58. *The Hydrolysis of Acetonesemicarbazone.*

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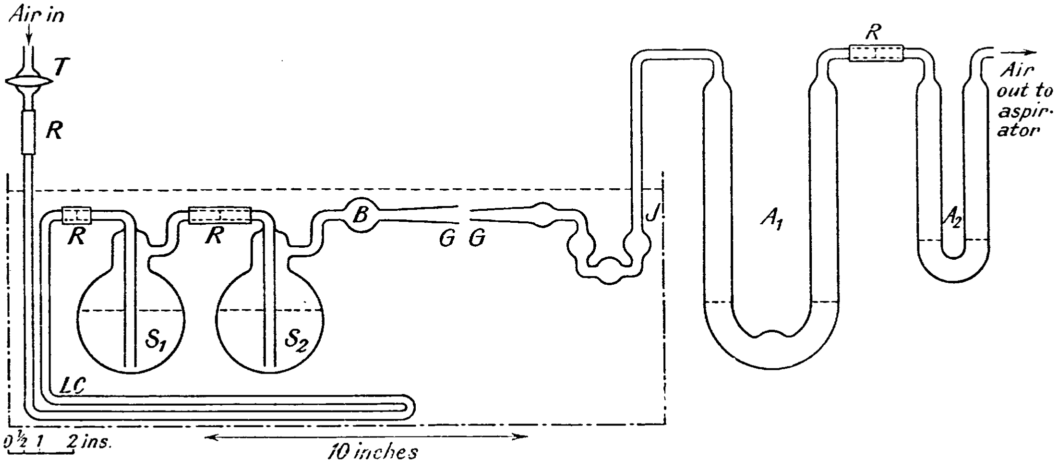
ACETONESEMICARBAZONE was found to be extensively hydrolysed in aqueous solution, and it was decided to measure its degree of hydrolysis by comparing the partial pressure of acetone vapour over the solution with that over an aqueous solution of pure acetone of known concentration. By working at two temperatures, it was possible, by means of the van 't Hoff isochore, to calculate the heat of the reaction between acetone and semicarbazide; similarly, the heat of condensation of acetone vapour in acetone solutions of known concentration was evaluated by the Clausius–Clapeyron equation.

I. *The Partial Vapour Pressure of Acetone in Aqueous Solutions.*

The dynamic method appeared to be the most suitable, although it has been criticised by Tammann (*Wied. Ann.*, 1888, **33**, 322); with suitable apparatus and correct calculation, however, it has been shown by Menzies (*J. Amer. Chem. Soc.*, 1920, **42**, 1951) to give the same results as those obtained by the static method. Partington and his collaborators (J., 1911, **99**, 467; 1923, **123**, 160; 1930, 635) have also used this method successfully but with a somewhat different technique. The most important points to be considered were (1) the design of the jet, (2) the admissibility or otherwise of rubber joints, and (3) distillation during heating and premature condensation during a run.

FIG. 1.



(1) The size of the bubble must not be too small (Jones, J., 1911, **99**, 160), since the internal pressure exceeds the external by $2\gamma/r$, where γ = surface tension and r = radius of bubble; hence, on theoretical grounds, the capillary type of jet and Schott's sintered silica "gaseinleitungsrohr," which breaks up the gas stream into a multitude of fine bubbles, are open to objection; they were tried (see p. 206), but their use is not recommended. A further disadvantage of the latter is the very high hydrostatic pressure required to force the air through the disc. In both cases it is not known at what pressure the air becomes saturated with acetone, as the gas pressure is falling while the acetone is evaporating.

(2) Rubber joints are condemned by Partington (J., 1911, **99**, 467), but he gives no data as to errors caused by their use. It is difficult to dispense with them entirely, but in the later experiments they were used only on butt joints (see *R*,*R*; Fig. 1). Direct experiment failed to reveal any absorption by the rubber, but since a very small amount of absorption would affect the results in the most dilute solutions, a ground-glass joint (*GG*) was used in most of the experiments to join the saturating system to the absorbers.

(3) The third source of error is more serious. The distillation leads to a lowering of

the concentration of acetone in the saturator before the experiment starts, so this concentration should always be measured *after* a run. The condensation may arrest acetone before it reaches the absorbing system, and cause it to return to the saturator, giving rise to low and variable results. The tube *J* (Fig. 1) overcomes this difficulty : the condensed acetone runs back into the bend of the tube which is in one piece with the first part (A_1) of the absorbing system. During the preliminary heating, a little distillation takes place, so it is necessary to dry out the ground-glass joint and attached splash bulb *B* with filter-paper; neglect of this precaution leads to irregular results, as the condensate tends to be richer in acetone than the bulk of the solution.

