illustrates $(\partial x/\partial y)_T$ which is proportional to $(\partial \bar{E}/\partial \bar{V}^0)_T$, Fig. 3 gives xy which is proportional to a, and Fig. 4 illustrates $(\partial xy/\partial y)_T$ which is proportional to $(\partial a/\partial \bar{V}^0)_T$. For these illustrations, eq. 13 has again been used with z taken as 1.18.

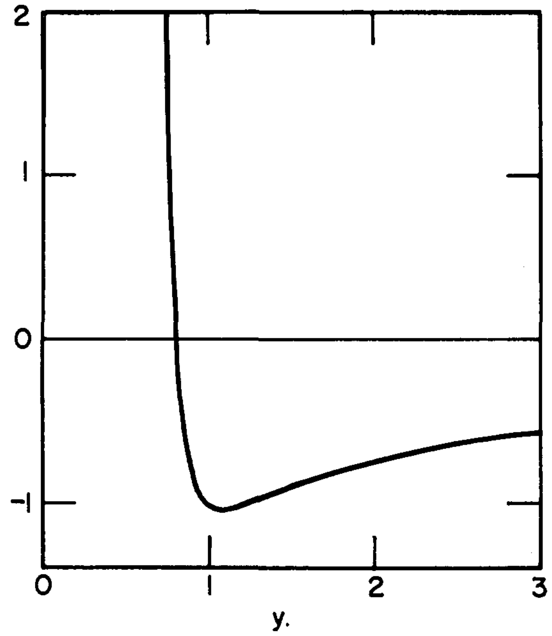

Fig. 3.—The quantity a as a function of the volume.

Very similar results are obtained when an exponential term of the form $C_1e^{l(\bar{V}^0{}_m - \bar{V}^0)/\bar{V}^0{}_m}$ is used for the repulsive term instead of the inverse power. When l is taken as 8, the point of inflection of the two constant equation ($C_3 = 0$) occurs at z equal to 1.24. For the three constant equation z can have values only between 1.20 and 1.24. Again z is limited to a very narrow range of values and the effect of the third constant is to steepen the walls of the potential well.

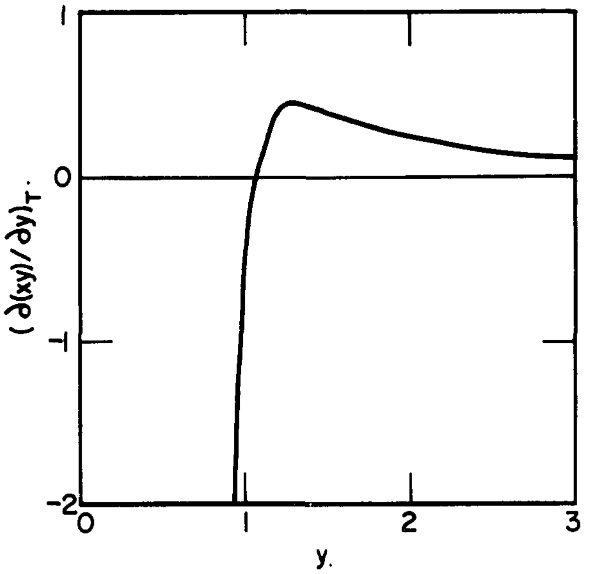

Fig. 4.—The change of a with volume as a function of the volume.

An expression alternative to eq. 12

$$\bar{E} = \bar{E}_0 + [C_1/(\bar{V}^0)^l] - [C_2/(\bar{V}^0)^m] \quad (17)$$

might have been used. This equation is similar to that used by Hildebrand,[28] in which l and m were given the values of 9 and 1, respectively. However, in order to obtain positive values of $(\partial a/\partial V)_T$ at large volumes, m must be greater than 1. When m is given values greater than 1, the corresponding curves of x, xy, $(\partial x/\partial y)_T$, and $(\partial xy/\partial y)_T$ have the same general form as given in the four figures. The point of inflection depends upon the values of l and m. One difference between these equations is that according to eq. 12 a approaches a negative value as the volume approaches infinity in agreement with the behavior of a real gas below its inversion temperature, while, according to eq. 17 a approaches zero. If the relation, $\bar{E} = \bar{E}_0 + k/(\bar{V}^0)^n$, is compared to eq. 17, it is found that both k and n must be functions of the volume. Further, n depends upon the values of l and m is such a way that n must be less than m and approaches m only as the volume approaches infinity. Thus, n includes the effect of the repulsive forces as well as that of the attractive forces. Only further experimental studies of the P-V-T properties of liquids can give a final answer to the question of the variation of a with volume.

The Effect of Temperature.—The dependence of a on the temperature can be determined by differentiation of eq. 8 with respect to temperature at constant volume, giving

$$\bar{C}_V = \bar{C}^0{}_V + \frac{1}{\bar{V}^0}\left(\frac{\partial a}{\partial T}\right)_V \quad (18)$$

The last column of Table I gives $(\partial a/\partial T)_V$ in units of ml. cal. per deg. for the substances listed there. Certainly a is a function of the temperature. The rather small range of the values of $(\partial a/\partial T)_V$ in contrast to the larger range of values of $(\partial a/\partial V)_T$

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(27) K. S. Pitzer, THIS JOURNAL, **77**, 3428 (1955).

