[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

A Semi Micro Gas Evolution Apparatus Applied to Kinetic Studies in Heavy Water[1]

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The rate of decomposition of nitramide ($H_2N_2O_2 = N_2O\uparrow + H_2O$) in solution recently has been subjected to an extensive experimental investigation by Marlies and La Mer[2] using a macro apparatus requiring a minimum of 100 ml. of solvent. This reaction seemed especially suited, from both an experimental and a theoretical point of view, to a precision study in heavy water media to ascertain the effects of deuterium substitution on prototropic reactions. The experimental problem, essentially, is to determine the rate of evolution of the gaseous decomposition product (nitrous oxide) with high precision despite the small quantities of heavy water available. The principle adopted in the later forms of macro apparatus,[2,3] *viz.*, of measuring the time change of pressure in a constant volume, was followed. Details of specific changes and improvements incorporated in the micro apparatus are given below.

The apparatus was immersed in a large glass-walled thermostat (T), as shown in Fig. 1, thus ensuring a constant temperature for the manometers as well as for the reaction flasks. Reaction flask (F), of 25-ml. capacity, was connected with the manometer system by four turns of 1-mm. i. d. thin-walled glass capillary, permitting a 1.9 cm. stretch of this glass spring. Several factors must be considered in designing the flask. The ratio of the space occupied by gas and by liquid (10-ml. samples of heavy water were used) should be as small as possible in order to keep the concentration of nitramide low and to permit rapid response of the manometer to pressure changes. Although this might be accomplished by using a flask of volume slightly larger than the contained solution, it is not advisable since the flask must be shaken vigorously, and sufficient surface exposed during shaking to secure rapid equilibrium between the solution and the gas phase. Furthermore, splashing of the liquid into the glass spring during shaking must be prevented. In the present apparatus these objects were attained simultaneously by pushing in the neck of the flask (N). Very vigorous shaking failed to cause any splashing into the side arm since the indented neck acts as an excellent baffle. The bottom center of the flask was blown out into a small depression (D), permitting removal of the last traces of solution after a measurement or during cleaning. The flask was fitted with the male part of the ground joint (B) (8–9 mm. i. d.) and a collar (C) for mercury. This arrangement gave a mercury sealed joint which prevented mercury from falling into the flask when the stopper was removed.

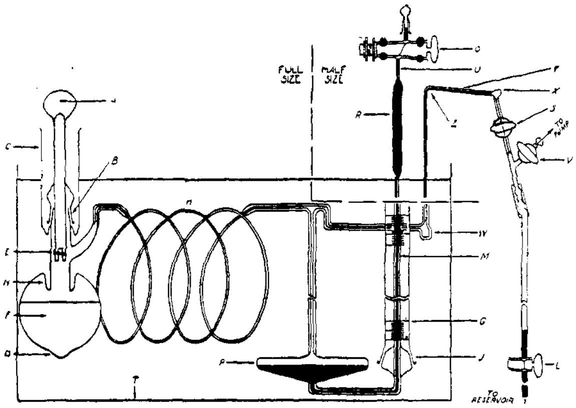

Fig. 1.

The manometer system consisted of a "pancake" (P) and a 1-mm. i. d. capillary (M) filled with mercury. The capillary (M) (33 cm. long) was not itself graduated but was surrounded by a graduated outer tube (G), (graduated in mm. with graduations at least half way around tube to prevent parallax errors) concentrically seated on the capillary by ground joint (J). The "dead space" increase caused by the mercury drawn from the "pancake" into the capillary as the pressure increases, necessitates a correction to the readings (Formula 6, Marlies and La Mer); the correction (column 3 of the table) amounted to 0.30 cm. for a pressure change of 30 cm. To make pressure changes register completely in the *capillary*, it is necessary to keep the "pancake" mercury level constant despite this flow of mercury. Therefore the ratio of "pancake" diameter (6 cm.) was made as large as feasible compared to the capillary diameter (1 mm.). The capillary tube was surmounted by an enlarged tube (R) of approximately 4-ml. capacity which served to minimize the effect of changing mercury level (or volume) on gas pressure at the blank end of the manometer. The upper end of the manometer was closed off with a diagonal-bore mercury-sealed pressure stopcock (O). The stopcock permits one to change the air pressure in the blank end of the manometer and thus adapt the outfit for measurements on solutions of high vapor pressure; in which case R should be immersed in the thermostat. The filling of the manometer is also simplified by stopcock O.

