413. *The Measurement of Gas Solubilities.*

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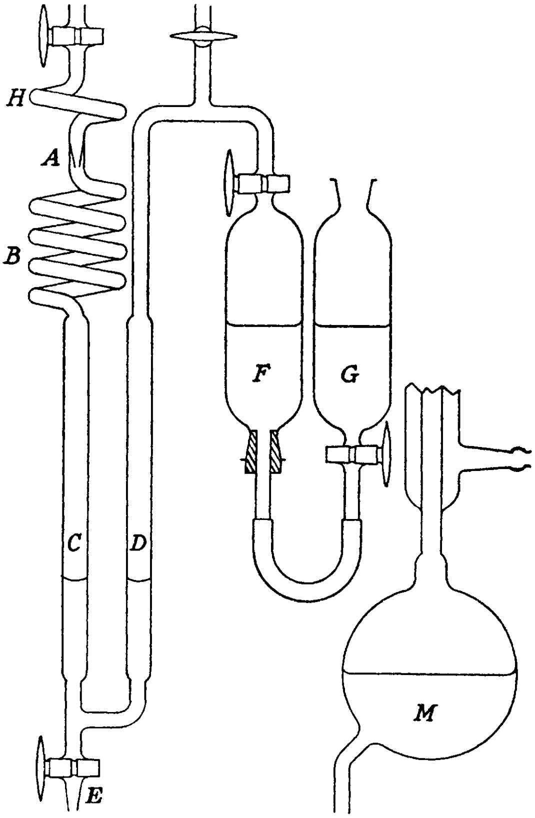
An apparatus based on the flow of a liquid film through the gas has been developed for the study of gas solubility problems, including the salting-out effect. The method compares favourably with the normal Ostwald technique in rapidity and accuracy.

The type of apparatus used in most of the work is shown in Fig. 1, though various modifications were tried initially. The thoroughly boiled-out solvent from *M* is injected drop by drop at *A*. The spiral *H* is necessary to preheat the solvent in work at higher temperatures. After flowing through spiral *B*, the liquid passes into the gas burette *C*. The levelling burette *D* is sealed into the bottom of *C*, and saturated solvent is allowed to drop from tap *E* at such a rate that the levels in *C* and *D* are kept the same. Solvent from *E* is collected and measured. Readings of *C* give the volume of gas dissolved, while the volume of solvent is the amount collected at *E* together with the volume accumulating in *C* and *D*. The absorption section is contained in a thermostat. The dimensions are not critical, but a spiral *B* of about 5 turns of 10-mm. tubing with a diameter of about 7 cm. was found suitable; *C* and *D* may be ordinary 50-ml. burette tubes.

Fig. 1.

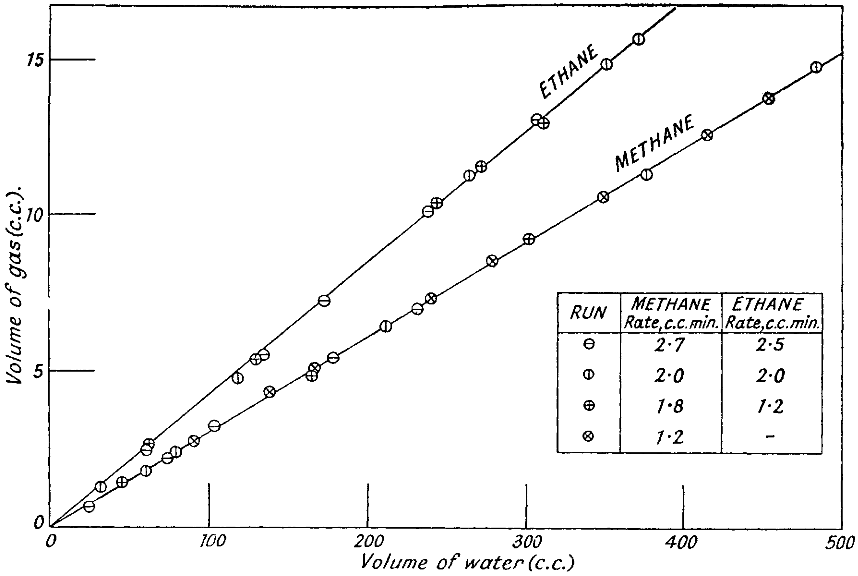


Samples of gas obtained and purified as indicated in the table are stored over saturated water in inverted separating funnels with reservoirs (*F*, *G*). The gas supply is connected to *D* throughout so that constant pressure can be maintained in the absorption section. The absorption apparatus is initially filled with gas either by evacuation or by displacing air-free solvent.

