CXLV. THE MANOMETRIC ESTIMATION OF VOLATILE SUBSTANCES SOLUBLE IN WATER, WITH SPECIAL REFERENCE TO ETHER

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In connexion with work on the effects of ethyl ether on respiration of surviving tissues by means of the Warburg manometric method [Jowett & Quastel, 1937], a simple method has been devised for the estimation by manometric means of the concentration of ether in manometric vessels.

The method depends on the variation with temperature of the solubility of volatile liquids or gases in water. It may be of use with substances other than ether, which have partition coefficients in a suitable range in relation to the concentration to be estimated.

THEORY

The theory is applied to the Warburg constant-volume manometer, bound to a vessel containing both an aqueous and a gaseous phase.

The pressure varies with temperature for three main reasons: (1) the effect of temperature on gas pressure according to the gas law, (2) the varying vapour pressure of water and (3) the effect of temperature on the distribution of substances between gas and liquid. If a substance with a suitable partition coefficient is present in one manometer and not in another, the difference in the variation with temperature of the pressure exerted by the contents of the two vessels will be a measure of its concentration.

Let x mg. of a volatile substance (S) soluble in water be present in one manometer vessel (A) and absent from another (B) which serves as a control. The distribution of S between liquid and gaseous phases is measured by its Ostwald partition coefficient λ, which is the ratio of its concentration in the liquid to that in the gas. If the volume of the liquid present is v_F (ml.) and that of the gas v_G (ml.), the total amount of the substance in the gaseous phase at the temperature T_1 is

$$x_G = \frac{x v_G}{\lambda_1 v_F + v_G}.$$

If the temperature is raised to a higher value T_2, the Ostwald coefficient will decrease and the quantity of S in the gaseous phase will increase, the amount of the increase being

$$\Delta x_G = \frac{x\, v_G\, (\lambda_1 - \lambda_2)}{v_F \left(\lambda_2 + \frac{v_G}{v_F}\right)\left(\lambda_1 + \frac{v_G}{v_F}\right)}.$$

The pressure in vessel A will therefore rise more than that in B. If in A and B the total pressures are originally equal, the gas present in both at temperature T_1 will cause equal rises in pressure in both vessels, according to the gas law. The pressure of water vapour will usually (as in the case of the ether solutions that concern us) undergo the same rise in both vessels.

The difference between the pressure increments in vessels A and B will then arise solely from the change in distribution of volatile substances between

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liquid and gas. To obtain the simplest equation, we must have only one substance of high λ value present in different amounts in vessels A and B. In our application this condition is satisfied, for apart from ether and water vapour the only gases present are carbon dioxide-free air or oxygen. The effect of changes of temperature on the values of λ for oxygen and nitrogen is negligibly small.

The extra rise in pressure due to the volatile substance S is calculated from the gas law to be

$$\Delta p = \Delta x_G \cdot \frac{22{\cdot}4}{Mv_G} \cdot \frac{T_2}{273} \cdot P_0 .$$

$$= \frac{22{\cdot}4\, P_0 T_2 x}{273M} \cdot \frac{(\lambda_1 - \lambda_2)}{v_F \left(\lambda_2 + \frac{v_G}{v_F}\right)\left(\lambda_1 + \frac{v_G}{v_F}\right)} .$$

Pressures are measured in mm. of manometric fluid, of which P_0 mm. equal one atmosphere, and M is the molecular weight of S. Rearranging the last equation,

$$x = \frac{273 M\, \Delta p\, v_F}{22{\cdot}4\, P_0 T_2} \cdot \frac{\left(\lambda_2 + \frac{v_G}{v_F}\right)\left(\lambda_1 + \frac{v_G}{v_F}\right)}{(\lambda_1 - \lambda_2)} . \qquad \ldots\ldots(1)$$

