ethylene glycols from monoethylene to heptaethylene glycol and of seven of their derivatives have been measured over a range of approximately 100°. The series constant of 72 ± 1 erg for the total surface energy is attained at triethylene glycol. This series constant closely approaches the value for the total surface energy of ethylene oxide, namely, 73.2 ergs.

A continuous increase in the value of the Ramsay and Shields constant is exhibited as the polyethylene glycol series is ascended. A similar increase in the positive direction for the percentage difference of the calculated and observed values of the parachor is noted. Some phenomenon presumably is taking place in the liquid surface of the polyethylene glycols which affects the surface in an abnormal manner, possibly the result of partial orientation of the surface molecules.

The algebraic difference between the calculated and observed values of the parachor is negative in ethylene and diethylene glycols, becoming continuously positive in triethylene and the higher polyethylene glycols. This suggests that a definite relation exists between the valence forces in operation, and each addition of an ethylene oxide group to the polyethylene glycol molecules. The positive anomalies are unusual and cannot be accounted for on the basis of Sugden's interpretation of the parachor and its relation to valence forces. A possible explanation of the association of the polyethylene glycol molecules arising through coördination, or other intermolecular attractive forces of the ethylene oxide groups, is advanced to account for the positive anomalies.

Attention is drawn to the fact that the parachor anomalies for the fatty acids show a behavior identical with that for the polyethylene glycols.

The molecular volumes of the polyethylene glycols exhibit large negative anomalies between the calculated and observed values. Evidence is obtained which possibly supports a zig-zag structure for the ethylene oxide chain in the polyethylene glycol molecules, the ether oxygen angle in the chain being similar to that present in the ethylene oxide molecule.

MONTREAL, CANADA RECEIVED OCTOBER 11, 1937

[CONTRIBUTION FROM THE DIVISION OF INDUSTRIAL AND CELLULOSE CHEMISTRY, MCGILL UNIVERSITY]

Studies on Reactions Relating to Carbohydrates and Polysaccharides. LV. Vapor Pressures of the Polyethylene Glycols and their Derivatives[1]

BY A. F. GALLAUGHER AND HAROLD HIBBERT

In the preceding papers of this series[2,3] surface tension and other measurements on polyethylene glycols and their derivatives were considered in relation to the question of molecular association. The present study continues the investigation to cover the vapor pressures of these substances.[4]

Measurement of the Vapor Pressure.[5]—The apparatus used in the measurement of the vapor pressure is shown in Fig. 1 and is a modified form of that devised by Sutherland and Maass.[5]

A and B are safety bulbs, introduced to minimize possible errors in the manometer readings due to leaks in the stopcocks. C represents a manometer of 20-mm. diameter tubing, the scale used being found correct to 0.1 mm. It was read by means of a hand-lens to 0.2 mm.

The constant temperature bath J is identical with that previously described.[3] I is a differential manometer and E the bulb containing the liquid of which the vapor pressure is to be determined. This is fitted with a magnetic stirrer operated by the coil G, housed in the glass container as shown and actuated by a metronome. The system may be evacuated at N and air admitted through the stopcocks M and K and the reservoir L.

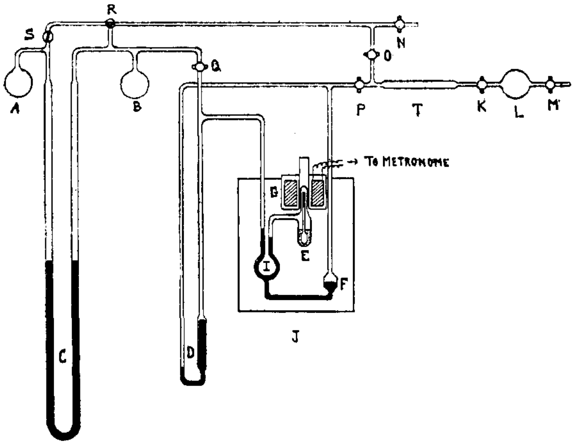

Fig. 1.—Apparatus.

