

Studies in Chemical Kinetics

a Thesis by

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Part 1.

Studies of Exchange Reactions of Radioactive Isotopes

Introduction:

A process in which interchange of atoms of the same element takes place between two different compounds of that element we shall call an isotopic exchange reaction. The study of these reactions is made possible by the fact that the isotopes of a given element differ from one another in their chemical properties to only a very small extent. In order to carry out such a study, however, methods must be available for varying and for determining the amount of one isotope which is present in a mixture of isotopes of the same element. The method which was used in the investigations reported in the following pages is based on the fact that radioactive isotopes of most of the elements can be artificially produced by methods recently developed in nuclear physics - e.g. by bombardment of an element with neutrons or fast deuterons. If a radioactive isotope is to be useful for the study of an exchange reaction it is of course necessary that the "half-life" of the radioactive indicator be of the order of magnitude of the time required for the exchange reaction to occur to an appreciable extent and for the experimental manipulations to be made.

A detailed disquisition on the results at present available from the investigation of exchange reactions will not be given here, since excellent summaries of the experimental data so

far obtained by the use of radioactive isotopes as well as by other methods have recently been published (1,2). A brief description of the type of work which has been done will be given, however, in order to relate the results presented in the present dissertation to those obtained by other investigators.

The elements whose exchange reactions have been studied by the use of their radioactive isotopes include chlorine (with a radioactive isotope whose half-life is 37 minutes), bromine (three isotopes: half-lives of 18 minutes, 4.2 hours and 36 hours), iodine (25 minutes), sulphur (80 days), phosphorus (14 days), arsenic (26 hours), and manganese (166 minutes). Most of the work done has been of a qualitative nature; the results have shown whether a given exchange occurs rapidly, slowly, or not at all (within the time limits imposed by the half-life of the isotope used). Some very significant quantitative results have however been obtained by Hughes, Topley, and their co-workers who have shown that the rate of exchange of halogen between lithium bromide and α -phenyl ethyl bromide or between sodium iodide and secondary octyl iodide is equal to the rate of racemisation of the optically active organic halide by the metallic halide. This result gives fairly direct experimental evidence for the validity of the theory that racemisation proceeds by an exchange mechanism, with one inversion of the optical activity per exchange. Another investigation from whose results some significant conclusions can be

drawn has been carried out by Polissar, who showed on the basis of a study of exchange reactions of manganese between some of its compounds that the previously accepted mechanism for the oxidation of oxalic acid by permanganate could not be entirely correct. Some results of biological importance have been obtained by various investigators from a study of exchange reactions of phosphorus in organic compounds such as the phospholipids. These experiments have been conducted both in vitro and in living animals.

The investigations reported in the following pages include a study of the iodine-catalysed exchange of arsenic between arsenious and arsenic acids, an attempted exchange of phosphorus between phosphoric and phosphorous acids, and a study of a number of exchange reactions of bromine. It was possible to follow the arsenic reaction in detail, and to conclude that the kinetics of the reaction between arsenious acid and iodine are the same at equilibrium as they are remote from equilibrium. The phosphorus exchange was not found to occur to any measureable extent. No quantitative study was made of the rates of the exchange reactions of bromine which were investigated, but some new qualitative results were obtained.

Technique of Radioactivity Measurements:

The radioactive isotopes of bromine and of arsenic used in the experiments were prepared by the irradiation of appropriate materials with slow neutrons from a radon-beryllium source containing from fifty to two hundred and fifty millicuries of radon. Both source and target were placed near the centre of a paraffin sphere about 30 inches in diameter. The material was irradiated for a time chosen to give maximum activity in the sample, according

to the equation

$$t_{\max} = \frac{T_R}{0.693(T_R - T)} \ln_e \frac{T_R}{T}$$

where T_R and T are respectively the half-lives of radon and of the radioactive isotope being produced. The radioactivity measurements were made by means of a sensitive Lauritsen quartz-fiber electroscope filled with air at atmospheric pressure, with a capacity of about 0.13 cm. and a measured sensitivity of 1.0 volts per scale division, or about 5×10^5 ion-pairs per division. The sample to be measured was converted to a form in which it could be finely powdered; this powder was evenly packed into a cylindrical depression about one millimeter deep and five or seven centimeters in diameter in a flat brass sheet which could be placed in a reproduceable position directly below the aluminum window of the electroscope. The aluminum window was about 3.3×10^{-3} centimeters thick. The electroscope was calibrated for non-linearity of scale by the use of a uranium source. Several investigations which were carried out with the apparatus just described are reported in the following pages.

[Reprint from the Journal of the American Chemical Society, 59, 1358 (1937).]

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 592]

Measurement of a Reaction Rate at Equilibrium by Means of a Radioactive Indicator. The Reaction between Arsenic Acid and Iodine

BY J. NORTON WILSON AND ROSCOE G. DICKINSON

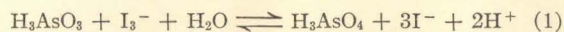
In the study of chemical kinetics and equilibrium, it is customary to correlate the specific rates k_f and k_r for a pair of forward and reverse reactions with the corresponding equilibrium constant K , in accordance with the equation

$$k_f/k_r = K$$

In making empirical tests of this relation, however, the specific rates k_f and k_r are in general measured with the system considerably displaced from equilibrium in order that accurate values may be obtained more easily. Hence it is of interest to appreciate that such methods do not eliminate the possibility that k_f and k_r might actually change as equilibrium is approached, but in such a way as to keep the ratio k_f/k_r approximately constant. The use of radioactive indicators, which have become an important chemical tool, permits the measurement of rates at equilibrium and thus makes it possible to place the ki-

netic theory of equilibrium on a sounder experimental foundation.

In the present paper are described some experiments involving reactions on which previous rate¹ and equilibrium² measurements have been made by customary methods; these reactions are the oxidation of arsenious acid by iodine, and its reverse



Experimental Procedure.—A radioactive arsenic with a half period of twenty-six hours is formed from ordinary arsenic by neutron capture.³ To utilize this we exposed 15 to 20 g. of pure crystalline arsenic (Kahlbaum) for two to three days to a radon-beryllium source of neutrons whose initial strength was 200 to 300 millicuries; the exposure occurred in a large block of paraffin. The arsenic

(1) J. R. Roebuck, *J. Phys. Chem.*, **6**, 365 (1902); **9**, 727 (1905); W. C. Bray, *ibid.*, **9**, 578 (1905); H. A. Liebhafsky, *ibid.*, **35**, 1648 (1931).

(2) E. W. Washburn and E. K. Strachan, *ibid.*, **35**, 681 (1931).

(3) F. A. Paneth and J. W. J. Fay, *Nature*, **135**, 820 (1935).

was then burned to arsenious oxide in a stream of air and a weighed amount of oxide dissolved in a measured volume of 1 N standard sodium hydroxide solution, which was then diluted to the desired concentration. The reaction mixtures were then prepared from standard solutions of arsenic acid, hydrochloric acid, and the radioactive arsenite.

The mixtures so prepared were brought to thermostat temperature and a measured volume of standard potassium iodide at the same temperature was added. The mixtures were such that at equilibrium comparatively little free iodine should be present. The color due to free iodine developed immediately on the addition of the potassium iodide and became constant within a minute or two, indicating a rapid approach of equilibrium.

The solutions were kept at a temperature constant to within 0.1° for a measured period of from four to seventeen hours. During this period exchange of radioactive arsenic between the tri- and pentavalent states occurred presumably through reactions with iodide and iodine. The exchange was then quenched by dilution with water and addition of an excess of ammonium hydroxide sufficient to make the solution 0.6 N in the latter reagent. The arsenate was then immediately precipitated as magnesium ammonium arsenate by the addition of magnesium-ammonium nitrate solution. The precipitate was washed with 0.6 N ammonium hydroxide, filtered, dried, and ignited to magnesium pyroarsenate which was then ground to a fine powder.

A fixed weighed amount of the powder was placed in a shallow cylindrical depression 0.1 cm. deep and 5 cm. in diameter in a thick sheet of brass; the powder was pressed down to fill the depression fully and evenly. The brass sheet was then placed in a reproducible position under a quartz fiber electroscope and the activity of the arsenic measured. Separate fillings of the brass container gave results with a maximum deviation from the mean of about 3% of the net activity. The electroscope was calibrated for linearity of scale. Natural leak was measured frequently and corrected for.

About one-fifth of the original radioactive arsenite solution was oxidized to arsenate with sodium hypobromite and was then precipitated, ignited, and its activity measured just as with the exchange samples. All activities were corrected to the same time using the half period twenty-six hours.

In some preliminary experiments the usual reaction mixtures containing arsenate, radioactive arsenite, and hydrochloric acid were made up with the omission of iodide. Even after the solution was boiled for three hours, the subsequently precipitated arsenate exhibited no activity. This shows that any direct exchange between the tri- and pentavalent arsenic is negligibly slow, and that the method of separating the arsenate did not itself induce exchange. Incidentally, a similar lack of exchange in alkaline solution (~1 N sodium hydroxide) was also found after three hours of boiling.

Treatment of Results

In the experiments described here, the initial concentrations of trivalent and pentavalent arsenic were not significantly different from the

equilibrium concentrations, and it is assumed that substantially all of the exchange occurred under equilibrium conditions; further justification for this is given below. We shall accordingly first obtain relations valid for the case where the initial solution is at chemical equilibrium.

Let α and β be the respective fractions (corrected for radioactive decay) of pentavalent and trivalent arsenic which are radioactive at any time t measured from the beginning of exchange; if initially only the trivalent arsenic is radioactive then at $t = 0$, $\beta = \beta_0$ and $\alpha = 0$. Let (As^V) and (As^{III}) be the total concentrations (at. wts. \times vol.⁻¹) of arsenic in the respective valence states. The total concentration of radioactive arsenic (corrected for decay) is $\alpha(As^V) + \beta(As^{III})$; since this remains constant, it follows that

$$\alpha(As^V) + \beta(As^{III}) = \beta_0(As^{III}) \quad (2)$$

Let R be the (constant) rate (atomic wts. \times vol.⁻¹ \times time⁻¹) at which arsenic passes from the trivalent to the pentavalent state or the reverse. Without reference to the orders of the reactions involved, the rate at which radioactive pentavalent arsenic is formed is given by the rate R at which trivalent arsenic passes to the pentavalent state multiplied by the fraction β of trivalent arsenic which is radioactive, *i. e.*, βR . Similarly the rate at which radioactive pentavalent arsenic disappears is αR . The net rate at which the concentration $\alpha(As^V)$ of pentavalent radioactive arsenic increases is the difference between these two terms, *i. e.*

$$(d\alpha(As^V)/dt) = (\beta - \alpha)R \quad (3)$$

Writing $(As) = (As^{III}) + (As^V)$, and substituting for β from (2), we obtain

$$\frac{d\alpha}{dt} = \frac{R}{(As^V)} \left[\beta_0 - \frac{(As)}{(As^{III})} \alpha \right] \quad (4)$$

Integrating, and inserting the condition $\alpha = 0$ at $t = 0$

$$R = - \frac{1}{t} \frac{(As^V)(As^{III})}{(As)} \ln \left[1 - \frac{\alpha}{\beta_0} \frac{(As)}{(As^{III})} \right] \quad (5)$$

Since α/β_0 as well as the other quantities on the right are measurable, R may be calculated for the particular solution used. In the present experiments the quantity α/β_0 has been taken as the ratio of the electroscopic activity of pyroarsenate from a solution which has exchanged for a time t to that of pyroarsenate from the original unexchanged arsenite.

