UNIVERSITY OF TORONTO STUDIES

PAPERS FROM THE CHEMICAL LABORATORIES

No. 70: AN IMPROVED FORM OF APPARATUS FOR THE RAPID ESTIMATION OF SULPHATES AND SALTS OF BARIUM, BY W. R. LANG AND T. B. ALLEN

(REPRINTED FROM THE JOURNAL OF THE CHEMICAL SOCIETY OF LONDON, VOL. XCI.)

No. 71: A BENZENE MODEL ON ONE PLANE FOR LECTURE PURPOSES, BY W. R. LANG

(REPRINTED FROM THE JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, VOL. XXIX.)

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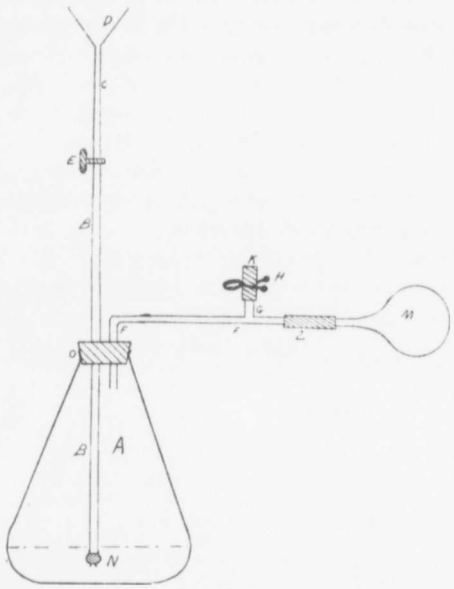
CXXVII.—*An Improved Form of Apparatus for the Rapid Estimation of Sulphates and Salts of Barium.*

By William Robert Lang and Thos. Boles Allen.

N. Tarugi and G. Bianchi (*Gazzetta*, 1906, **36**, i, 347) describe an apparatus for the rapid and exact estimation of sulphates and salts of barium by a volumetric method based on the rapid clearing of turbid solutions in narrow tubes. (For a short description of their apparatus



see Abstr., 1906, **90**, ii, 627.) The authors have modified this apparatus materially; the following short description and diagram will serve to explain it.

The vessel, *A*, containing the acidified sulphate is placed on a flat burner, the approximate amount of barium chloride solution, ascertained by previous rough experiments, run directly into the flask, the stopper, *O*, with its attachments, inserted, and the contents kept at the boiling point. *FF* is a T-tube, on the branch, *G*, of which is fixed a small piece of rubber tubing with a pinchcock, at this stage of the experiment left open to the air. *N* is a small thistle-shaped tube filled with glass-wool which is found materially to clear the turbid solution as it passes up to the narrow tube. The pinchcock, *H*, is then

closed and a slight pressure on M forces a portion of the contents of the flask through N and up B until the portion C is filled, when the stopcock, E, is closed. The whole pressure on the flask can then be relieved by opening the pinchcock, H. The liquid in C clears very rapidly and the standard barium chloride solution may be added. If this produces a turbidity, E is opened and the solution washed down into the flask ; a very complete mixing is then obtained by alternately compressing M, with G open to the air, placing the finger on the orifice of the short rubber tube, K, and releasing M, thus causing air to be drawn through N and to bubble through the solution.

The process of forcing the liquid up the tube, titrating, washing it down again, and mixing is repeated until a further addition of barium chloride solution causes no turbidity. The mean between the number of c.c. used up to the point of having an evident turbidity and the quantity necessary to the point where none is perceptible is taken as the amount of barium chloride solution consumed in the precipitation of the sulphate. As the amounts of barium salt and sulphate in solution approximate to each other, so the rapidity of the clearing increases, and when the reaction has almost reached the end-point this clarification is very nearly instantaneous.

Experiments were undertaken in this apparatus with the solutions of sulphates and barium salts given in the following tables :

TABLE I.