In general, the apparatus should be designed to work with a low hydrostatic pressure (see p. 204), for which a correction has to be applied, and this makes **U**-tubes inferior to wash-bottles as saturators, since the latter have a larger capacity for a given head of liquid. Further, the volume of air passing through the saturator is increased by water vapour taken up, and most of the latter is condensed before the air is measured, hence a correction must also be applied for the aqueous vapour tension.

EXPERIMENTAL.

Apparatus.—Early expts. varied in certain respects which are mentioned later. The standard apparatus is shown in Fig. 1, $\frac{3}{16}$ in. jets being used in the saturators. In order that there might be only a small fall in concn. in the acetone solution during a run, two saturators (S_1, S_2) were used; the first nearly saturated the air, so that little was removed from the second.

The air was heated in the thin lead coil *LC*, which was about 10 ft. long. Two absorbers (A_1, A_2) sufficed to trap all the acetone, as shown by tests with a third; these were connected to a $2\frac{1}{2}$-l. aspirator provided with a scale graduated to read in c.c. and with a bottle for levelling. Before a reading, the tap on the inlet tube (*T*) is closed, then a screw clip between the aspirator and the absorbers; the vol. of air in the aspirator is then measured after suitable levelling.

The acetone was purified by redistn. until the b. p. was const., and the middle fraction of the last distn. alone was used. Known vols. of this were diluted to definite vols. with H_2O, and the concns. of the solutions estimated iodometrically by Messinger's method.

Procedure.—The saturators are about half filled with an aq. acetone solution and the tube *J* attached, the vaseline used in the joint being so placed that it does not come into contact with the acetone-laden air. (Without vaseline, the joint tends either to come apart when the thermostat is stirred or to bind.) The union between the saturators and the lead coil is so arranged that the joint *GG* may be brought above the surface when required. The whole is immersed in a thermostat and maintained at a steady temp. for at least an hr. (longer if the acetone is produced by a slow reaction), the joint *GG* raised, disconnected, and the tubes *J* and A_1 rapidly flushed out with distilled H_2O; A_1 is then filled to the level shown, the joint remade, and A_2 also filled with H_2O to the level indicated and attached. The other side of A_2 is then connected to the aspirator, full of water.

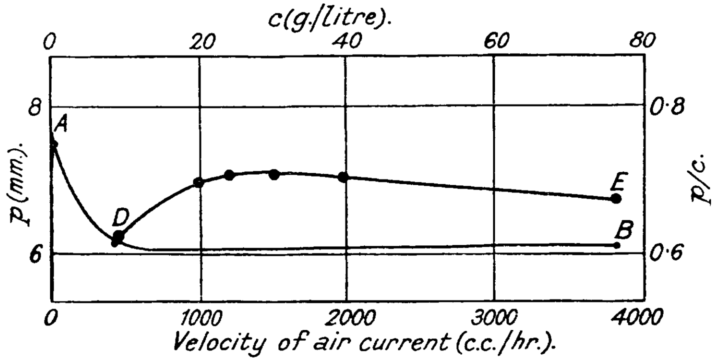
The stopcock *T* being still closed, the aspirator clip is opened and the vol. of air in the aspirator (derived from the expansion of the air in the rest of the apparatus) read. It is usually 25 c.c., and as only a small part of it is due to expansion in S_2, the error in neglecting its acetone content is inappreciable. The stopcock *T* is then opened, the screw clip adjusted to give a suitable rate of flow, and 500—4000 c.c. of air passed through; *T* is now closed, then the clip on the aspirator. The joint *GG* is broken and the contents of the absorbers washed into stoppered bottles. The saturators are also removed, quickly cooled, and a suitable vol. is withdrawn from S_2 for analysis. To each bottle and also to a blank are added 10 c.c. of $2N$-NaOH and a 2-fold excess of I; after 1 hr. the solutions are acidified and titrated with $Na_2S_2O_3$: 1 c.c. $0{\cdot}1N$-I = 0·000967 g. acetone. The temp. of the air in the aspirator, and also its vol. after levelling to atm. press., are recorded.

The v. p. is calc. by means of the formula $p = 760(P - h - \pi)v/P(V + v)$, where p = partial v. p. of acetone; P = atm. press.; V = vol. of air; v = vol. of acetone vapour evaporated at t° and 760 mm. (calc. from the wt. of acetone found); h = hydrostatic diff. of press. between the air in S_2 and the atm. (measured in a separate expt. to avoid the loss of acetone which would be trapped in a manometer if one were included in the apparatus); π = diff. between the aq. v. p. at the temp. of the thermostat and the temp. at which the air was measured.

Results.—Table I shows the connexion between the rate of flow of air ($\frac{3}{16}$ in. jet) and acetone evaporated, the latter being tabulated in terms of partial v. p. These results, plotted in Fig. 2, show that the rate of flow has little effect between 1000 and 2000 c.c./hr.; above and below these limits the apparent v. p. decreases.