On the assumption that a given arsenic atom passed from one valence state to another only

through oxidation or reduction by iodine or iodide, the rate R may now be identified with the rate of the oxidation of arsenious acid by iodine or the equal rate of reduction of arsenic acid by iodide.

The results of such experiments are given in the table. Columns 2 to 6 give the empirical composition of the solutions as made up. The empirically measured rates are given in moles \times liters $^{-1} \times$ min. $^{-1}$ in the column headed R .

oxidation may be tested by determining whether the rates of exchange depend on concentrations in the manner to be expected from Roebuck's kinetic studies. In order to do this, we have calculated specific rate constants for the reduction of As^{V} by placing $R = k(\text{H}_3\text{AsO}_4)(\text{H}^+)(\text{I}^-)_e$ the right-hand member being Roebuck's expression. As was done by Roebuck, we have taken $(\text{H}_3\text{AsO}_4) = (\text{As}^{\text{V}})$ and (H^+) as the formal hydrochloric acid concentration. The values of k thus

MEASUREMENT OF THE RATE OF
OXIDATION AND REDUCTION AT EQUILIBRIUM AND THE CALCULATION OF SPECIFIC RATE CONSTANTS

No.	H_2AsO_3	H_3AsO_4	Formula weights per liter			$(\text{I}^-)_e$	$(\text{I}_3^-)_e$	Activity, α/β_0	Time t , min.	Rate R , $\times 10^4$	Temp., $^\circ\text{C}$.	$k \times 10^4$, corr.
			HCl	NaCl	KI							
1	0.120	0.119	0.130	0.121	0.0091	0.0091	2.5×10^{-7}	0.062	952	0.85	25.0	6
2	.114	.113	.236	.114	.0086	.0086	6.5×10^{-7}	.072	617	1.43	25.0	6.2
3	.107	.100	.196	.100	.0408	.0407	4.5×10^{-5}	.226	555	5.38	25.2	6.7
4	.105	.098	.107	.100	.100	.099	1.9×10^{-4}	.333	732	7.80	25.2	7.4
5	.125	.273	.098	.081	.100	.099	4.5×10^{-4}	.265	789	20.3	24.6	7.9
6	.125	.406	.098	.081	.100	.098	7.1×10^{-4}	.208	657	31.1	24.6	8.2
7	.125	.203	.098	.081	.100	.099	2.6×10^{-4}	.280	839	12.6	24.6	6.5
8	.125	.273	.163	.081	.100	.097	1.0×10^{-3}	.212	361	27.8	24.6	6.6
9	.107	.099	.196	.100	.0405	.0403	6.1×10^{-5}	.256	278	12.6	35.0	16.1
10	.105	.098	.107	.100	.100	.099	3.1×10^{-4}	.350	408	14.1	35.0	13.7
11	.151	.096	.079	.074	.0536	.0536	1.8×10^{-5}	.342	713	6.75	35.1	16.5
12	.151	.096	.237	.074	.0107	.0107	1.2×10^{-5}	.231	1001	2.78	35.1	11.3

In the columns headed $(\text{I}_3^-)_e$ and $(\text{I}^-)_e$ are given the concentrations of I^- and of I_3^- in the various solutions at equilibrium. These were calculated for the runs at 25° using the constant²

$$K = \frac{(\text{H}_3\text{AsO}_4)(\text{H}^+)^2(\text{I}^-)^3}{(\text{H}_3\text{AsO}_3)(\text{I}_3^-)} = 5.5 \times 10^{-2}$$

For the runs at 35° a value of K (3.8×10^{-2}) was estimated from that at 25° , and that at 0° (1.6×10^{-1}) measured by Roebuck.¹ Here (H_3AsO_4) and (H_3AsO_3) have been taken as (As^{V}) and (As^{III}) , respectively, and (H^+) as the formal concentration of hydrochloric acid. This is adequate since $(\text{I}_3^-)_e$ was in all cases small and is needed only to calculate a small correction to $(\text{I}^-)_e$ and to show the small amount of reaction required to reach chemical equilibrium.

A more detailed analysis of the rate of exchange which considered the fact that I_3^- was initially absent rather than at its equilibrium concentration, led to an expression similar to (5) but with t replaced by $t - (1/a)(1 - e^{-at})$ where $a = R/(\text{I}_3^-)_e$. Because of the small values of $(\text{I}_3^-)_e$ in the experiments the use of this expression gives values of R differing by less than 1% from those given by equation (5).

The assumption that radioactive exchange occurred only through iodine-iodide reduction and

obtained are given in moles $^{-2} \times$ liters \times min. $^{-1}$ under k (corr.); a small temperature correction to 25° (or 35°) has been applied when the experiments were made at temperatures slightly different from these. At a given temperature the values of k show reasonably good constancy.

The assumptions may be further examined by comparing the absolute values of the constants with those of Roebuck.¹ As recalculated by Liebafsky, Roebuck's measurements of this specific rate give the values 6.3×10^{-3} at 0° and 1.6×10^{-2} at 10° (units: moles $^{-2} \times$ liters \times min. $^{-1}$). If these be extrapolated to 25° using the Arrhenius equation, the value 0.057 is obtained in satisfactory agreement with the mean value 0.071 from the exchange measurements; extrapolated to 35° , Roebuck's values give 0.125 and the exchange measurements 0.154.⁴ The Arrhenius heat of activation is calculated from Roebuck's measurements to be 14,300 cal. per mole; the exchange measurements give the value 14,100. It appears then that the radioactive exchange occurs mainly through the oxidation and reduction of the iodine, and that the kinetics of the oxidation and reduction at equilib-

(4) In calculating the mean values of k the results of experiments 1 and 2 have been omitted because of the small precision of α/β_0 ; experiment 12 also has been omitted.

rium are the same as those remote from equilibrium.

The authors are indebted to the W. K. Kellogg Radiation Laboratory at this Institute for the preparation of neutron sources used in this investigation.

Summary

Radioactive trivalent arsenic does not exchange with non-radioactive pentavalent arsenic in dilute acid or alkaline solutions in the absence of other easily oxidizable or reducible substances. In the presence of iodine in acid solution, however, an

exchange takes place at a measurable rate. On the assumption that the exchange occurs through the oxidation and reduction of the iodine, we have calculated the rates of oxidation and reduction at chemical equilibrium from measurements of rates of exchange in systems containing iodide ion and small amounts of free iodine. The rates of oxidation and reduction measured in this way are in agreement with the kinetic expressions shown by Roebuck to hold for the same reactions remote from equilibrium, and lead to specific rate constants which agree with those measured by him.

PASADENA, CALIF.

RECEIVED APRIL 7, 1937

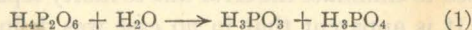
[Reprinted from the Journal of the American Chemical Society, 60, 2697 (1938).]

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 652]

An Attempted Exchange of Phosphorus between Phosphorous and Phosphoric Acids

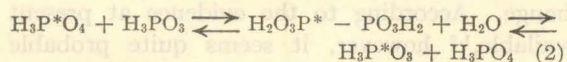
BY J. NORTON WILSON

The hydration of hypophosphoric acid, which takes place according to the equation



has been shown^{1,2} to proceed at a rate which is first order with respect to hypophosphoric acid and increases with increasing hydrogen ion concentration. It has been suggested¹ that this reaction is irreversible, but it seems probable that an equilibrium may be reached in which the concentration of hypophosphoric acid remaining is too small to be detected readily by chemical methods. If the structure of hypophosphoric acid is such that the phosphorus atoms are equivalent, as in the structure $(\text{HO})_2\text{P}-\text{P}(\text{OH})_2$, which has been

suggested on the basis of X-ray absorption spectra and chemical properties by Nylen and Stelling³ and by Hantzsch,⁴ the reverse of reaction (1) should lead to an exchange of radioactive phosphorus between phosphorous and phosphoric acids according to the following mechanism (the radioactive phosphorus atom is denoted by an asterisk)



An attempt has been made to detect this exchange using radioactive phosphorus⁵ obtained

- (1) Van Name and Huff, *Am. J. Sci.*, **45**, 103, 18 (1918).
- (2) Blaser, *Z. physik. Chem.*, **A167**, 441 (1934).
- (3) Nylen and Stelling, *Z. anorg. allgem. Chem.*, **212**, 169 (1933); *ibid.*, **218**, 301 (1934).
- (4) Hantzsch, *ibid.*, **221**, 63 (1934).
- (5) This material was supplied through the generosity of Professor Edwin McMillan of the Radiation Laboratory of the University of California.

as a by-product of the formation of radio-sulfur by bombardment of sulfur with fast deuterons. The material was separated from most of the accompanying sulfur and oxidized to phosphoric acid; a small amount of ordinary phosphoric acid was added as a carrier. The phosphate was precipitated as magnesium ammonium phosphate and converted to lead phosphate which was treated with hydrogen sulfide to liberate radioactive phosphoric acid. The reaction mixtures were made up from this material and "c. p." phosphorous and phosphoric acids. The phosphorous acid used was found to contain a small amount of phosphoric; this was determined and corrected for.

In order to determine whether exchange had occurred the mixture was diluted and the phosphate precipitated as magnesium ammonium phosphate; this was dissolved in acid and reprecipitated to remove co-precipitated phosphite. The phosphate precipitate was dried and its electroscopic activity measured. The phosphite contained in the filtrates was oxidized with bromine and similarly precipitated; the electroscopic activity of this precipitate was determined as before. Occurrence of activity in the latter precipitate would be evidence either of exchange or faulty separation.