It was necessary to use a few drops of a mercury lubricant[4] consisting of dibutyl phthalate saturated with mercury *p*-ditolyl to prevent sticking of mercury in the capillary.

The pumping outlet consisted of a "Y" tube fitted with stopcocks. Evacuation was performed with the mercury control stopcock (L) closed, (S) and (V) being open until

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[1] Original manuscript received July 10, 1936.

[2] Marlies and La Mer, THIS JOURNAL, **57**, 1812 (1935).

[3] Brönsted and Duus, *Z. physik. Chem.*, **117**, 299 (1925).

[4] Hickman, *J. Opt. Soc. Am.*, **19**, 190 (1929); Marlies and La Mer, ref. 2, p. 1813.

the mercury in (R) fell to the level J; (L) was then opened and the mercury allowed to rise above (S) and (V). When the mercury reached point (Y), all stopcocks were closed, thus giving a mercury-sealed pumping outlet. Gas trap (X) and mercury well (W) were provided to take care of possible gas leakage from sealing mercury or accidental splashing of mercury around bend (Z).

With first order reactions, the bucket and sample may be dropped into the flask *before* the system is evacuated. The bucket dropper (Fig. 2) was used for this purpose. Since for second order reactions the initial concentration or time of addition is important, the system must be evacuated and sealed before the bucket is dropped into the solution. This was achieved by a magnetically controlled bucket release located in the stopper (A) of the flask. A rod (E), slotted vertically at its lower end, was sealed into the top of stopper (A)—incidentally, further reducing the "dead space." A hole was drilled across this groove at a 30° slope to the horizontal. A short platinum plated iron nail (with head) fitted the hole and supported the bucket; the weight of the platinum bucket and the downward tilt of the nail kept the bucket seated despite vigorous shaking. The sample was suspended on this mechanism, the stopper seated and the entire system sealed and evacuated.

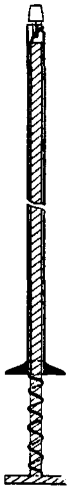


Fig. 2.

An electromagnet was applied outside the flask near the head of the nail to release the bucket. By adjusting dimensions so that its head touched the flask wall when the other end of the nail was not quite half way across the slot, the nail was prevented from falling into the solution.

A battery of four such instruments was used in this work, common pumping and mercury sealing manifolds being employed. The flasks, supported by brass clamps connected, through eccentrics, with a common shaft, were motivated by a rheostat control motor through a pulley drive.

Pedersen[5] has shown that for the prevention of supersaturation there is an optimum shaking speed and amplitude, depending upon the size and shape of the flask and upon the volume of solution employed. Individual amplitude adjustment for each flask was secured through the use of adjustable eccentrics (Fig. 3). The common shaft held a slotted brass disk. A grooved disk (3B), held against the face of (3A) by two set screws, was capable of being set at any point along the slot, varying the distance off center and thus the travel of the flask. A collar (3C) rode in the groove of this adjustable plate; it, in turn, was connected with the bearing supported rod (3D) holding the flask clamps. It is suggested that future models provide for interrupting the shaking of any one flask without affecting the others. In our work a speed and amplitude were chosen to make the liquid "break" over the indented flask neck.

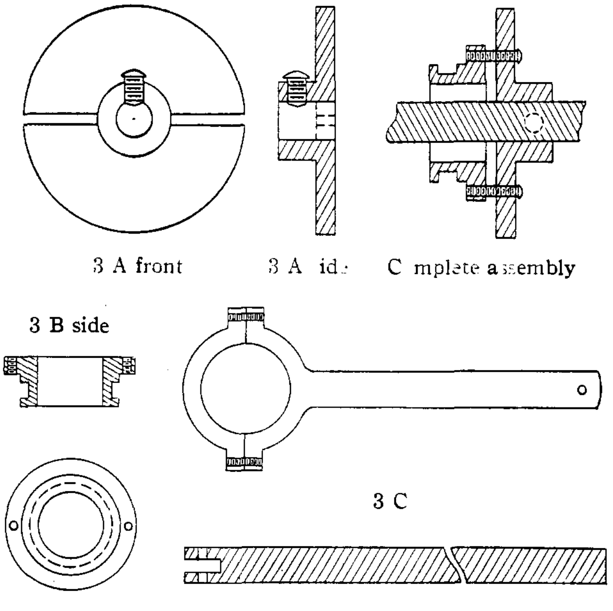
The capillary manometers were clamped together with strip brass at (P). A 110-volt a. c. buzzer was arranged to tap this strip during readings; the vibration transmitted to the four instruments offered additional assurance against sticking of mercury. A large grid type mercury regulator in conjunction with a vacuum tube relay, which controlled bulb heaters on the heating cycle, and a fan on the cooling cycle, maintained the temperature constant to ± 0.002° at 25°.