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[1] Contribution from a thesis presented by A. F. Gallaugher to the Faculty of Graduate Studies, McGill University, in May, 1932, in partial fulfilment of the requirements for the Degree of Doctor of Philosophy. Original manuscript received March 9, 1936.

[2] Gallaugher and Hibbert, THIS JOURNAL, **58**, 813 (1936).

[3] Gallaugher and Hibbert, *ibid.*, **59**, 2514 (1937).

[4] The preparation and purification of the materials used have been described previously.[3]

[5] Sutherland and Maass, *Trans. Roy. Soc. Can.*, **20**, 499 (1926).

The actual procedure was as follows: the cell E was partly filled with the required liquid and then sealed off at the top. The bulb F was next filled with mercury and the system IEF sealed on to the rest of the apparatus as shown in Fig. 1. The stopcocks S, R, Q, P, O and N were then opened and the whole apparatus evacuated at N. When the evacuation was complete, stopcocks S, Q and N were closed, and air, dried by the phosphorus pentoxide tube T, was admitted to F through the stopcock P, the mercury rising in both arms of the differential manometer I. In order to maintain zero vapor pressure in the case of the more volatile derivatives of the polyethylene glycols such as ethylene dichloride and 1,4-dioxane, the bulb E was surrounded with a freezing mixture during evaporation. The vapor pressure of the polyethylene glycols is almost zero at room temperature, but it was found necessary to remove completely any dissolved air prior to admitting air to the arms of the differential manometer I. This was accomplished by vigorous stirring of the compounds, their temperature being increased simultaneously to 40–80°, depending upon the relative volatility of the liquid under investigation. At this point, air was admitted to F and the temperature of the bath was then raised, the liquid in the bulb E being well stirred throughout. In order to maintain the mercury at the same level in both arms of the differential manometer, the pressure of the vapor in E was compensated by closing P and admitting air through O, this being controlled by the trap D which contained mercury in such quantity that the pressure difference between the two sides could not exceed that required to keep the mercury at about the middle of the two arms of the differential manometer. When the levels in the latter were the same, the vapor pressure of the liquid in E was equal to that of the air as given by the manometer C, and the temperature was read from a thermometer[6] suspended near E in the bath.

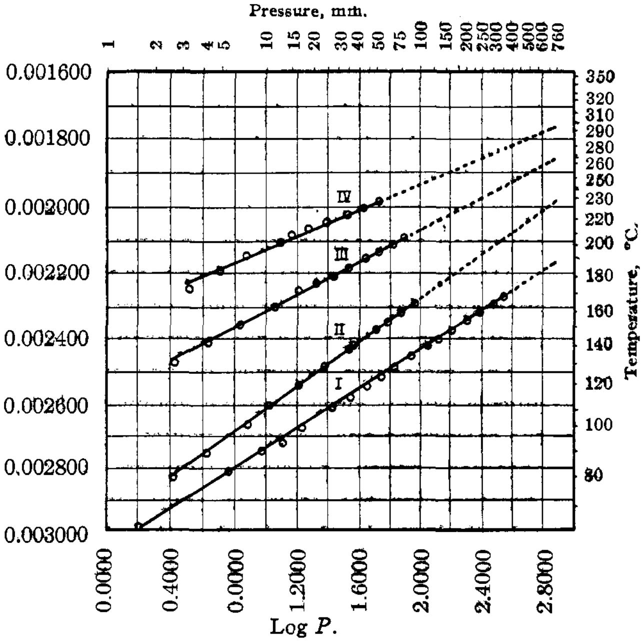

Fig. 2.—I, ethylene glycol; II, diethylene glycol; III, triethylene glycol; IV, tetraethylene glycol.

In this manner the vapor pressures were determined at intervals of 5 or 10°. Where the compounds did not decompose, the observed values for the vapor pressure were checked with both ascending and descending temperatures. The vapor pressures of those compounds undergoing decomposition were determined, up to the initial temperature of decomposition, from observations on at least three different samples of the same liquid.