The reaction mixtures were made up in duplicate; one of the pair, used as a blank, was subjected immediately after mixing to the separation process and radioactivity measurements described above; the other was sealed in a glass

ATTEMPTED EXCHANGE OF PHOSPHORUS BETWEEN PHOSPHOROUS AND PHOSPHORIC ACIDS: EXPERIMENTAL RESULTS

No.	(H ₃ PO ₄)	(H ₃ PO ₃)	Other reagents	<i>t</i> , min.	<i>T</i> , °C.	Activity PO ₃ , div./min.	Activity PO ₄ , div./min.	β/α_0	β/α_0 , blank
I	0.76	0.72		1440	100	+0.004 ± 0.005	0.79	(5 ± 6) × 10 ⁻³	± 6 × 10 ⁻³
II	.46	.43	NaOH, 2.86	1400	100	-.002 ± .005	0.92	(-2 ± 5) × 10 ⁻³	± 5 × 10 ⁻³
III	.60	.68	HCl, 5.31	11,500	100	+.006 ± .006	4.85	(1 ± 1) × 10 ⁻³	± 1 × 10 ⁻³
IV	.62	.70	HCl, 5.51	21,200	20-25	+.013 ± .006	4.20	(3 ± 1) × 10 ⁻³	± 1 × 10 ⁻³
V	.36	.35	HCl, 5.63	18,900	25	+.010 ± .010	49.0	(2 ± 2) × 10 ⁻⁴	(1 ± 1) × 10 ⁻⁴
VI	.36	.35	HCl, 5.63	37,900	25	+.006 ± .004	24.8	(2 ± 2) × 10 ⁻⁴	(1 ± 1) × 10 ⁻⁴

ampoule and allowed to stand for a convenient time before separation.

The probability of error due to faulty separation was greatly decreased in experiments V and VI in which after the precipitation and separation of the radioactive phosphate some inactive phosphoric acid equal in amount to that originally present in the solution was mixed with the phosphite in the filtrates and precipitated in the same way. This treatment should remove practically all of any radioactive phosphoric acid left in solution after the first precipitation. Measurement of the activity of the resulting precipitate indicated that about 0.1% of the radiophosphoric acid originally present was left in solution after the first precipitation. After the extra precipitation the phosphite in the filtrate was oxidized and precipitated as in the earlier experiments.

From the observed extent of an exchange occurring during the time *t* in accordance with the mechanism suggested in (2), one can calculate the rate at which reaction (1) and its reverse proceed at equilibrium. If the first order rate constant *k*₁ for the hydration of hypophosphoric acid is known, one can calculate from this result the equilibrium constant *K*, defined as $K = (\text{H}_4\text{P}_2\text{O}_6) / (\text{H}_3\text{PO}_4)(\text{H}_3\text{PO}_3)$. It may be shown that for the case where exchange occurs to a very small extent over a long time a good approximation is

$$K = \frac{2}{(\text{H}_3\text{PO}_4)_{k_1 t}} \frac{\beta}{\alpha_0} \quad (3)$$

where α_0 is the fraction of phosphoric acid initially radioactive corrected for radioactive decay to the time *t* and β is the fraction of phosphorous acid radioactive at time *t*.

In the following table are listed the concentrations, in formula weights per liter, of the reagents used in the experiments; the time *t* between the original mixing of the solutions and the separation of the phosphate; the temperature; the electroscopic activities of equal weights of the precipitates from the phosphite and phosphate fractions, corrected for radioactive decay and for the normal leak of the electroscopes; and the values of β/α_0 ,

which has been taken as the ratio of these activities. The values of β/α_0 for the "blank" experiments are also included. The normal leak of the electroscopes was about 0.07 division per minute; fluctuations about this value were large enough to make a comparatively large uncertainty in the value of the activity of the phosphite precipitate. This uncertainty was estimated from the root mean square deviation from the mean of a number of alternate measurements of the normal leak and the phosphite activity. The results of experiments V and VI are the most reliable because of the care used to eliminate the error due to faulty separation.

It is apparent that in no case was definite evidence of exchange obtained. It can be stated, however, that the extent of exchange was less than a certain value determined by the estimated uncertainty; on the basis of the assumptions made a limit can then be placed on the value of the equilibrium constant *K*. Thus in experiment VI, β/α_0 was very probably less than 5×10^{-4} ; *k*₁ for the given conditions may be estimated from the data of Van Name and Huff¹ to be 1.0×10^{-3} min.⁻¹. Then $K < 8 \times 10^{-5}$ mole⁻¹ liters at 25° in 5.6 formal hydrochloric acid.

Unfortunately, an alternative conclusion is possible: that the phosphorus atoms in hypophosphoric acid are not equivalent, as for instance in the structure $(\text{HO})_2\text{P}-\overset{\text{O}}{\parallel}-\text{P}(\text{OH})_2$ proposed on the basis of some slight chemical evidence by Blaser and Halpern.⁶ If this is the case it is unlikely that the reverse of reaction (1) would lead to exchange. According to the evidence at present available,^{1,2} however, it seems quite probable that the molecule contains two equivalent phosphorus atoms bonded to one another.

The author is grateful to Professor R. G. Dickinson for his advice, criticism and encouragement in connection with this investigation.

Summary

No exchange of radioactive phosphorus between

(6) Blaser and Halpern, *Z. anorg. allgem. Chem.*, **215**, 33 (1933).

Nov., 1938

ATTEMPTED EXCHANGE OF PHOSPHORUS IN ITS ACIDS

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phosphorous and phosphoric acids in acid or alkaline solution was found to occur beyond the limits of experimental error. The results indicate that if the phosphorus atoms in hypophosphoric acid are equivalent, the equilibrium constant for the

formation of hypophosphoric acid from phosphorous and phosphoric acids is less than 8×10^{-5} mole⁻¹ liters at 25° in 5.6 formal hydrochloric acid.

PASADENA, CALIF.

RECEIVED JUNE 13, 1938

Part 1 (c)

Exchange Reactions of Radioactive Bromine

An attempt was made to find a simple isotopic exchange reaction whose rate could be conveniently measured, in the hope that the relative chemical simplicity of such a reaction might permit a straightforward interpretation of the observed rates. The attempt was not a successful one, but did lead to the discovery of some exchange reactions not previously reported. Brief investigations were made of exchange reactions of radioactive elementary bromine in carbon tetrachloride solution with the following substances: stannic bromide, arsenous bromide, ethylene dibromide, and trichlorobrom methane, the last both thermally and photochemically.

Preparation of reagents:-

Carbon tetrachloride:- A good grade of carbon tetrachloride which had been purified with aqua regia and carefully distilled was dried with P_2O_5 and redistilled. The fraction boiling within a temperature range of $0.2^\circ C$ was retained.

Ethylene dibromide:- A student preparation was washed with distilled water, dried over P_2O_5 and distilled, the fraction boiling in the range $130-132^\circ C$ being retained.

Bromine:- The best commercial grade obtainable was distilled over sodium bromide and then from P_2O_5 in an all-glass still.

Stannic Bromide:- This compound was prepared by cautiously adding small pieces of pure tin to a solution of 29 grams of

bromine in 72 grams of carbon disulfide. After 7.5 grams of tin had been added the mixture was allowed to stand at room temperature for four hours. The solution was decanted into an all-glass still and the carbon disulfide was distilled off, with some of the bromine. Attempts to remove the bromine completely by distillation resulted in appreciable losses of stannic bromide. The removal of bromine was therefore accomplished by adding carbon tetrachloride and distilling, the bromine being carried over with the carbon tetrachloride. The remaining material, which was nearly colorless, was distilled, the fraction boiling between 202° and 203.5°C being retained. Redistillation of this material yielded a colorless material with a sharp melting point and a distillation range of 0.2°C.

Arsenic tribromide:- A Kahlbaum product was purified roughly by distillation, the fraction boiling between 211 and 217°C being retained.

Trichlorobrom methane:- A solution of sixty grams of sodium hydroxide in 250 ml. of water was added at room temperature to 30 cc. of alcohol-free chloroform. The mixture was cooled to 5°C and 85 grams of bromine were added. Preliminary experiments showed that unless a considerable excess of sodium hydroxide is present the reaction is agonizingly slow; under the conditions described above the reaction is about two-thirds complete in thirty hours. The mixture was stirred for three days in an ice-bath; the non-aqueous layer was separated and

distilled, dried with barium perchlorate and twice distilled through a fractionating column. The final product was colorless and boiled at 104.8°C, the boiling point being constant within 0.2°C.

Radioactive Bromine:- For the experiments with ethylene bromide, arsenous and stannic bromides, radioactive bromine was prepared by direct exposure of elementary bromine in a soft-glass container to slow neutrons in paraffin. About 15 grams were irradiated at a time. Solutions of this material in carbon tetrachloride were made up by direct weighing.

Exchange Experiments with Ethylene Bromide:-

Solutions of ethylene bromide and radioactive bromine in carbon tetrachloride were prepared by direct weighing. Weighed amounts of these solutions were mixed in a glass ampoule which was then sealed, brought to an appropriate temperature in the dark, and kept under these conditions for a convenient time. The ampoule was cooled and opened; its contents were transferred to a glass-stoppered flask and shaken with 4 N. sodium nitrite solution until the organic liquid was colorless. This process required about four minutes. Preliminary experiments showed that the effect of sodium nitrite on the alkyl bromide under these conditions was negligible. The aqueous layer was then separated from the organic material and made approximately 1 N in ammonium hydroxide. The bromide was then precipitated as silver bromide; the solution was heated to boiling and filtered. The precipitate was washed with hot water, dried in an oven at 130°C, weighed, and powdered in a mortar. The

electroscopic activity of a known weight of this powder was then determined and compared with that of a sample of silver bromide prepared in the same way from an equal quantity of the original solution of radioactive bromine used as a "blank". The apparent extent to which exchange had occurred could be determined by a comparison of the electroscopic activities of the two precipitates per gram of silver bromide, corrected for radioactive decay to the same time.

As is shown in the detailed results tabulated below, no exchange beyond the limits of experimental error was found to occur. The precision of the experimental method was not sufficiently great to allow any significance to be attached to the increase in apparent extent of exchange with increasing temperature and time of reaction. The extent of exchange is expressed as percent of complete exchange.

Table

Results of Thermal Exchange Experiments with Bromine and Ethylene Bromide.

	Conc. of Br_2 in solvent (mol percent)	Conc. of $\text{C}_2\text{H}_4\text{Br}_2$ (mol percent)	Temperature $^{\circ}\text{C}$	Time (min).	Apparent Exchange (percent)
a)	7.0	8.8	25	114	0.0 ± 5
b)	24	28	100	30	0.6 ± 5
c)	24	28	100	65	3.3 ± 5

Exchange Experiments with Arsenous and Stannic Bromides:-

Reaction mixtures were made up as before by mixing weighed amounts of carbon tetrachloride solutions of radioactive bromine and the metallic bromide, but were subjected immediately after mixing to vacuum distillation at 20°C, the temperature being maintained roughly constant by means of a water bath, until all the bromine had been removed. This process was completed about thirty-five minutes after the original mixing of the solutions had occurred; the stannic or arsenous bromide remained in the distilling flask. In the case of stannic bromide the residue was dissolved in cold water; the resulting solution was hydrolysed by boiling and decanted through a filter. The bromide in the filtrate was precipitated as silver bromide and prepared for radioactivity measurements in the manner previously described. The residue of arsenious bromide was dissolved in hot water and the solution was made alkaline with ammonium hydroxide. Silver bromide was then precipitated directly from this solution. The occurrence of radioactivity in these precipitates would give direct evidence of the occurrence of an exchange. As before, a precipitate of silver bromide was prepared for comparison purposes from an appropriate quantity of the original solution of radioactive bromine.