Dead Space Determination.—The "dead space" was determined by decomposing a weighed sample of zinc with 10 ml. of dilute hydrochloric acid; 0.0096 g. of zinc produced a pressure change of 11.77 cm. From these data one calculates the "dead space" to be approximately 23.2 ml.

Gas–Liquid Phase Equilibrium.—The rate of attainment of this equilibrium was determined at the conclusion of several of our experiments. The reactions studied reached completion in periods of from three to ten days. Since the thermostat and shaker were not in operation during such intervals, the solutions became either supersaturated or unsaturated with respect to the nitrous oxide. For the equilibrium determinations, these solutions were brought to 25° *without* shaking. Upon attainment of temperature equilibrium a reading ($t = 0$) was taken. Then a stop watch and shaker were started simultaneously and pressure readings observed at one minute intervals thereafter. A typical experiment gave

t	0	1	2	3	4	5	7	10
p	24.97	26.80	26.97	27.00	27.01	27.02	27.02	27.02

Equilibrium, here attained within four to five minutes, depending on the speed and amplitudes chosen, varied between two and five minutes. This is a rather long period and may be the origin of the fluctuations of the individual rate constants from the average (see below).



3 A front 3 A side Complete assembly

3 B side

3 C

3 B front 3 D

Fig. 3.

Leakage Tests.—No change in final readings greater than the experimental error of operation (± 0.01 cm.) was observed over periods of twenty-six days.

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(5) Pedersen, This Journal, **49**, 2681 (1927).

NITRAMIDE IN APPROXIMATELY 0.01 MOLAR HYDROCHLORIC ACID MEDIUM, 45.83% D_2O. $T = 24.84 \pm 0.002°$

$t_{\text{min.}}$	p	p, corr. for vol. change	$10^6k^* = \frac{\log(p_\infty - p_1)_{\text{corr.}} - \log(p_\infty - p_2)_{\text{corr.}}}{\Delta t}$
0	4.47	4.47	
15	5.13	5.13	647
30	5.80	5.80	671
45	6.42	6.42	635
60	7.04	7.04	650
75	7.66	7.66	665
90	8.25	8.25	647
105	8.83	8.84	662
120	9.41	9.42	665
135	9.99	10.00	681
150	10.52	10.53	637
165	11.05	11.06	651
180	11.58	11.60	679
195	12.09	12.11	656
210	12.60	12.62	671
225	13.10	13.12	674
240	13.56	13.59	647
255	14.01	14.04	635
270	14.48	14.51	677
285	14.91	14.94	634
300	15.35	15.39	679
315	15.79	15.83	679
330	16.20	16.24	647
345	16.60	16.65	662
360	16.99	17.04	645
375	17.36	17.41	625
390	17.72	17.78	639
405	18.10	18.16	671
420	18.48	18.54	687
435	18.82	18.89	647
450	19.17	19.24	662
465	19.50	19.57	705
480	19.81	19.88	613
495	20.15	20.23	709
510	20.47	20.55	663
525	20.77	20.85	635
540	21.07	21.16	672
555	21.36	21.45	635
570	21.64	21.73	635
585	21.91	22.01	649
∞	34.08	34.36	

(Least squares average) $10^6k^* = 657 \pm 18$
(A duplicate run) $10^6k^* = 647.7 \pm 3.8$

A typical experiment is given in the table.

It is important to emphasize that, although the individual fluctuations in one experiment are large, the results when submitted to the severe test of the difference calculation employed in column four of the table, are of a form which may arise through slow response of the manometer to pressure changes of the system. Thus a "sticking" of the mercury during one reading is canceled by an "overshot" subsequent reading, so that the averages of duplicate experiments are of much higher precision than are the individual values during any one experiment. Two experiments with the same solution were always performed simultaneously. The two values of the average rate constants, depending upon the solution used, agreed to within 0.1 to 2%. The micro apparatus thus yields results that approach closely in precision those obtained by the customary macro apparatus which requires ten times as much solvent.

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Summary

An all glass semi-micro apparatus suitable for high precision measurements on the rate of evolution of gases from 10 ml. of solution has been developed. Details of design are described, together with control tests and a typical experiment on the rate of decomposition of nitramide in heavy water solution.

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