(28) J. H. Hildebrand, *Phys. Revs.*, **34**, 984 (1929); see also ref. 13, p. 99, Fig. 8.

is rather surprising. While the basic equation, in its interpretation of potential energy, is not strictly applicable to water and methanol, these substances do not show any marked departure from the other substances.

The Entropy.—Since $(\partial S/\partial T)_V = C_V/T$, it is possible to obtain a formal expression for the entropy of a liquid. The integration of eq. 18 yields

$$\bar{S} = \bar{S}^0 + \frac{1}{\bar{V}^0}\int\frac{1}{T}\left(\frac{\partial a}{\partial T}\right)_V \mathrm{d}T + s(V,n) \qquad (19)$$

Here $\bar{S}^0$ is the entropy due to the translational, vibrational and rotational modes of motion in the ideal gas but does not contain any term involving the concentration. The term $s(V,n)$ is the integration constant and is a function of the volume and the number of moles. Throughout this paper the partition function for the liquid has been considered to be the product of independent partition functions for translational, vibrational, and rotational motion, and for the potential energy. The last two terms of eq. 19 then result from the partition function for the potential energy. Following the suggestion of Eyring and Hirschfelder[29] for this partition function, the integration constant may be written as $-R\ln(n/\mathcal{V})$, so that

$$\bar{S} = \bar{S}^0 + \frac{1}{\bar{V}^0}\int\frac{1}{T}\left(\frac{\partial a}{\partial T}\right)_V \mathrm{d}T - R\ln\frac{n}{\mathcal{V}} \qquad (20)$$

Here $\mathcal{V}$ is a volume which might be called a free volume defined by this equation.

Equation 20 can only be considered as a formal, semi-empirical equation at the present time and the same information would be required for further study as for the energy. Obviously, it means that the coefficients of the separate terms of eq. 12 or 17 are functions of the temperature. It does afford an opportunity, however, of estimating the entropy of mixing for solutions as will be shown in the following paper.

[29] H. Eyring and J. Hirschfelder, *J. Phys. Chem.*, **41**, 249 (1937).

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The Estimation of the Properties of Solutions from Those of the Pure Components[1,2]

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Expressions for the change of the energy and of the entropy on mixing have been developed by a method similar to that of Hildebrand and Scatchard. In this development the interaction parameter a, defined by the equation $\bar{E} = \bar{E}_0 + (a/\bar{V})$, is taken to be a function of the volume and the temperature. The volume is taken as one of the independent variables rather than the pressure, thereby permitting calculations for any chosen change of state, the two most important cases being mixing at constant volume and mixing at constant pressure. It is necessary to assume that the a's are independent of the composition and that a_{12} is determinable from a_{11} and a_{22}. The geometrical mean is used in this paper. Other methods are suggested, but they require more information than is available at the present time. Calculations have been made for the three binary systems composed of benzene, carbon tetrachloride and cyclohexane. The calculations for the energy of mixing show improvement over the Hildebrand–Scatchard equation, although the agreement with the observed values is still not good. Except for the benzene–carbon tetrachloride system, the excess entropy of mixing is positive but smaller than the observed values. The agreement of the excess free energy, while not exact, is surprisingly good because of a cancellation of errors.

The Hildebrand–Scatchard equation[3,4] has attained great prominence for the estimation of the properties of solutions from those of the pure components, but it does have a few outstanding difficulties. The entropy of mixing at constant volume must be assumed to be that of an ideal solution of the same concentration or use must be made of the Flory–Huggins theory expressing the entropy in terms of the volume fraction rather than the mole fraction. Also, the energy of mixing at constant volume is usually much smaller than the observed value. Great progress has been made in the theoretical treatment of solutions by Guggenheim,[5] Kirkwood,[6] Prigogine[7] and many others. Since a complete, theoretical treatment of the problem is so difficult, a method of estimating the properties of solutions from those of the pure components is still important. This paper presents such a method, very similar to that of Hildebrand and Scatchard, but which appears to be a considerable improvement. The estimates of the energy of mixing at constant volume and the heat of mixing at constant pressure are in closer agreement with the observed values. An estimate of the entropy of mixing both at constant volume and at constant pressure is obtained, but with only fair agreement with the observed values. The free energies of mixing at constant pressure are in rather surprising agreement with the observed values for the systems studied. The method is strictly applicable only to non-polar liquids.

The Energy of Mixing.—As in the preceding paper,[8] the energy of n moles of a pure liquid at a given volume and temperature may be expressed as

$$E_i^0 = n_i\bar{E}_{0i} + \frac{n_i^2 a_{ii}'}{V^0_i} \qquad (1)$$

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[2] Presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society at the Dallas meeting, April, 1956.

[3] G. Scatchard, *Chem. Revs.*, **8**, 321 (1931).

[4] J. H. Hildebrand and S. E. Wood, *J. Chem. Phys.*, **1**, 817 (1933).

[5] E. A. Guggenheim, "Mixtures," Oxford University Press, London, 1952.

[6] J. G. Kirkwood and F. P. Buff, *J. Chem. Phys.*, **19**, 774 (1951); Z. W. Salsburg and J. G. Kirkwood, *ibid.*, **20**, 1538 (1952).

[7] I. Prigogine and G. Garikian, *Physica*, **16**, 239 (1950).

[8] S. E. Wood, O. Sandus and S. Weissman, THIS JOURNAL, **79**, 1777 (1957).