The results obtained were as follows:

- (a) With a solution which was 2.3 mol % AsBr_3 and 3.6 mol % Br_2 at 25° C., the time elapsing between the initial mixing of the solution and the con-

clusion of the bromine distillation was 30 minutes. The apparent extent of exchange was 101 %.

- (b) With a solution which was 2.0 mol % SnBr_4 and 4.2 mol % Br_2 at 25°C , the time required for separation was 35 minutes and the apparent extent of exchange was 110 %.

In both these cases then the exchange was apparently complete in the time required for separation. The possibility must not be forgotten, however, that a small amount of water present as an impurity may have been responsible for the rapidity of the exchange.

Experiments with Trichlorobrom methane.

The first experiments were conducted in the same way as the experiments with ethylene bromide, except that the bromine was extracted from the organic material by shaking with 1 N sodium hydroxide solution. This extract was treated with nitrous acid to reduce the hypobromite to bromide which was then precipitated from ammoniacal solution as silver bromide. If any exchange occurred in these experiments it was within the limits of experimental error.

Experiments were then made to determine whether the exchange could be induced photochemically. A photochemical exchange was indeed found to occur, but its detailed study was abandoned because of experimental difficulties. The experimental technique will be described in some detail, however, since some of the methods which were developed for handling radioactive bro-

mine may be of value to anyone interested in a further study of this, or similar reactions.

The high absorption coefficient of bromine for visible light and the length of time required for the experiments necessitated the preparation of dilute solutions of highly radioactive bromine. For this purpose the radioactive bromine resulting from the exposure of 200 to 300 grams of ethylene bromide in a soft glass vessel to slow neutrons for a period of 24 to 48 hours was extracted according to the method of Erbacher and Philipp (4) by shaking the liquid for about ten minutes with a dilute aqueous solution of sodium bromide (about 3×10^{-4} formal). This extract was then evaporated to a volume of one or two cc., cooled, and shaken for twenty minutes with 10 to 20 cc. of a solution of bromine in carbon tetrachloride (0.01 to 0.1 formal). In the resulting exchange reaction most of the radioactivity went into the carbon tetrachloride solution. The solution of radioactive bromine thus obtained was separated from the aqueous layer, dried by shaking with P_2O_5 , and distilled in an all glass still. The time elapsing between the removal of the ethylene bromide from the neutron source and the conclusion of the distillation of the radioactive bromine solution was about one hour and thirty minutes. The amount of activity to be expected in the bromine solution resulting from such a treatment may be estimated from the results of an experiment in which a 150 gram sample of ethylene bromide was exposed to a neutron source, initially estimated to contain 35 millicuries of radon, for 74 hours,

this being the time required for the bromine isotope with 36-hour half period to reach its maximum concentration. The radioactive bromine was extracted by shaking the liquid for six minutes with a solution of 1.0 gram of sodium bromide in 30 cc. of water. The aqueous layer was separated and the sodium bromide obtained by evaporation to dryness. Analysis of the measured radioactivity of this sodium bromide as a function of time enabled an estimate to be made of the total electroscopic activity at the time exposure to neutrons ceased, and of the distribution of the responsibility for this activity among the various radioactive bromine isotopes.

Half period of bromine isotope	Estimated electroscopic activity at time exposure stopped	Fraction of total activity
18 minutes	8.15 div./min.	0.74
4.2 hours	2.14 div./min.	0.19
36 hours	0.77 div./min.	0.07
"Normal leak" of electroscope	0.07 div./min.	

By way of comparison it may be remarked that exposure of 15 grams of pure bromine to the same neutron source, using the methods described for the preparation of radioactive bromine for the experiments with ethylene bromide, would be expected to yield a total activity of 1.5 div. per minute or less: a much smaller total activity distributed over a much larger amount of bromine. Evidently the use of the concen-

tration technique described above is well worth while, in spite of the extra time involved.

Since the preliminary experiments previously described had shown the rate of the thermal exchange reaction to be negligibly small, the photochemical experiments were conducted as follows:- The reaction solution was made up in a blackened 50 cc. volumetric flask using the dilute solution of radioactive bromine, a measured volume of a standard solution of trichlorobrom methane, and enough carbon tetrachloride to make the total volume 50 cc. After mixing, the solution was analysed for bromine by titrating a few cc. with thiosulfate after treatment with potassium iodide. The solution was then separated into halves, one for use as a "blank", the other for exposure to light. In view of the fact that the presence of oxygen is known to exert an important influence on the rate of some photochemical halogenation reactions (5)(6)(7) an effort was made in most of the experiments to eliminate most of the air from the reaction vessels in the following way: the whole solution of trichlorobrom methane and bromine was sealed in a 250 cc. Erlenmeyer flask connected by glass tubing to a vacuum system and to two smaller flasks, one of these being a photochemical reaction vessel. The solution was frozen with liquid air and the system was evacuated by means of a Hyvac mechanical pump. It is doubtful whether the partial pressure of air in the system was reduced below about 1 mm. of mercury. The three interconnected flasks were then sealed off from the vacuum

system; the solution was allowed to melt, was mixed by shaking, and transferred to the smaller flasks, approximately half the solution going to each. The smaller flasks were then sealed off from the rest of the system. All these operations were performed in semidarkness. The photochemical reaction vessel, which now contained half the solution, was transferred to a thermostat and, after a suitable time had elapsed for temperature equilibrium to be reached (about twenty minutes) was exposed to light. The flask containing the other half of the solution, which was to serve as a blank, was kept in the dark at approximately the same temperature during this time. After the exposure to light was completed, both solutions were cooled with ice. The flasks were then opened and their contents were transferred to glass-stoppered dark bottles; each of the solutions was then analysed for bromine by titrating a few cc. with thiosulphate in the presence of potassium iodide. Equal volumes of the two bromine solutions were now measured out with a pipet and shaken with 5 cc. of 1 N sodium hydroxide solution until colorless. The aqueous extracts were diluted to 100 cc. and separated from the organic material. These operations were also carried out in semidarkness. Since the amount of bromine in these extracts was insufficient to yield a convenient amount of silver bromide precipitate for radioactivity measurements, 25.0 cc. of 1 N sodium bromide (non-radioactive) was now added to each solution. This was followed

by 5 cc. of 1 N sodium nitrite. Each solution was made slightly acid with nitric acid, boiled, and made alkaline with 5 cc. excess of 6 N ammonium hydroxide. Silver nitrate solution was added and the resulting precipitate of silver bromide prepared for radioactivity measurements. The extent to which exchange had occurred was calculated from the relative electroscopic activities of equal weights of the precipitates prepared from the "blank" and from the solution which had been exposed to light, corrected for the difference, if any, in the measured concentrations of bromine in the "blank" and the "reaction" solutions.

The photochemical reaction cell had the shape of a flat cylinder about 2.0 cm. thick and 3.7 cm. in diameter, with a glass side-tube which served for filling the cell and also for the accommodation of a magnetically operated stirrer. The reaction cell was suspended in an air thermostat and illuminated with the roughly collimated beam from a 500 watt tungsten lamp running at 100 volts. It is estimated that about 0.8 % of the radiation emitted by the lamp entered the collimating system where it was passed through a filter transmitting chiefly in the spectral region from 5000 to 6100 Å. No measurements of the amount of light absorbed in the reaction cell were made, for reasons which will appear later.

A test of the technique was made by carrying out a thermal exchange reaction in the same way: the solution was prepared

as for the photochemical experiments and separated in vacuo into two parts, one of which was immediately subjected to the extraction process described above, while the other was kept in the dark at a high temperature for a convenient time before receiving the same treatment. As was expected from the preliminary experiments, the radioactivity measurements indicated that no exchange beyond the limits of experimental error had occurred. Nevertheless, it was not found possible to reproduce the results of the photochemical experiments, and the attempt to study the photochemical reaction in detail was abandoned because of the excessive labour involved in each experiment and the difficulty of doing precise work with the speed necessitated by the short half-life of radioactive bromine. If further work is to be done with this reaction a set of conditions will have to be found under which rate measurements can be made, and some improvements in technique will be required. The difficulty in reproducing the experiments may be partly due to a difference in the concentration of CCl_3Br in the two portions into which the original solution is divided, corresponding to the observed difference in the corresponding bromine concentrations. This effect may be overcome by proper temperature equalisation in the system in which the ^{division}~~separation~~ is made. The need for and effectiveness of the treatment for the removal of oxygen must also be studied.

The experimental results given in the following tables indicate that a photochemical exchange does occur, and that

under the conditions of experiments 8 to 13 inclusive it is practically complete in the time allowed. Comparison of experiment 2 with experiments 4 to 9 inclusive suggests a reasonably high temperature coefficient. The result of experiment 3 is probably due to some gross experimental error. Comparison of the results with one another indicates that in experiments 9 and 12 exchange was probably 100 % complete, and that the experimental error is of the order of 15 %.

Results of Exchange Experiments with Bromine and Trichlorobrommethane

Thermal Experiments

Experiment	Conc. of Br ₂ in Reaction Solution (moles/liter)	Conc. of Br ₂ in blank (moles/liter)	Conc. of CCl ₃ Br (moles/liter)	Temp. °C.	Time (min.)	Apparent Ex- tent of Ex- change (percent)	Estimated Un- certainty
1	0.36		0.62	25°	4	-5 ± 10	10%
2	0.6		0.62	95°	40	7 ± 10	10%
3	0.3		1.00	115°	50	9 ± 10	10%
4*	0.00320	0.00328	0.0824	76°	70	-3 ± 10	15%

*The same technique was used in this experiment as in the photochemical experiments

Photochemical Exchange Experiments with Bromine and Trichlorobromethane

Experiment	Conc. of Br ₂ in reaction solution (moles/liter)	Conc. of Br ₂ in blank (moles/liter)	Conc. of CCl ₃ Br (moles/liter)	Temp. °C	Time of ex- posure to light (min.)	Apparent ex- tent of Exchange
5*	0.0035	-----	0.040	30	40	86%
6	0.008	-----	0.039	30	160	4%
7	0.0054	0.0063	0.0412	76	25	11%
8	-----	0.0033	0.0324	76	75	98%
9	0.0034	0.0038	0.0206	76	20	86%
10	0.0033	0.0037	0.0206	76	20	97%
11	0.0031	0.0036	0.052	76	40	100%
12	0.0045	0.0048	0.040	100	25	85%
13	0.0051	-----	0.039	100	86	100%

* The light used in this experiment was not filtered.