The initial decomposition temperature was obtained by observing the temperature at which the vapor pressure no longer remained constant but increased with time, the rate of increase being measured by recording the observed pressures at intervals of five minutes for half an hour. The initial decomposition temperature and the rate of decomposition were checked carefully in each case in the course of the subsequent vapor pressure measurements on other samples of the same liquid. In the latter instances, the temperature of the bath was raised slowly and maintained constant for five minutes at 5° intervals in the neighborhood of the previously established decomposition temperature, in order to detect any possible decomposition below the latter.

The observed vapor pressures were corrected to 0° and allowance made for the vapor pressure of the mercury in the right arm of the differential manometer. The necessary corrections were applied for the portion of the thermometer thread not immersed in the bath liquid.

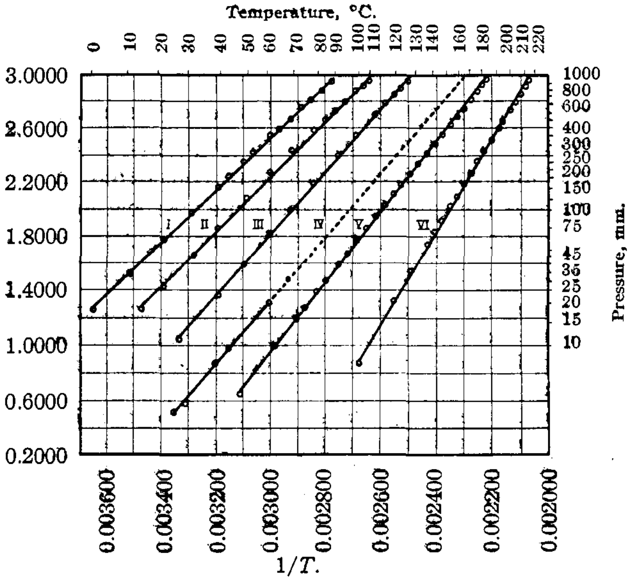

Fig. 3.—I, ethylene dichloride; II, 1,4-dioxane; III, ethylene glycol monomethyl ether; IV, ethylene glycol dimethyl ether; V, β,β'-dichloroethyl ether; VI, trimethylene glycol.

The results of plotting $1/T$ against $\log_{10} P$ for the polyethylene glycols and their derivatives are

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(6) Calibrated at the Reichsanstalt, Germany.

TABLE I

Compound	Equation connecting vapor pressure with temperature
Ethylene glycol	$\log_{10} P = -2976.6/T + 9.2087$
Diethylene glycol	$\log_{10} P = -2727.3/T + 8.1527$
Triethylene glycol	$\log_{10} P = -3726.2/T + 9.6396$
Tetraethylene glycol	$\log_{10} P = -4649.4/T + 10.886$
Trimethylene glycol	$\log_{10} P = -3018.8/T + 9.0767$
Ethylene glycol monomethyl ether	$\log_{10} P = -2157\ /T + 8.3077$
Ethylene dichloride	$\log_{10} P = -1769.4/T + 7.8462$
1,4-Dioxane	$\log_{10} P = -1866.7/T + 7.8642$
β,β'-Dichloroethyl ether	$\log_{10} P = -2359.6/T + 8.1040$
Diethylene glycol dimethyl ether	$\log_{10} P = -2251.5/T + 8.0837$
Tetraethylene glycol monochlorohydrin	$\log_{10} P = -3576.0/T + 9.3293$

T is temperature in °A. P is pressure in mm.

shown in Figs. 2 and 3, respectively. In these the data were plotted on a large scale. As may be seen, no difficulty was encountered in drawing a smooth curve through the experimental points. The dotted lines indicate the extrapolated vapor pressures of those compounds which underwent decomposition.