Using 0·0958 N – H_2SO_4, 1 c.c. = 0·0046 gram (SO_4).
„ 0·1101 N – $Ba(NO_3)_2$, 1 „ = 0·00485 „ (SO_4).

No. of c.c. of H_2SO_4 taken.	Equal to gram (SO_4).	No. of c.c. of $Ba(NO_3)_2$ taken.	Equal to gram (SO_4).	Error in per cent.
10·42	0·0479	10·00	0·0485	−1·0
10·60	0·0488	10·00	0·0485	+0·6
10·52	0·0484	10·00	0·0485	−0·2
10·58	0·0487	10·00	0·0485	+0·4
16·80	0·0773	16·00	0·0776	−0·3
15·71	0·0722	15·00	0·0727	−0·7

Average error −0·55 and +0·5, giving a mean error of 0·025 per cent.

TABLE II.

Using 0·9981 N – H_2SO_4, 1 c.c. = 0·0479 gram (SO_4).
„ 0·1101 N – $Ba(NO_3)_2$, 1 „ = 0·00485 „ (SO_4).

No. of c.c. of H_2SO_4 taken.	Equal to gram (SO_4).	No. of c.c. of $Ba(NO_3)_2$ taken.	Equal to gram (SO_4).	Error in per cent.
5·05	0·2419	50·00	0·2425	0·4
5·08	0·2433	50·00	0·2425	0·4
5·09	0·2438	50·00	0·2428	0·5
			Average error.....	0·43

TABLE III.

Using 0·2039 N – H_2SO_4, 1 c.c. = 0·0099 gram (SO_4).
,, 0·1101 N – $Ba(NO_3)_2$, 1 ,, = 0·00485 ,, (SO_4).

No. of c.c. of H_2SO_4 taken.	Equal to gram (SO_4).	No. of c.c. of $Ba(NO_3)_2$ taken.	Equal to gram (SO_4).	Error in per cent.
14·75	0·1460	29·95	0·1453	1·0
14·81	0·1466	30·00	0·1455	0·9
17·35	0·1717	34·90	0·1700	0·6
9·90	0·0980	20·10	0·0975	0·5
			Average error.....	0·75

Solutions of coloured sulphates, such as those of copper and nickel. were also tried, the error in these cases ranging from 0·1 to 0·8 per cent. of the theoretical.

From a study of these results it appears that a single titration will come within 1 per cent. of the value found by gravimetric estimation, and, if a sufficient number of titrations are made, the results can be obtained to within 0·5 per cent. of the gravimetric value (compare Table I.). It may be added that the presence of free acid materially aids the precipitation, greatly increasing the rate of precipitation of the turbid liquid in the narrow tube.

The determination of sulphur in iron pyrites by this method gave :

	Gravimetric.	*Volumetric.*
Iron salts present.....	52·13 per cent.	52·20 per cent.
Iron salts absent	52·24 ,,	52·09 ,,

It would seem that this method might be used in cases where speed is of more importance than absolute accuracy. It has this great advantage, that an estimation agreeing within 0·5 per cent. of the best gravimetric method can be made in from three-quarters to one hour ; that is, by taking the mean of four or five volumetric readings.

The Determination of Sucrose by Fehling's Solution.

Experiments with this apparatus were made to determine the best conditions under which the above could be most accurately carried out.

TABLE IV.