Summary:-

The results of this section may be summarised as follows: no definite evidence was found for the occurrence of thermal isotopic exchange of bromine between bromine and trichlorobrom methane or ethylene dibromide in carbon tetrachloride solution. A thermal exchange between bromine and arsenous bromide or stannic bromide, and a photochemical exchange between bromine and trichlorobrom methane were found to occur readily in carbon tetrachloride solution.

Part 2:-

The Rate of the Reaction between Phosphorus
Trifluoride and Chlorine.

Many years ago Moissan (8) discovered that gaseous phosphorus trifluoride combines in glass vessels with chlorine according to the equation



The reaction was later studied by C. Polenc (9), who was unable to find any other products and demonstrated by very rough volume measurements that the reaction appears to go to completion according to the above equation at room temperature.

In the present report are presented the results of a study of the kinetics of this reaction, which was investigated in the hope that it might be bimolecular. Unfortunately for this hope, the reaction proved to be heterogeneous.

The phosphorus trifluoride used in these experiments was kindly prepared by Prof. Don M. Yost by a method which he has described elsewhere (10). The purified material was obtained as needed from a large Pyrex storage bulb through a stop-cock. Moissan (8) has shown that in the presence of a trace of water vapour phosphorus trifluoride attacks glass rapidly; since the storage bulb used in these experiments showed no evidence of such action even after several months, the gas was probably quite dry. Commercial tank chlorine was used; the gas was washed with potassium permanganate solution, passed through

a long calcium chloride tube and was condensed by means of liquid air into small weighed Pyrex bulbs with capillary tips.

The reaction was followed in an all-glass system by pressure measurements made by means of a glass diaphragm "click" gauge backed by a mercury manometer.

Experiments 2 to 10 inclusive were made at 0°C according to the following technique: a Pyrex reaction vessel, whose volume was about 300 cc., was evacuated by means of a mercury diffusion pump to a pressure of 10^{-5} mm. while being baked at 150°C. A dry-ice trap was interposed between the reaction vessel and the pumps. The connection to the pumps was then closed off by means of a stop-cock, and a sample of phosphorus trifluoride was introduced from the storage bulb into the reaction vessel and its connecting tubing, whose volume was about 30 cc. The pressure of the gas at room temperature was then measured, and the sample was condensed by means of liquid air into a small side tube sealed into the reaction vessel. A glass bulb containing a known weight of chlorine was then broken with a magnetic hammer which was located near the reaction vessel as part of the connecting tubing referred to above. The chlorine diffused into the reaction vessel where it was condensed with the phosphorus trifluoride. When pressure measurements showed that all the chlorine had been condensed the reaction bulb was sealed off from the rest of the apparatus and the reactants were allowed to evaporate into the reaction vessel which was immediately surrounded by an ice

bath. The reaction was then followed by means of pressure measurements.

The initial pressures of the reactants were calculated from the initially measured pressure of phosphorus trifluoride in the reaction vessel and its connections, the known weight of chlorine, and the accurately known volumes of the reaction vessel and of its connections. The vapors were assumed to act as perfect gases.

After the completion of an experiment the products were condensed in the side-tube which was then sealed off. It was observed that the condensed products on warming up to room temperature formed a liquid which rapidly attacked the glass containing it; small flocks of fluffy white material began to appear in the liquid and increased in amount until within a few hours the initially clear liquid contents of the tube were replaced by a gelatinous mass which was white or yellow depending on whether phosphorus trifluoride or chlorine had been present in excess in the reaction mixture. The nature of this reaction was not investigated; its occurrence may indicate that a trace of water vapor was present. Polenc (9) observed that dry gaseous PF_3Cl_2 does not attack glass noticeably at room temperature; slight etching of the reaction vessel used in these experiments was noticed only after several runs had been made, each extending over several days.

When the reaction vessel was opened after a run a faint cloud of smoke usually formed from the hydrolysis of PF_3Cl_2

which had not been frozen out with liquid air. For this reason the reaction vessel was washed with distilled water between successive runs. This precaution was not taken between runs 2 and 3; the hydrolysis products present on the walls of the reaction vessel accelerated the reaction in run 3 considerably.

When the technique just described was used it was found that from 20 % to 50 % of the reaction occurred before the first pressure measurement could be made, presumably because of a rapid reaction taking place in the liquid phase while the reactants were evaporating from the side-tube in which they had been condensed together. This rapid reaction in the liquid was also observed in a separate experiment in which chlorine and excess phosphorus trifluoride were condensed together in a small glass tube which had been evacuated. The tube was then sealed off and allowed to come to room temperature. The yellow color of chlorine in the liquid disappeared very rapidly.

That part of the reaction which could be followed by means of pressure measurements appeared to be roughly first order with respect to each reactant, with a specific rate roughly proportional to the specific surface of the vessel. In order to study this latter effect the specific surface was varied from about 0.9 cm.^{-1} to 5.7 cm.^{-1} , the larger value being obtained with a reaction vessel packed with thin glass rods over which the gaseous contents were circulated

by means of a glass piston with an iron core actuated by a solenoid. Some attempts were made to vary the nature of the surface: in experiment 9 the reaction vessel was rinsed with a solution of potassium chloride, drained, dried, and baked in vacuum; in experiment 10 the inside of the reaction flask was silvered chemically and treated with chlorine to leave a coating of silver chloride, and was then rinsed with distilled water, dried, and baked under vacuum. The results of experiments 2 to 10 will be discussed later and the technique used in carrying them out will be referred to as the "first technique".

With such a large part of the reaction occurring in the liquid phase it appeared unlikely that it would be possible with the technique just described to study the reaction in a satisfactory way over a wide range of initial pressures. Experiments were then carried out using a reaction vessel within which the chlorine bulb could be broken. A convenient amount of phosphorus trifluoride was introduced into the previously evacuated reaction vessel and condensed in a side-tube. The reaction vessel was then sealed off from the rest of the apparatus and the phosphorus trifluoride was allowed to evaporate. A water thermostat operating at 25°C was then raised around the reaction vessel by means of pulleys and a counterweight, and the initial pressure of phosphorus trifluoride was measured. The glass bulb containing a weighed amount of chlorine was broken, and the initial pressure was measured as soon as the chlorine had vaporised. In this case very little

reaction occurred before the first pressure measurement was made; hence the whole course of the reaction could be followed. Unfortunately, however, the experiments carried out according to this procedure were much less reproducible than those made with the first technique, possibly because it was now impossible to bake out the reaction vessel since it contained a bulb of liquid chlorine. A small and variable amount of water remaining adsorbed on the glass surfaces may have been responsible for the variations which were observed in both the magnitude of the specific rates and in the character of the kinetics.

The specific rates measured at 25°C by this method, and calculated on the basis of a rate first order with respect to each reactant, were considerably smaller than those measured at 0°C by the first technique; to ascertain whether the apparent negative temperature coefficient was entirely due to the change in experimental procedure an experiment (No. 15) using the second technique was run for a time at 25°C and the temperature was then lowered to 0°C, whereupon the rate of reaction increased by nearly a factor of two. In the same experiment the reaction mixture was later illuminated for a time with a 100 watt electric light and reflector placed adjacent to the reaction vessel; the resultant increase in specific rate indicated that the reaction is somewhat photosensitive. In all other experiments made with either the first or second technique, the reaction vessel was protected from light by means of a black cloth. Experiment 16 was conducted using

a reaction vessel whose inner surface was coated with paraffin. In this case the decrease in pressure was very slow, and may well have been due to reactions other than the combination of chlorine and phosphorus trifluoride. This result indicates that the rate of the homogeneous reaction is negligible compared to that of the heterogeneous reaction at 25°C.

In the following table are listed the temperature, the initial pressures p° of the reactants, and the average apparent second order rate constant \bar{k}_2 , an average of the values calculated from point to point by means of the expression $k_2 = \frac{-1}{P_{PF_3}P_{Cl_2}} \frac{\Delta p}{\Delta t}$. In the column headed $\bar{k}_2 \frac{V}{S}$ are tabulated the values of \bar{k}_2 divided by the specific surface (here V is the total volume of the reaction vessel and S its total surface.) The extent of the deviations from a second order rate expression is shown in the curves in Figure 1, in which the reciprocal of $k_2 \frac{V}{S}$ is plotted against the total pressure p . These curves cover the range over which measurements were made, and may therefore be used to calculate the fraction of the reaction which occurred before pressure measurements were started. Additional information of this kind is furnished by columns in the table which contain values of k_2 averaged over various ranges of the reaction: 0 to 20 % completion, 20 to 40 % etc.

A study of the table and the curves leads to the following observations: at 0°C there is approximate agreement between experiments 2, 4, and 8, which were made in vessels whose surfaces had been treated in approximately the same way,

i.e. by washing with distilled water after a previous run, drying, and baking under vacuum. In these experiments the apparent second order specific rate remained approximately constant during the run, and there is fair agreement between values of $\bar{k}_2 \frac{V}{S}$ from one experiment to another, though the specific surface varied from 0.90 in experiments 2 and 4 to 5.7 in experiment 8. The rate therefore appears to be proportional to the specific surface so long as the nature of the surface remains the same. In experiment 5, in which the reaction took place on new glass, the value of $k_2 \frac{V}{S}$ is seen to increase as the pressure decreases in approximately a linear manner; in experiment 7, in which the surface was 25 % glass which had been treated as in experiment 2, and 75% new glass, the curve is seen to be intermediate between 2 and 5, and perhaps by coincidence to be very nearly the curve which would be obtained by adding 25 % of 2 and 75 % of 5. These results indicate that the rate on new glass follows a different expression from that on used and washed glass, and that it can be represented at the pressures used as

$$-\frac{dp}{dt} = A \frac{P_{PF_3} P_{Cl_2}}{1 - ap}$$

where "A" and "a" are constants. The reaction was not studied over a sufficient range of initial pressures to allow the significance of the constant "a" to be determined. The rate expression just given may however be reasonably interpreted as indicating that the reaction is retarded by adsorption of

PF_3Cl_2 on the new glass surface.

The reaction appears to go faster on a silver chloride surface than on glass (Experiment 10). On the other hand the behaviour of the reaction on glass treated with KCl (Experiment 9) is surprisingly similar to that on glass treated as in experiments 2, 4, and 8. This fact is in contrast with the results of Pease (11) who found that the same treatment of the surface of glass reaction vessels with KCl decreased the velocity of oxidation of methane by a factor of ten.