The vapor pressures of the penta-, hexa-, and hepta-ethylene glycols were not measured because of experimental difficulties involved in obtaining a constant temperature bath which would function efficiently at temperatures from 230 to 350°.

The vapor pressure curve of tetraethylene glycol monochlorohydrin is not represented in Fig. 3 since, due to its low decomposition temperature, only three readings could be obtained.

The particular equation connecting vapor pressure with temperature (derived by substituting the calculated constants in the integrated Clausius–Clapeyron equation) is given in Table I.

Table II contains a summary of the vapor pressure data. The boiling points were obtained from the integrated Clausius–Clapeyron equation by substituting the calculated constants, the latent heats of evaporation being calculated by similarly substituting the coördinates of two points on the vapor pressure–temperature curve. Trouton's constant follows at once from the relation ML/T.

The values of T_1 and T_2 and the ratio T_1/T_2, where T_1 and T_2 are the temperatures at vapor pressures of 76 and 20 cm., respectively, have been interpolated from the vapor pressure–temperature curves.

TABLE II

SUMMARY OF THE VAPOR PRESSURE DATA

Compound	B. p. calcd., °C.	M. L., calcd.	L., calcd.	Trouton's constant	T_1, °A.	T_2, °A.	T_1/T_2
Ethylene glycol	197.40	13633	219.7	28.98	470.6	430.8	1.092
Diethylene glycol	244.33	12491	117.8	24.14	517.2	466.0	1.110
Triethylene glycol	278.31	17066	113.7	30.95	551.6	507.7	1.086
Tetraethylene glycol	307.8	21294	109.7	36.66	580.7	540.4	1.075
Trimethylene glycol	214.22	13826	181.8	28.37	487.2	445.4	1.094
Tetraethylene glycol monochlorohydrin	281.54	16378	77.0	29.53	554.3	508.0	1.091
Ethylene glycol monomethyl ether	124.43	9879	129.9	24.86	397.5	359.0	1.107
Diethylene glycol dimethyl ether	159.76	10312	76.9	23.83	432.8	389.2	1.112
Ethylene dichloride	83.24	8104	81.9	22.74	356.5	318.8	1.118
β,β'-Dichloroethyl ether	178.75	10807	75.6	23.92	451.8	406.3	1.112
Ethylene oxide[7]	10.73	6000	136.3	21.14	283.7	253.5	1.119
1,4-Dioxane	101.58	8550	97.1	21.90	374.6	335.4	1.117

M. L., the molecular heat of evaporation. L., the latent heat of evaporation per gram. T_1 and T_2 are the temperatures at vapor pressures of 76 and 20 cm.

TABLE III

THE RATIO T_{BP}/T_C[8]

Compound	T_C, °A.	T_{BP}, °A.	T_{BP}/T_C
Ethylene dichloride	579.3	356.2	0.62
1,4-Dioxane	585.0	374.6	.64
Ethylene oxide[9]	465.0	283.7	.61

T_C is the critical temperature in °A. T_{BP} is the calculated boiling point in °A.

Table III contains the boiling points and critical temperatures in absolute degrees, and the value of the ratio T_{BP}/T_C where T_{BP} is the calculated boiling point and T_C is the critical temperature, both in absolute degrees. The latter were calculated from the surface tension equation

$$\gamma(M/d)^{2/3} = K(T_C - T - 6)$$

These data are listed for ethylene dichloride and 1,4-dioxane only, since with the other compounds the value of the Ramsay and Shields constant was found to be a function of the temperature.[3]

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[7] The values given for ethylene oxide were taken or calculated from the data of Maass and Boomer [THIS JOURNAL, 44, 1709 (1922)] and have been inserted in this table for purposes of comparison.

[8] Calculated from the Ramsay and Shields equation.

[9] See note (7) under Table II.