It is readily deduced that

$$C_2 = \frac{273\, \Delta p}{22{\cdot}4\, P_0 T_2} \cdot \frac{\lambda_2 \left(\lambda_1 + \frac{v_G}{v_F}\right)}{(\lambda_1 - \lambda_2)} \qquad \ldots\ldots(2)$$

and

$$C_1 = \frac{273\, \Delta p}{22{\cdot}4\, P_0 T_2} \cdot \frac{\lambda_1 \left(\lambda_2 + \frac{v_G}{v_F}\right)}{(\lambda_1 - \lambda_2)} , \qquad \ldots\ldots(3)$$

where C_2 and C_1 are the concentrations of S in the solution (in moles per litre) at temperatures T_2 and T_1 respectively. The equations also apply when the temperature is lowered instead of being raised; C_2, λ_2, T_2 are always the values at the higher temperature.

It may sometimes be convenient to employ the last three equations in differential form. The equations derived are:

$$x = -\frac{273 M v_F \frac{dp}{dT}}{22{\cdot}4 T P_0} \cdot \frac{\left(\lambda + \frac{v_G}{v_F}\right)^2}{\frac{d\lambda}{dT}} , \qquad \ldots\ldots(4)$$

$$C = -\frac{273 \frac{dp}{dT}}{22{\cdot}4 T P_0} \cdot \frac{\lambda \left(\lambda + \frac{v_G}{v_F}\right)}{\frac{d\lambda}{dT}} . \qquad \ldots\ldots(5)$$

APPLICATION TO ETHYL ETHER

The method described can be calibrated and used empirically without any knowledge of partition coefficients. Over a given temperature range, provided that v_G/v_F is kept constant, the terms containing λ will be constant.

As values of λ are available or can be calculated for ether, a comparison between measurement and calculation has been made.

Values of λ have been calculated from data [*International Critical Tables*, 1928] for the composition and vapour pressures of saturated solutions of ether in water, on the assumption that ether behaves as a perfect gas ($M = 74$, mol. vol. $= 22{\cdot}4$ l. at N.T.P.). Sufficient data for the density of the solutions were not available, and these were calculated from the assumption, which is true at 20–25°, that a contraction of 0·20 ml. per g. of ether occurs when ether dissolves. From the total vapour pressures of the solutions the vapour pressures of water are subtracted to obtain the vapour pressures of ether over the solutions; the depression of the vapour pressure of water by dissolved ether can be neglected. From the vapour pressures of ether the concentrations in the vapour phase are calculated.

Table I. *Values of λ for ether*

Temp. ° C.	Calc.	From equation	Shaffer & Ronzoni
0	142·8	142·9	—
5	101·9	102·1	—
10	73·0	73·2	—
15	53·11	52·83	48·7
20	38·73	38·57	39·9
25	28·68	28·56	31·0
30	21·52	21·54	23·0
34·1	17·26	17·37	18·3
40	13·12	13·13	14·0
50	8·73	(8·98)	—

The values of λ so calculated (calc. Table I) were found to be represented, over the range 0–40°, with an average deviation of $\pm 0{\cdot}3\,\%$ by the equation

$$\log_{10}\lambda = 2{\cdot}1550 - 0{\cdot}02928\,t + 0{\cdot}0000021\,t^3,$$

t being the temperature (° C.). The agreement is shown in Table I. In the table are also given values of λ interpolated from the data of Shaffer & Ronzoni [1923], which were obtained by direct chemical analysis with more dilute solutions. The figures of these authors are rather higher than the calculated values. The latter, however, are probably themselves too high, since the densities of saturated ether vapour at 35° upwards are 7 % or more higher than the densities calculated from gas theory. The values of λ calculated from the equation have been used for comparison with experiment.

Calibration. A few ml. of an aqueous solution of ether of known composition are measured into a manometric vessel, which is at once attached to its manometer. The central cylinder contains 0·05 ml. of $N/2$ NaOH to absorb traces of carbon dioxide. Several such vessels, together with a control vessel, are shaken in a thermostat at room temperature, and after 20 min. the manometers are read. The temperature is raised a few degrees (so as just to keep the manometer levels on the scale), and after 20 min. readings are again taken. 20 min. are ample for obtaining constant readings. The taps are opened to release the pressure, and 10 min. later the manometers are read afresh and the raising of the temperature repeated. In this way a number of values of Δp over a temperature range of about 16–42° are obtained. Each time the taps are opened a little ether vapour is lost, the loss being calculated from the values of λ and gas theory.