The lack of consistency among the results of the experiments at 25°C is very evident from the table and graphs presented at the end of this section. The occurrence of extrema in the curves showing the reciprocal of $k_2 \frac{S}{V}$ as a function of the total pressure p indicates that the data for any one experiment made with the second technique cannot be fitted by a single term of the familiar Langmuir rate expression(12). This last statement may be verified by investigating whether the expression $\frac{d}{dp} \left\{ \frac{P_{\text{PF}_3} P_{\text{Cl}_2}}{dp/dt} \right\}$ may become zero if the rate expression has the form

$$-\frac{dp}{dt} = K \frac{P_{\text{PF}_3} P_{\text{Cl}_2}}{\left\{ 1 + a_1 P_{\text{PF}_3} + a_2 P_{\text{Cl}_2} + a_3 P_{\text{PF}_3} \text{Cl}_2 \right\}^n}$$

where a_1 , a_2 , a_3 and K are constants at a given temperature, n is an integer which may assume the values 0, 1, or 2, and the partial pressures P_{PF_3} etc. are given in terms of the initial pressures $P_{\text{PF}_3}^0$ etc. and the total pressure p by the equations:

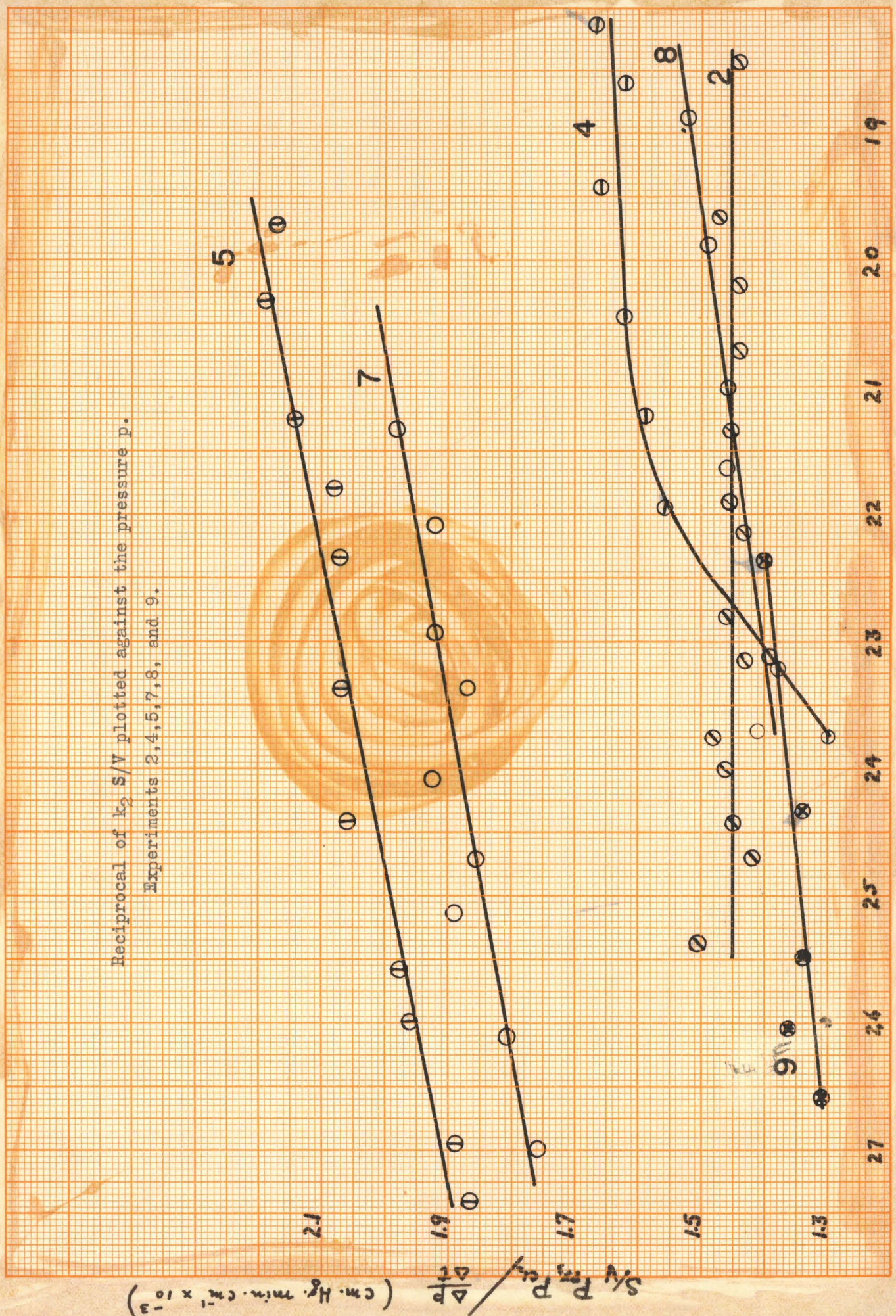
$$P_{\text{Cl}_2} = p - P_{\text{PF}_3}^0; P_{\text{PF}_3} = p - P_{\text{Cl}_2}^0$$

$$P_{\text{PF}_3} \text{Cl}_2 = P_{\text{PF}_3}^0 + P_{\text{Cl}_2}^0 - p$$

In all the experiments at both 0°C and 25°C (except that in the paraffined vessel) the final pressure approached within 1 % the pressure calculated for complete reaction. No analysis was made of the products.

Because of the difficulty of even approximately reproducing the experiments unless observations were limited to only the latter part of the reaction the work was discontinued. No attempt will be made to discuss the mechanism of this apparently very complicated reaction on the basis of the meagre experimental results reported here.

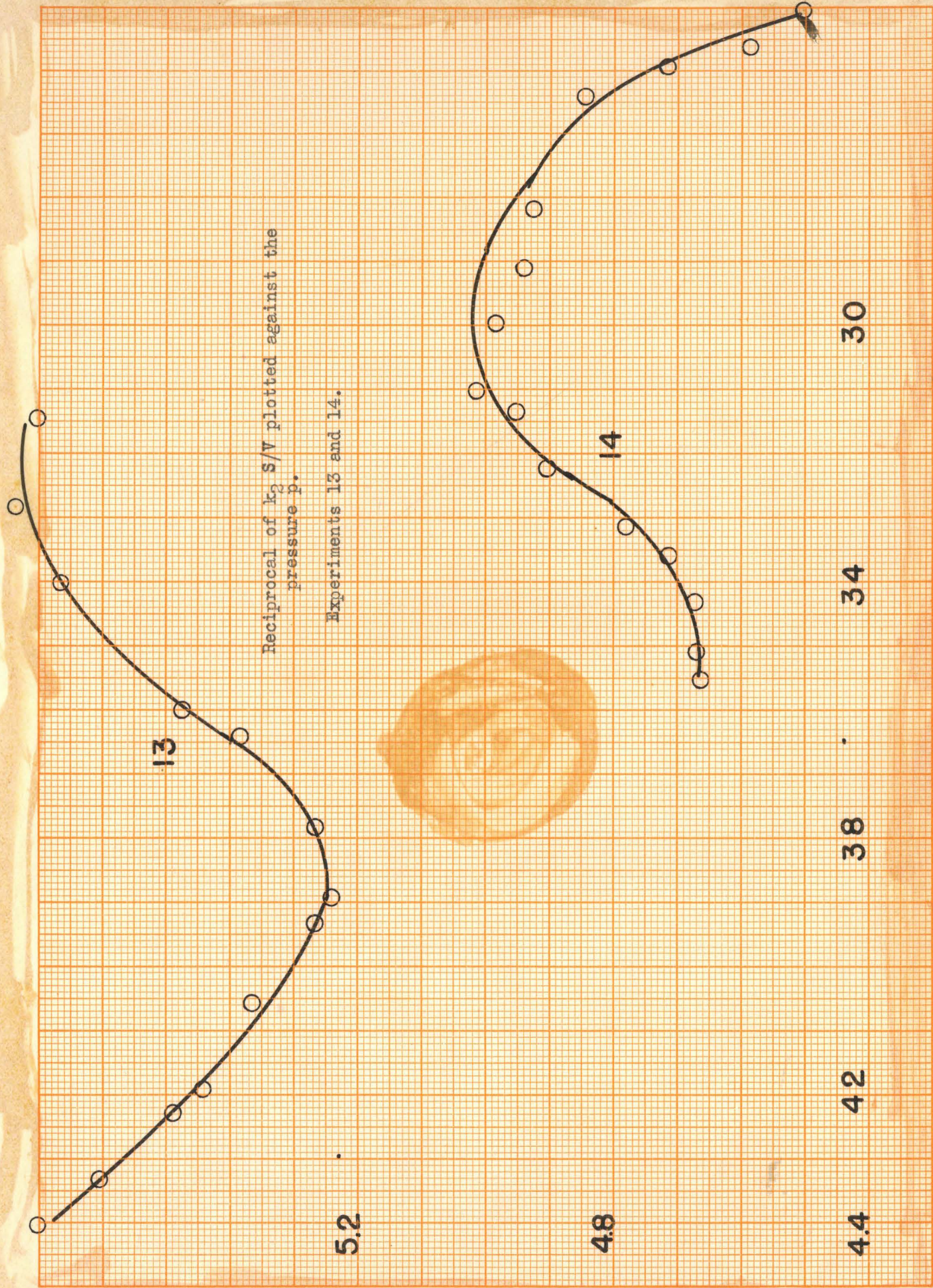
Reciprocal of $k_2 S/V$ plotted against the pressure p .
 Experiments 2, 4, 5, 7, 8, and 9.



p (cm. Hg)

$S/V P \text{ cm. Hg. min. cm}^2 \times 10^{-3}$

$\frac{1}{V} P_{F_3} P_{O_2} / \Delta t$ (cm. Hg min. $cm^{-1} \times 10^{-3}$)



Reciprocal of $k_2 S/V$ plotted against the pressure p.
Experiments 13 and 14.

p (cm. Hg)

Rate of the Reaction between PF_3 and Cl_2

Experiment	Temperature °C	$P_{Cl_2}^0$ (cm. Hg)	$P_{PF_3}^0$ (cm. Hg)	\bar{k}_2 V/S $\frac{cm^3 \text{ moles}^{-1}}{sec}$	Values of k_2 during the reaction: $k_2 = - \frac{1}{P_{PF_3} P_{Cl_2}} \frac{dP}{dt}$ ($cm^3 \text{ moles}^{-1} \text{ sec}^{-1}$)			
					0-20%	20-40	40-50	50-70
2	0	16.00	12.16	19.6	18.2	17.8	17.8	17.2
3	0	15.00	15.75	29.8		22	26	33
4	0	13.28	14.26	18.2	19.2	16.3	15.7	15.2
5	0	16.28	16.90	14.0		24.2	22.7	21.6
7	0	17.20	19.56	15.3			89	86
8	0	14.35	16.49	19.6			113	108
9	0	17.52	18.58	21.2			19.3	18.8
10	0	20.80	21.40	41.2				34 to 43
11	25	26.44	19.78	15.9	12.5	14.5	16.0	16.6
12	25	9.45	18.16	6.61	6.32	6.26	6.39	6.35
13	25	27.30	20.03	5.63	5.15	5.50	5.61	5.26
14	25	21.0	16.06	6.4	6.3	6.1	5.9	6.0
15 (a)	25	21.60	17.11	13		11		13
15*(b)	25	21.60	17.11	32*			30*	
15**(c)	0	21.60	17.11	23**				22*
16	25	25.0	19.5	0.5				

*Reaction vessel illuminated with 100 watt lamp.