TABLE IV

THERMAL DECOMPOSITION DATA

Compound	Temperature of initial decomposition, °C.	Rate of decomposition, mm. change of press./minute at initial decomp. temp.
Ethylene glycol	164.9	1.30
Diethylene glycol	164.5	0.30
Triethylene glycol	206.5	.38
Tetraethylene glycol	237.9	.89
Tetraethylene glycol monochlorohydrin	139.6	.09
Diethylene glycol dimethyl ether	60.0	.22

Table IV contains the initial decomposition temperature, together with the rate of decomposition at this temperature, of the polyethylene glycols and their less stable derivatives.

Discussion of Results

From the vapor pressure measurements on the polyethylene glycols and their derivatives, the following characteristic constants have been derived:

1. **The Boiling Point T_{BP} and the Ratio of the Boiling Point to the Critical Temperature T_{BP}/T_C.**—It may be noted that in the polyethylene glycols the boiling point increment decreases continuously in ascending the series. The low boiling points of ethylene dichloride, 1,4-dioxane and ethylene oxide indicate an absence of association of the molecules in the interior of the liquid.

It was not possible to determine the critical temperature of the polyethylene glycols and their derivatives which undergo decomposition, but an attempt was made to calculate their critical temperatures from the surface tension equation

$$\gamma(M/d)^{2/3} \doteq K(T_C - T - 6)$$

Inasmuch as the value of K has been shown to be a function of the temperature for all the compounds in question, with the exception of ethylene dichloride, ethylene oxide and 1,4-dioxane, the application of this equation leads only to absurd results in the other cases. The values of the ratio T_{BP}/T_C found with 1,4-dioxane (0.64), ethylene dichloride (0.62) and ethylene oxide (0.61) lie very close to the mean found in normal liquids and indicate that these may be regarded as such.

2. **The Ratio T_1/T_2.**—According to Ramsay and Young's rule, the ratio of the boiling points for any two substances in the vertical columns under T_1 and T_2 in Table II must be equal, so that the quotient T_1/T_2 should be a constant in all cases. Deviations from this law imply nonobedience to the law of corresponding states.

In the polyethylene glycols examined, the ratio T_1/T_2 is low (1.075–1.092) except in the case of diethylene glycol where it has the more normal value of 1.110. If these deviations are sufficiently large, they may mean that the tendency to association is less in the case of diethylene glycol than in the other glycols, a fact in accordance with the spatial structure postulated above for the former in the previous paper.[2]

3. **The Molecular Latent Heat of Evaporation.**—With the exception of diethylene glycol the molecular latent heat of evaporation of the polyethylene glycols increases as expected with each addition of an ethylene oxide group. The anomalous value of 12,491 calories found with diethylene glycol, as compared with 13,633 calories for ethylene glycol may be explained by the structure assumed for the former in the previous paper.[2] The consequent intramolecular neutralization of the polar forces of the hydroxyl groups in the diethylene glycol molecule would involve a lower degree of association than is the case with ethylene glycol.

The molecular latent heats of ethylene glycol (13,633 cal.) and its monomethyl ether (9879 cal.) indicate the influence on volatility of substitution by a methoxyl group. However, with diethylene glycol (12,491 cal.) and its dimethyl ether (10,312 cal.), the expected increase in volatility is not observed, due no doubt as before to the anomalous structure of diethylene glycol.

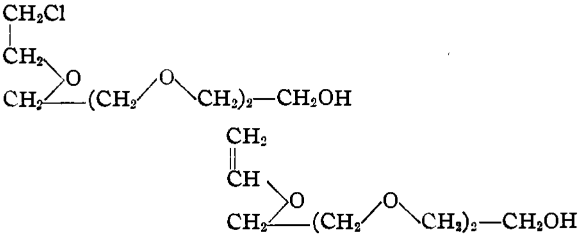
4. **Trouton's Constant.**—Again with the exception of diethylene glycol, the values for Trouton's constant exhibit a constant increase with each addition of an ethylene oxide grouping. If Trouton's constant may be regarded as an indication of the degree of association, then diethylene glycol is less associated than ethylene glycol, these compounds having values for this constant of 24.14 and 28.98, respectively.