Table II shows results obtained in the same way with a porous septum (see p. 204); they agree with those in Table I. Table III shows the effect of substituting a ground-glass joint for the rubber joint used in the previous expts., and the effect of using a capillary jet in place of a $\frac{3}{16}''$ jet: the differences are of the order of the exptl. error. Table IV gives results obtained with different concns. of acetone solution at 49·7°; the quotient p/c rises as the concentration falls instead of remaining const. as required by Henry's law.

FIG. 2.



AB, p/c *plotted against* c (*g./litre*). *DE*, p (*mm.*) *plotted against rate of flow of air* (*c.c./hr.*).

Table V records numerous expts. at 30·8°; the rise in p/c as concentration falls is more marked at this lower temp. The mean value of this ratio for various concns. is recorded in Table VI. In the very dil. solutions the larger exptl. error is offset by taking the mean value of a number of expts. If log p is plotted against log c, the points lie well on a straight line corresponding to the empirical relation

$$\log c = (\log p + 0{\cdot}1494)/0{\cdot}95 \text{ or } p = 0{\cdot}709\, c^{0{\cdot}95},$$

where c is in g./l. and p in mm. of Hg. Hence the value of p at 30·8° for a concn. of 3·97 g./l. is calculated to be 2·655 mm. At 49·7° the mean of 12 concordant expts. gives $p = 6{\cdot}94$ mm. for the same concn., whence, from the Clausius–Clapeyron equation, the heat required to remove 1 g.-mol. of acetone as vapour from this aq. solution = 10,000 g.-cal., a result noticeably higher than the value 9,000 g.-cal. obtained at 56° by Wirtz (*Wied. Ann.*, 1890, **40**, 446) for pure acetone.

TABLE I.

Hydrostatic press., 4 mm.; temp., 49·7°; acetone = 3·97 g./l.

Rate of air flow, c.c./hr.	2000	3840	1200	835	1520	418
V. p. (calc. from acetone evap.)	6·95	6·72	7·05	6·94	7·06	6·22

TABLE II.

Hydrostatic press., 26 mm.; temp. and concn. as in Table I.

Rate of air flow, c.c./hr.	3000	2370	2880	3900
V. p. (calc. from acetone evap.)	7·02	6·81	6·82	6·90

TABLE III.

Temp., 49·7°; acetone concn. = 3·97 g./l.

Rate of air flow, c.c./hr.	1600 *	4000 †	4000 †
V. p. (calc. from acetone evap.)	6·88	6·95	6·87

* Hydrostatic press., 4 mm.; ground-glass joint and $\frac{3}{16}''$ jet.
† ,, ,, 6·6 mm.; capillary jets.

TABLE IV.

c, g./l.	3·97	0·863	0·1625	0·067
p, mm.	6·94	1·524	0·310	0·1263
p/c	1·75	1·75	1·91	1·90

TABLE V.

	Temp.	c.	w.*	p, corr. to 30·8°.	p/c.		Temp.	c.	w.*	p, corr. to 30·8°.	p/c.
g	30·8°	76·60	0·1625	50·2	0·619	r	30·8°	0·744	0·00431	0·577	0·775
u	30·0	9·68	0·02590	5·98	0·618	r	30·8	0·752	0·00420	0·543	0·722
u	30·5	9·68	0·01959	5·71	0·590	r	30·5	0·467	0·00258	0·341	0·730
u	30·5	9·68	0·02350	5·74	0·593	g	31·16	0·388	0·00182	0·284	0·732
u	30·5	8·66	0·02380	5·53	0·638	r	30·8	0·2395	0·001386	0·204	0·851
g	30·9	3·72	0·01622	2·512	0·676	r	30·5	0·2395	0·001426	0·182	0·760
g	30·9	3·80	0·01242	2·568	0·676	r	30·45	0·2395	0·001436	0·1985	0·864
g	30·9	3·76	0·02017	2·497	0·664	r	30·45	0·2395	0·001227	0·1760	0·754
g	30·7	3·55	0·01503	2·335	0·659	r	30·5	0·1600	0·000833	0·1175	0·735
r	30·8	1·340	0·00683	0·972	0·724						

Type of apparatus: *u*, second saturator a U-tube; *r*, second saturator a CO_2 flask with capillary jet, saturators joined to absorbers by rubber joint; *g*, second saturator an all-glass wash-bottle with $\frac{3}{16}''$ jet joined to absorbers by a ground-glass joint.

* w = Wt. (g.) of acetone carried over.