	No. of c.c. of sucrose taken.	Equal to gram sucrose.	Dilution in c.c.	Time of heating in minutes.	No. of c.c. of solution used.	Equal to gram sucrose.	Error in per cent.
(1)	10·00	0·2278	200	5	45·50	0·2275	0·2
(2)	10·00	0·2278	150	5	45·65	0·2283	0·3
(3)	5·00	0·1136	100	5	22·75	0·1138	0·2
(4)	10·00	0·2278	150	5	45·64	0·2282	0·2
(5)	10·01	0·2280	150	5	45·58	0·2279	0·1
(6)	10·00	0·2278	175	5	45·62	0·2281	0·1
(7)	10·00	0·2278	150	8	45·65	0·2283	0·3
(8)	2·00	0·0456	200	5	9·02	0·0451	1·0
(9)	5·00	0·1136	450	5	22·90	0·1145	1·0
(10)	10·00	0·2278	450	5	45·92	0·2296	0·9
(11)	10·00	0·2278	150	15	45·82	0·2292	1·0
(12)	5·00	0·1136	100	20	23·20	0·1160	2·0

These results are some of a number of determinations, and they show that, if suitable conditions are obtained, the results give excellent agreement with the theoretical. The conditions are, first, that the Fehling's solution should be added to the boiling liquid to within 1 c.c. of the correct amount, this being obtained by previous rough titrations; secondly, that the strength of the sucrose in the flask should not be more than 0·15 gram in from 75—100 c.c. of water, and thirdly, that the time of heating should not be more than from five to eight minutes.

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A Benzene Model on One Plane for Lecture Purposes.

W. R. Lang.

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A Benzene Model, on One Plane, for Lecture Purposes.—This model is intended as an aid to teachers in explaining the theory of the constitution of benzene. Any theory regarding its constitution must account for and explain the behavior of benzene towards reagents and its power of forming derivatives. In the aliphatic series it is usual to represent the hydrocarbons graphically with the carbon and hydrogen atoms arranged as in an open chain. The model held as in Fig. 1 would thus represent benzene, showing eight unsatisfied affinities.

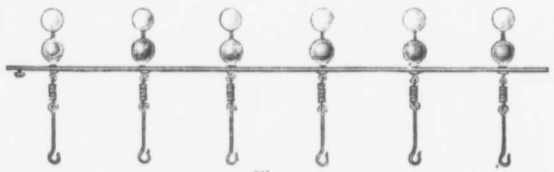

Fig. 1.

But the following summarized characteristics of this body cannot be reconciled with such an open-chain representation, namely :

(*a*) That each of its hydrogen atoms bears the same relation to the molecule, as is evident by the non-existence of isomeric mono-substitution compounds.

(*b*) The formation of benzene as a constant product of the decomposition of the other members of the aromatic series.

(*c*) The formation of hexa-additive compounds (and no more) and the ready breaking up of these into a tri-substitution product.

(*d*) The formation of three di-substitution products.

(*e*) The evident "saturated" nature of benzene.

It is clear from (*c*) that there can be only six unsatisfied affinities, so, if the model is bent round to form a circle, as in Fig. 2, thus linking the first carbon atom to the last, the number of unsatisfied affinities is shown as being reduced to six, and, in addition, each carbon and hydrogen atom is represented as bearing the same relation to the molecule, all being similarly linked.

FIG. 2

But the fourth valence of the carbon atoms still appears as unoccupied; these may be represented as acting *towards* the centre—as in the Armstrong-Baeyer formula, or the diagonally opposite atoms may be linked together (Claus); figure 3. If this is done, the model will then represent an exceedingly stable molecule.

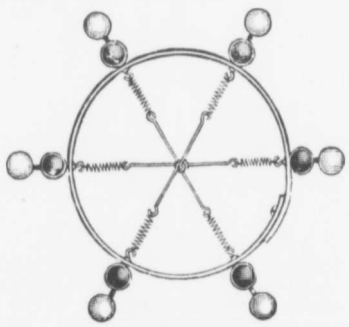

FIG. 3

Small spiral springs are used in the interior of the "ring," to permit of the rapid and secure fastening together of the diagonally opposite

linkings in the last position. The model can readily be constructed from a flexible brass band 1–2 cms. wide, with stiff wires soldered through holes in the rim, while corks of different colors serve admirably for the carbon and hydrogen atoms. It is, however, obtainable from Messrs. Baird and Tatlock, London, E. C.

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