5. **The Thermal Decomposition of the Polyethylene Glycols and their Derivatives.**—The data show that all the polyethylene glycols decompose when heated at relatively low temperatures yielding volatile decomposition products. The latter possess a sweet odor, and the residual product is colorless.

Diethylene, triethylene and tetraethylene glycols decompose at equal temperature intervals apart, indicating that the decomposition is a function of the length of the ethylene oxide chain.

Tetraethylene glycol monochlorohydrin and diethylene glycol dimethyl ether were the only two derivatives of the polyethylene glycols investigated in which decomposition on heating below the boiling point was noted.

The low decomposition temperature of tetraethylene glycol monochlorohydrin (140°) as compared with that of the corresponding tetraethylene glycol (238°) can only be ascribed to the substitution of the chlorine atom for the hydroxyl group. The decomposition may involve the removal of hydrochloric acid from a molecule with the formation of a vinyl derivative thus



although in this event it is difficult to understand why dichloroethyl ether does not show a similar ease of decomposition.

The decomposition temperature of 60° for diethylene glycol dimethyl ether is low compared with that of the corresponding diethylene glycol (165°). The instability of the former substance is remarkable when compared with the stability of β,β'-dichloroethyl ether.

Acknowledgment.—The writers wish to acknowledge the kind assistance of Dr. O. Maass in the designing of the apparatus used in the vapor pressure measurements and in the interpretation of the experimental results. They also desire to thank the National Research Council of Canada for the award of a Bursary to one of them (A. F. G.).

Summary

The vapor pressures of mono-, di-, tri-, tetraethylene glycols and certain derivatives have been measured.

Certain of these substances show negative deviations from the ratio T_1/T_2 expected according to the Ramsay and Young rule, indicating deviations from the law of corresponding states.

The molecular latent heat and the value for Trouton's constant increase on ascending the glycol series, abnormal values being found with diethylene glycol. Replacement of hydroxyl by methoxyl or chlorine results, as anticipated, in greater volatility. The normal values of Trouton's constant and the low molecular latent heats of ethylene oxide, ethylene dichloride and 1,4-dioxane indicate that these liquids are not associated.

The initial decomposition temperatures of the glycols are seen to be a function of the length of the polyethylene oxide chain. The relative ease of decomposition of diethylene glycol dimethyl ether is unexpected in view of the stability of β,β'-dichloroethyl ether.

MONTREAL, CANADA RECEIVED OCTOBER 11, 1937

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

The Aromatic Character of the Furan Nucleus. Preparation and Reactions of Simple 3-Aminofurans

BY H. B. STEVENSON[1] AND JOHN R. JOHNSON

A number of chemical reactions have been used as a basis for comparing the aromatic properties ("aromaticity") of the furan and benzene systems. From studies of the selective cleavage of organo-lead compounds[2] and the relative ease of nuclear substitution reactions (halogenation, nitration, metalation, and Friedel–Crafts reactions)[3] Gilman has drawn the conclusion that the furan nucleus possesses an enhanced aromatic character[4] ("super-aromaticity") with reference to benzene. However, furan and its simple derivatives take part in the Diels–Alder diene synthesis,[5] and certain other aspects of their

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[1] This paper is an abstract of a portion of the doctoral dissertation of H. B. Stevenson, submitted to the Graduate Faculty of Cornell University in June, 1937.

[2] Gilman and Towne, *Rec. trav. chim.*, **51**, 1054 (1932).

[3] (a) Gilman and Calloway, THIS JOURNAL, **55**, 4197 (1933); (b) Gilman and Young, *ibid.*, **56**, 464 (1934); (c) Gilman and Breuer, *ibid.*, **56**, 1123 (1934).

[4] Gilman and Wright, *Chem. Rev.*, **11**, 323 (1932).

[5] Diels and Alder, *Ber.*, **62**, 554 (1929); Van Campen and Johnson, THIS JOURNAL, **55**, 430 (1933).