In measuring the solubilities of very soluble gases (with Ostwald coefficients greater than 0·5), the levelling burette *D* is replaced by a second gas burette sealed in above spiral *B*. This contains gas over mercury or saturated solvent, and constant pressure is maintained by adding liquid to the levelling tube of the second burette.

Preliminary work with various modifications of the apparatus established the fact that equilibrium between the film of liquid and gas is attained with considerable rapidity. It was found that variation in rate of flow within wide limits and in the dimensions of the spiral had no appreciable effect on the solubility. Measurements were carried out with rates as low as

Fig. 2.



0·5 c.c./min. and as high as 5 c.c./min. At low rates, however, the time required for the absorption of sufficient gas becomes too great, and at very high rates the control of the apparatus becomes difficult. There was, however, no indication of any appreciable change in solubility in this range, provided that the drop rate is adjusted to a constant value while readings are being taken. For normal work a range of drop rate from 1·5 to 2·5 c.c./min. was found to be most suitable. A run of 4—6 hours corresponds to agitation for this length of time in the Ostwald method, with the certainty that fresh liquid is continuously exposed to the gas. The method has the marked practical advantage that a number of volume readings can be taken during a run, and the solubility determined graphically from the slope of the line obtained by plotting volume of gas (or burette reading) against volume of liquid. Plots of this type are presented for methane and ethane, on which gases most of the preliminary work was done (Fig. 2). It is also clear that any factor which affects the solubility, such as traces of impurities or incompletely boiled out solvent, will be detected by some curvature of the line. Runs which showed such a curvature were obtained in a few cases and rejected.

Discussion.

The table gives values for the absorption coefficients (calculated from the slopes by reduction to 273° K.) of several gases compared with the recorded values. The values obtained by the

Solvent: water. Temp. 25° ± 0·1°.
(Recorded values from I.C.T.; Seidell, "Solubilities"; and Landolt–Börnstein, "Tabellen.")
Col. ii: rate of flow, c.c./min. Col. iii: absorption coefficient × 10^3. Col. iv: recorded absorption coefficient. Col. v: Deviation, %. Col. vi: method of preparation and purification.

i. Gas.	ii.	iii.	iv.	v.	vi.
CH_4	2·7	27·9	30·1	7	(1) CH_3I and Zn–Cu couple; washed with alcohol and water. (2) $CH_3{\cdot}MgI$ and H_2O; washed as in (1)
	2·5	27·8			
	2·0	27·9			
	1·8	27·8			
	1·2	27·9			
C_2H_6	1·5 to 2·5	39·1	41·0	5	$C_2H_5{\cdot}MgI$ and H_2O; washed as for methane
O_2	1·5 to 2·5	28·0	28·3—28·9	1—3	(1) $KMnO_4$ and H_2O_2; washed with water (2) Action of heat on $KMnO_4$
N_2	1·5 to 2·5	14·05	14·3—15·0	2—6	$NaNO_2$ and NH_4Cl; washed with $K_2Cr_2O_7$ and water
C_2H_4	1·5 to 2·5	104·4	108	3	EtOH and H_3PO_4 at 220°; washed with H_2SO_4 and KOH

present method are consistently lower than those got by the Ostwald technique by a few units %. Examination of the literature shows, however, that deviations of this magnitude are not unusual in gas-solubility measurements. It may also be pointed out that the recorded values for the gases used are drawn from relatively old work, and it is suggested that the values obtained by the method described are more reliable because of the absence of any possibility of supersaturation, and possibly because no correction is necessary for change in volume of the solvent. The absence of any type of flexible connection and of stop-cocks in contact with the gas may also contribute to increased reliability. Although these difficulties are realised and overcome in modern applications of the Ostwald technique, yet they may have contributed to somewhat inaccurate results in older investigations. The difficulties experienced in the Ostwald method in bringing gas and solvent into contact without an initial loss due to solution in the upper layer of solvent are also absent. An objection raised by Horiuti (*Sci. Papers Inst. Phys. Chem. Res. Tokio*, 1931—32, **17**, No. 341, 168) to the " wet " method (*i.e.*, any method in which the gas is kept saturated with solvent vapour), *viz.*, the possibility of a change in composition when wet gas is transferred from the gas burette to the gas pipette at a different temperature, does not apply in the method described.

Since the method requires the same type of readings as the normal Ostwald method—measurement of a gas volume and of a solvent volume—the accuracy is at least equal to the older method, but confidence in the reliability of the results increases with the number of measurements taken and increasing length of run. We find that results are reproducible within limits of 0·5% and possibly less. The method is therefore presented as an alternative to the Ostwald method, giving at least equal accuracy and requiring rather simpler apparatus.

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