**Reaction vessel cooled to 0° after starting experiment 15a at 25°.

Nature of the Surface of the Reaction Vessels

Experiment	Specific Surface $S/V = \text{cm}^{-1}$	Treatment of Surface Before Reaction
2	0.90	Washed with distilled water after previous run. Baked out
3	0.90	Coated with products of hydrolysis of phosphorus halides from No. 2. Baked out.
4	0.90	Treated as in No. 2.
5	1.63	New glass, washed with conc. HNO_3 , distilled water. Baked out.
7	5.75	Vessel from No. 5 washed with distilled water, packed with new glass rods which had been washed with conc. HNO_3 and distilled water. Baked out
8	5.75	Washed with distilled water after experiment 7. Baked out.
9	0.90	Vessel from No. 2, rinsed with KCl , drained, dried, baked out.
10	0.90	Vessel from No. 2, coated with AgCl , washed with distilled water, baked out.
11	0.95	New glass, washed with conc. HNO_3 , distilled water. Not baked out.
12,13	0.95	Washed with distilled water after previous run. Not baked out.
14,15		
16	0.95	Coated with paraffin.

Summary:

The addition reaction between phosphorus trifluoride and chlorine takes place very rapidly in the liquid phase in glass vessels, and in the gas phase proceeds practically to completion at a measurable rate in glass vessels at 0°C and 25°C. The gas reaction is largely heterogeneous, as shown by the following observations:

- 1) The rate in glass vessels is approximately proportional to the specific surface.
- 2) The rate in a paraffin-coated vessel is less than one-tenth as great as in a similar glass vessel at 25°C.
- 3) The reaction on glass appears to have a negative temperature coefficient, being roughly twice as fast at 0° as at 25°C.
- 4) The rate in glass vessels varies with the history of the glass.

The rate of the gas reaction at 0°C in glass reaction vessels which have been washed with distilled water after a previous experiment, dried and baked under vacuum can be represented over a small range of initial pressures as $-\frac{d}{dt}(\text{PF}_3) = k\frac{S}{V}(\text{PF}_3)(\text{Cl}_2)$ where S/V is the specific surface of the reaction vessel and k is approximately $20 \text{ moles}^{-1} \text{ cm}^4 \text{ sec}^{-1}$. The rate measurements at 25°C are not well fitted by this expression, possibly because with the technique

employed in the experiments|the reaction vessel could not be baked out. The reaction is accelerated by visible light.

The product of the reaction in the liquid state at room temperature rapidly attacks glass.

Part 3:-

A Theoretical Discussion of the Liesegang Phenomenon.

In 1896 R. E. Liesegang discovered that if a precipitate was formed by the diffusion of one reagent into a gel which contained the second reagent, the precipitate in many cases was discontinuous, occurring in a series of discrete layers or bands. This phenomenon, named after its discoverer, is also known as "periodic" or "rhythmic" precipitation, and the discrete bands are known as "Liesegang rings".

A qualitative explanation of the effect was first proposed by Wilhelm Ostwald (13), who suggested that the phenomenon is essentially due to the formation in the gel of supersaturated solutions which become unstable after a certain limiting supersaturation is reached. He also suggested that this limiting supersaturation is characterised by a limiting value of an ion concentration product, similar in form to, but greater in magnitude than the solubility product of the substance being precipitated.

Since Ostwald's suggestion a number of alternative theories have been suggested (14), involving adsorption of solute from the gel by the newly formed precipitate (15), or proposing that the fundamental process is not crystallisation from a supersaturated solution, but rather involves some limiting concentration for the coagulation of a colloidal sol of the precipitate (16). Although there is evidence that these factors may

become important in special cases, it is probable that most examples of the Liesegang phenomenon are to be explained on the basis of Ostwald's suggestion, which will accordingly be made the basis for the work presented here.

Most quantitative studies of the phenomenon have been conducted in the following way: a long narrow tube is filled with a gel containing initially a constant concentration of one reagent which we may call the internal reagent. This tube is dipped into a bath containing a solution of the second reagent which is allowed to diffuse into the tube. We shall call this reagent the entering reagent. Its concentration at the entrance to the tube is kept constant by stirring and by the use of a sufficiently large volume of solution. To insure uniform results the system must be protected against variations in temperature and in light intensity. Under these conditions the following equations are found to hold:

$$\frac{x_n}{\sqrt{t_n}} = k_1 = \text{constant} \quad (1)$$

$$\frac{x_n}{x_{n-1}} = K = \text{constant} \quad (2)$$

where x_n is the distance from the end of the tube in contact with the solution to the n 'th ring, and t_n is the time, measured from the beginning of the experiment, when the ring first begins to form. This time can be precisely measured; the ring appears suddenly as a very thin band which then grows

in thickness until the next ring forms.

The first of the equations just mentioned was developed theoretically by Morse and Pierce (17) who tested it in a series of painstaking experiments and obtained excellent agreement. The second is an empirical relation which was suggested by Schleussner (18) and by Jablczynski (19).

The object of the present discussion is to present a derivation of equation (2) and to show how the value of K depends on the other constants of the ring system.

Let us consider the diffusion of the entering reagent from a region where its concentration has the constant value C_e^0 into a long tube containing the internal reagent which can form a precipitate with the entering reagent and is initially at a uniform concentration C_i^0 throughout the tube. Let C_e and C_i be the variable concentrations of the entering and internal reagents respectively within the tube. Let t be the time measured from the beginning of the experiment, and x the distance measured from the end of the tube which is in contact with the entering reagent.

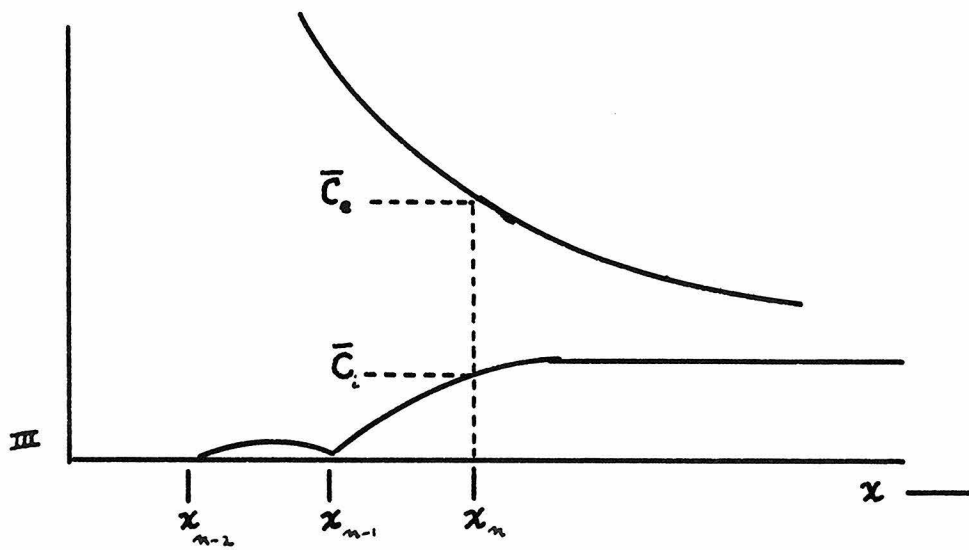
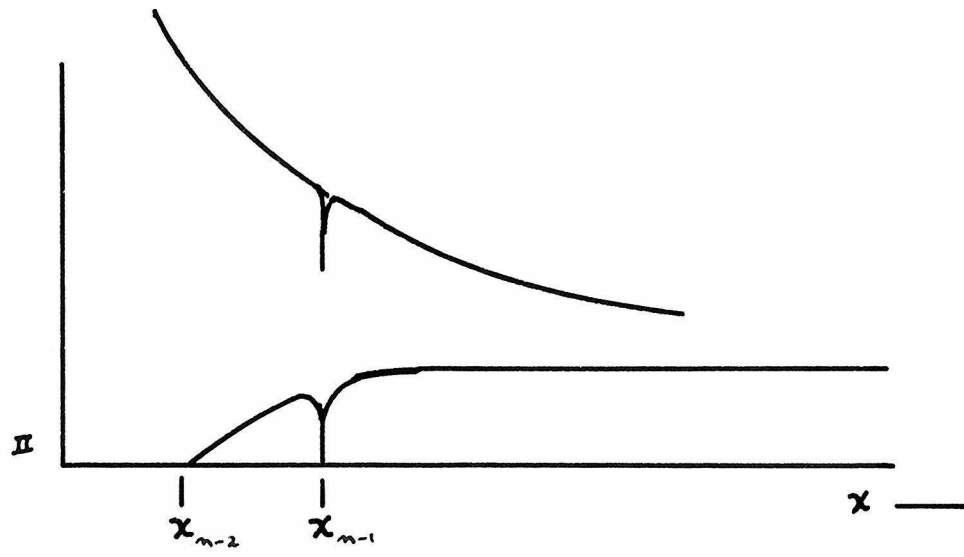
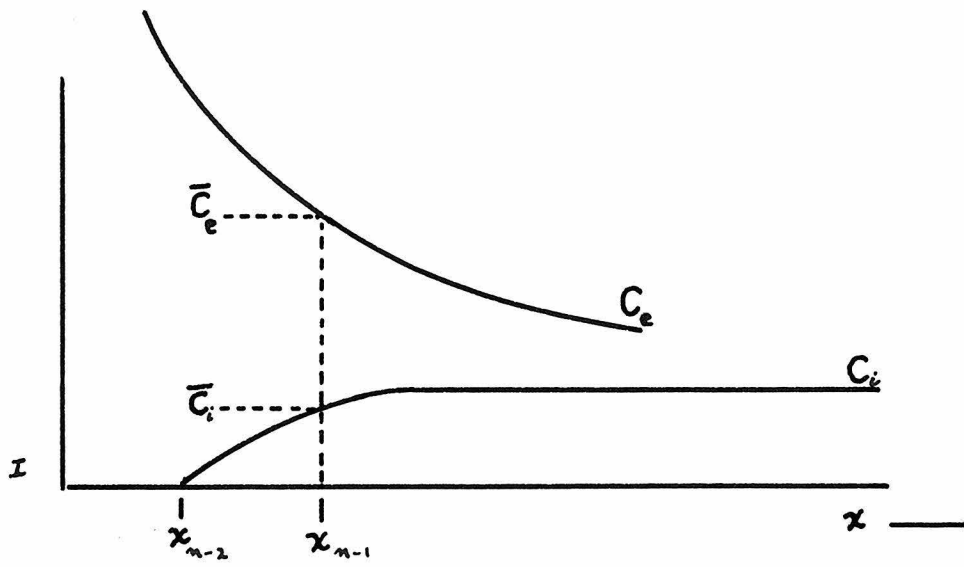
In accordance with the experimental fact that in order to produce ring systems for which equations (1) and (2) hold true it is usually necessary to use a low initial concentration of the internal reagent and a relatively high concentration of the entering reagent, we shall restrict our discussion to the case where $C_e^0 \gg C_i^0$. It then seems reasonable to assume that immediately preceding the formation of a ring

the concentration of internal reagent at the place where the ring is to form is not very different from the initial concentration C_i^0 ; this assumption receives support from the experimental work of Hughes (20) who has conducted quantitative analyses of thin sections of gels in which ring systems were forming. The assumption which we shall actually use will be considerably more drastic, however: we assume