TABLE VI.

c	76·6	9·68	3·72	1·34	0·744	0·467	0·2395
p/c (mean)	0·619	0·610	0·669	0·724	0·748	0·730	0·772

Discussion.—If acetone obeyed Henry's and Raoult's laws in dilute solution the value of p/c at 30° would be 0·35 instead of the values found, *viz.*, 0·61—0·77, and at 50° it would be 0·80 instead of 1·75—1·90; *i.e.*, the activity coefficient in the dilute solutions is much greater than that of pure acetone (taken as 1·00). This might be explained by supposing that pure acetone is highly self-associated, and that the breakdown of these complexes is still proceeding even in 0·1% solution. Solvation of the acetone also probably occurs. The net heat effect of these changes is of the order of 1000 cal.

II. *The Hydrolytic Constant of Acetonesemicarbazone and the Heat of Reaction between Acetone and Semicarbazide.*

The partial v. p.'s of acetone at 30·8° and 49·7° over solutions of its semicarbazone were measured; from the results at 30·8° the corresponding concns. of free acetone were calculated from the empirical formula $p = 0{\cdot}709c^{0{\cdot}95}$ (p. 206). The results for 49·7° covered a smaller range of v. p., and the concns. were given with sufficient accuracy by the relation $p = 1{\cdot}75c$, which is permissible because at this temp. Henry's law is nearly true over a small concn. range.

The semicarbazone was made from pure redistilled acetone and semicarbazide hydrochloride, and recryst.; its acetone content was checked by analysis. To 50 c.c. of a solution containing not more than 0·2 g. of semicarbazone, 2·5 c.c. of dil. H_2SO_4 (1 : 5) were added, and the solution heated to 100° in a current of air in an apparatus of the same type as that used for v. p. measurements. The acetone liberated was absorbed in three U-tubes containing H_2O. From four such portions, the acetone thus recovered corresponded to 0·748 g. of semicarbazone, whereas 0·75 g. was taken. The acetone remaining after a v. p. expt. was occasionally checked in the same way, in order to prove that the acetone–semicarbazide equilibrium had not been seriously disturbed during the experiment.

Hydrolysis of Acetonesemicarbazone at 30·8°.

V.	b.	b′.	p.	c.	h.	K × 10⁵.
2125	15	0·13044	0·828	0·02030	15·6	374
2429	10	0·08696	0·692	0·01680	19·3	402
* 2255	10	0·08696	0·729	0·01743	20·0	437
2605	5	0·04348	0·478	0·01111	25·6	382
† 2200	5	0·04348	0·442	0·01041	24·0	(328)
2474	2·5	0·02174	0·317	0·00739	34·0	380
4421	1·25	0·01087	0·216	0·00493	49·3	409
2582	1·25	0·01087	0·215	0·00491	49·1	404
						Mean 398

b and *b′* = concn. of semicarbazone in g./l. and g.-mol./l. respectively; *h* = degree of hydrolysis %; *K* = hydrolytic const.; *V*, *p*, and *c* have their former significance.

* At 30·65°. † At 30·55°.

Hydrolysis of Acetonesemicarbazone at 49·7°.

V.	b.	b'.	p.	c.	h.	$K \times 10^5$.
1000	20·0	0·1739	3·78	0·03725	21·4	1060
1005	20·0	0·1739	3·69	0·0364	20·9	964
1985	7·5	0·06522	2·135	0·02103	40·3	1001
1994	4·0	0·03478	1·420	0·01399	40·3	942
§ 1613	20·0	0·1739	3·70	0·03645	20·95	992
‡ 1510	20·0	0·1739	3·73	0·03678	21·1	1002
2348	5·0	0·04348	1·64	0·01617	37·2	957
1537	5·0	0·04348	1·614	0·01592	36·6	920
						Mean 974

§ At 49·2°. ‡ At 49·4°.

For these two expts., the values of K were corr. to 49·7° by the use of the experimentally determined temperature coeff.

Application of the van 't Hoff isochore gives the heat of the reaction between semicarbazide and acetone as $2{\cdot}3(\log 0{\cdot}00974 - \log 0{\cdot}00398) \times 303{\cdot}8 \times 322{\cdot}7 \times 1{\cdot}98/18{\cdot}9 =$ 9179 g.-cal.

SUMMARY.

A dynamic or transpiration method has been worked out for the measurement of partial vapour pressures, acetone being used as an example.

Henry's law is not obeyed over a concentration range of 76·6—0·16 g. per litre at 30° and 50°.

The heat of evaporation of acetone from an aqueous solution containing 4 g. per litre is greater than that of anhydrous acetone.

Both these effects may be due to self-association and solvation of acetone—the former in concentrated and the latter in dilute solutions.

The method has been applied to determination of the hydrolysis of acetonesemicarbazone at 30·8° and 497°, and from the data obtained the heat of reaction of its generators has been calculated.

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