From the equation for λ and equation (1) the quantities of ether present are calculated. A typical calculation is as follows:

	t	p_A	p_B	λ
Initial	17·11	-61·5	-65·1	46·19
Final	21·79	111·7	43·3	34·57

The pressures stated are with reference to atmospheric pressure as zero point. Δp, the pressure change in A less that in B, has the value 64·7. Also P_0 (for a lead perchlorate solution) is 4945, $M = 74$, $v_F = 3{\cdot}05$, $v_G = 15{\cdot}25$.

Hence
$$x = \frac{273 \times 74}{22{\cdot}4 \times 4945} \cdot \frac{64{\cdot}7 \times 3{\cdot}05}{294{\cdot}8} \cdot \frac{(46{\cdot}19 + 5{\cdot}00)\,(34{\cdot}57 + 5{\cdot}00)}{11{\cdot}62}$$
$$= 21{\cdot}28 \text{ (mg.)}.$$

In this experiment the data may be summarized as follows:

Range of t	Δp	x calc.	x present	$\frac{\text{Calc.}}{\text{Actual}}$
17·11–21·79	64·7	21·28	20·16	1·056
21·81–25·49	58·6	20·90	20·08	1·041
25·51–28·94	61·7	21·13	20·01	1·056
29·28–32·21	55·4	20·65	19·92	1·037
32·20–35·40	62·8	20·28	19·77	1·026
35·39–38·40	60·9	20·30	19·64	1·033
38·40–41·19	58·7	21·09	19·49	1·082

The mean value derived from each such experiment is inserted in the following summarizing table, together with the average deviation from the mean in each experiment.

Summary of results

v_F	$\frac{v_G}{v_F}$	mg. ether initially present	No. of observations	Mean $\frac{\text{Calc.}}{\text{Present}}$
2·05	7·58	20·16	7	1·032 ± 0·022
2·50	6·04	18·06	6	1·082 ± 0·008
3·05	5·00	20·16	7	1·047 ± 0·015
3·25	4·63	21·67	6	1·084 ± 0·010
4·56	3·13	20·16	6	1·133 ± 0·004
4·95	2·80	25·28	6	1·170 ± 0·012
5·05	2·73	28·86	8	1·127 ± 0·034
5·05	2·48	28·86	8	1·134 ± 0·017

The values calculated are rather higher than those actually present. On the average, however, the discrepancy remains constant over the temperature range investigated. The discrepancy is attributed to error in λ values and in the assumption that ether behaves as a perfect gas.

It appears that the ratio of calculated to actual values is about 1·06 for smaller values of v_F, about 1·14 for higher values. It is desired to apply the method (in the accompanying paper) to cases where $v_F = 3{\cdot}3$. This has been done by calculating values of the concentration of ether by equations (2) or (3), and multiplying the result by 0·94 as an empirical correction factor, which should be accurate within a few per cent.

It may be added that when the divergence between calculation and experiment was found, a number of sources of error were considered and found to be of little importance. Such, for instance, is the expansion of solutions with temperature, and the existence of some dead space. Absorption of ether by stopper grease is probably of little significance. The volume of stopper grease exposed to ether is of the order 0·01 ml., and the partition coefficient of ether between oil and water is about 4 according to Meyer and Overton.

Summary

A manometric method is described, applicable to constant-volume manometers, for determining volatile liquids or gases soluble in water, the partition of which between aqueous and gaseous phases varies considerably with temperature. The method is applied to the determination of ethyl ether.

REFERENCES

Jowett & Quastel (1937). *Biochem. J.* **31**, 1101.
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