- 1) The concentration of internal reagent at the place where a ring is just about to form has a critical value \bar{C}_i which is constant for all the rings in a system formed with given initial concentrations of reagents, and is not very different from the initial concentration C_i^0 .
- 2) In accordance with Ostwald's theory, we assume that when precipitation occurs, that some function of the concentrations C_e and C_i has a constant value. This assumption combined with assumption (1) leads us to state that for the formation of a ring the entering reagent must also be present in a critical concentration \bar{C}_e which is constant for all the rings in a given system. Let \bar{C}_e and \bar{C}_i have values such that just before precipitation occurs that a considerable degree of supersaturation exists.

- 3) We assume that $\bar{C}_e \gg \bar{C}_i$, so that the formation of a ring will not seriously affect the diffusion of the entering reagent. We assume further that the diffusion of each reagent obeys Fick's diffusion equation $\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}$, with a constant value of the diffusion coefficient D , though this coefficient is known to vary with the concentration.

We may now visualise the process of ring formation with the help of the following curves in which the concentrations C_e and C_i are plotted as functions of x at different times. In Curve I, precipitation is about to take place at x_{n-1} ; in Curve II precipitation has occurred and the concentration of internal reagent at x_{n-1} has fallen practically to zero. A large concentration gradient has been set up causing rapid diffusion of internal reagent from the surrounding region to x_{n-1} , where it is precipitated. At the same time the diffusion of entering reagent is somewhat disturbed; we shall ignore this effect in our quantitative considerations. In Curve III the diffusion of internal reagent to x_{n-1} has continued for some time; the disturbance in the diffusion of entering reagent caused by ring formation has smoothed itself out, and a new ring is ready to form at x_n . It is evident that one of the fundamental causes of the discontinuity in the precipitate is the great difference in the diffusion gradients



which control the diffusion of the reagents. Immediately after the formation of a ring, the abrupt change in the concentration of internal reagent causes it to diffuse toward the new ring so rapidly that a region beyond the ring is depleted of internal reagent sufficiently to prevent spontaneous precipitation of the supersaturated solution in that region. It is only after some time, when the large concentration gradients have been smoothed out, that the entering reagent is able to "catch up", so to speak, with the internal reagent and again bring about precipitation.

With this picture in mind we may now carry out an approximate mathematical treatment of the process. On the basis of our assumption (3) we may set up the following boundary conditions for the diffusion of entering reagent:

$$C_e = 0 \text{ for } t = 0, x \geq 0.$$

$$C_e = C_e^0 \text{ for } x = 0, t > 0.$$

The solution of Fick's equation for these boundary conditions is shown in the theory of heat conduction to be

$$C_e = \frac{2C_e^0}{\sqrt{\pi}} \int_0^{\frac{x}{2\sqrt{D_e t}}} e^{-\omega^2} d\omega \quad (3)$$

where ω is an integration variable. If for the formation of each ring $C_e = \bar{C}_e = \text{constant}$, then the lower limit of integration must be constant and we obtain

$$\frac{x_n}{\sqrt{t_n}} = k_1 = \text{const.}$$

This is the equation of Morse and Pierce and was obtained by them by a similar but in some respects incorrect treatment.

Some attempt will be made later to justify the approximation made in ignoring the influence of precipitation on the diffusion of entering reagent.

On the basis of assumption (1) and our qualitative discussion of the mechanism of the process we may set up the following approximate boundary conditions for the diffusion of the internal reagent during the formation of the (n-1)'st ring:

$$C_i = 0 \text{ for } x = x_{n-1}, t > t_{n-1}$$

$$C_i = C_i^0 \text{ for } x > x_{n-1}, t = t_{n-1}$$

The corresponding solution of the diffusion equation valid in the region $x_{n-1} \leq x \leq x_n$; $t_{n-1} \leq t \leq t_n$, is

$$C_i = \frac{2C_i^0}{\sqrt{\pi}} \int_0^{\frac{x - x_{n-1}}{2\sqrt{D_1(t-t_{n-1})}}} e^{-\omega^2} d\omega \quad (4)$$

where D_1 is the diffusion coefficient of the internal reagent.

In accordance with assumption (1), when precipitation next occurs at x_n , t_n , C_i will have the critical value \bar{C}_i . Then

$$\bar{C}_i = \frac{2C_i^0}{\sqrt{\pi}} \int_0^{\frac{x_n - x_{n-1}}{2\sqrt{D_1(t_n - t_{n-1})}}} e^{-\omega^2} d\omega = \text{constant} \quad (5)$$

This leads to the relation $\frac{x_n - x_{n-1}}{\sqrt{t_n - t_{n-1}}} = k_2 = \text{constant}$ (6)

Substituting in equation (6) for t_n and t_{n-1} in terms of x_n and x_{n-1} , by the use of equation (1), we obtain

$$\frac{x_n}{x_{n-1}} = \frac{k_1^2 + k_2^2}{k_1^2 - k_2^2} = K \quad (7)$$

This is the empirical relation of Schleussner and Jabliczynski (equation 2).

The most precise experimental data available seem to be those of Morse and Pierce (17) on the formation of silver chromate rings by diffusion of silver nitrate into gelatin gels containing potassium chromate. In Table I are shown values of k_1 , k_2 and K calculated from their data for a single experiment. It appears that k_2 is constant within the precision of $x_n - x_{n-1}$.

In Table II is presented a list of the values of k_1 , k_2 and K calculated from each of the experiments of Morse and Pierce and in Table III at the end of this section the mean values of these constants for given values of the initial concentrations. The experimental values of K are also compared with the values calculated from equation 7.

It should be emphasized that the relations presented in this discussion have been developed for very special boundary conditions. If \bar{C}_1 is much less than C_1^0 , the values of C_1

Table I

Compiled from Morse and Pierce's Data: Experiment 2.

1.0 N AgNO₃ diffusing into gelatin containing $\frac{1}{75}$ N K₂CrO₄

$\frac{x_n}{\sqrt{t_n}} \times 10^2$	$\frac{x_n - x_{n-1}}{\sqrt{t_n - t_{n-1}}} \times 10^3$	$\frac{x_n}{x_{n-1}}$	x cm.	t sec.
1.522	2.88	1.071	0.537	1245
1.526	2.63	1.063	0.575	1420
1.524	2.56	1.062	0.611	1607
1.519	2.88	1.069	0.649	1825
1.526	2.64	1.064	0.694	2068
1.524	2.66	1.064	0.738	2345
1.523	2.65	1.062	0.785	2658
1.523	2.72	1.062	0.834	3000
1.524	2.51	1.059	0.888	3395
1.520	2.64	1.062	0.940	3823
1.521	2.50	1.058	0.998	4305
1.518	2.81	1.065	1.056	4842
1.524	2.46	1.066	1.125	5443
1.520	2.60	1.061	1.188	6102
1.520			1.250	6870
=====				
1.523	2.65	1.063		

Table II

Calculations based on data by Morse and

Pierce on the formation of silver chromate rings in gelatin.

Experiment number	T C°	Conc. of $AgNO_3$ diffusing into gel (mol/l)	Conc. of K_2CrO_4 in gel (mol/l)	$\frac{x}{n} \times 10^2$ $\sqrt{t_n - t_{n-1}}$ cm. sec ^{-1/2}	$\frac{x_n - x_{n-1}}{\sqrt{t_n - t_{n-1}}} \times 10^3$	$\frac{x}{x_{n-1}}$
3	16.0	2.0	0.00667	1.656	2.63	0.9514
4	16.3	2.0	0.00667	1.663	2.63	0.9515
5	16.3	2.0	0.00667	1.671	2.68	0.9512
6	16.1	2.0	0.00667	1.700*	2.69	0.9508
2	15.7	1.0	0.00667	1.523	2.65	0.9411
7	15.5	1.0	0.00667	1.524	2.67	0.9385
8	17.0	1.0	0.00667	1.549	2.63	0.9444
9	16.7	1.0	0.00667	1.533	2.26*	0.9450*
17	16.6	0.50	0.00667	1.384*	2.02*	0.955 *
18	16.2	0.50	0.00667	1.377	2.61	0.9338
10	17.3	1.0	0.00333	1.462	2.89	0.9274
11	16.3	1.0	0.00333	1.466	2.74	0.9334
12	16.7	1.0	0.00333	1.467	2.74	0.9339
13	16.5	1.0	0.00333	1.462	2.80	0.9276
14	15.5	1.0	0.00333	1.453	2.76	0.9331
15	16.6	1.0	0.00333	1.477	2.82	0.9309
16	16.6	1.0	0.00333	1.468	2.78	0.9333
19	17.7	0.50	0.00333	1.311	2.85	0.9094
20	16.9	0.50	0.00333	1.292	2.81	0.9094
21	16.0	0.50	0.00333	1.335	2.81	0.9132
22	15.5	0.50	0.00333	1.313	2.76	0.9165
23	15.5	0.50	0.00333	1.299	2.81	0.9120

* Value not used in computing means

calculated from equation (4) will be too high, the error increasing as the ratio \bar{C}_i/C_i^0 decreases. If this ratio is in the neighborhood of 0.5, however, equation (4) should approximate the correct form fairly closely and the error will be partly compensated in the evaluation of D_i from experimental values of k_2 according to the method to be described later. If on the other hand $\bar{C}_e < \bar{C}_i$ the problem is much more difficult than the one treated here, because the diffusion of entering reagent is much more seriously disturbed. There appear to be available no precise data for a case of ring formation in which $\bar{C}_e < \bar{C}_i$, and it seems probable that such data would require a different treatment from that given here. It will be shown later that in all the experiments of Morse and Pierce the condition $\bar{C}_e \gg \bar{C}_i$ is met.

In connection with the disturbance of the diffusion of entering reagent by precipitation, it should be mentioned that an equation equivalent to equation (6) of the present paper has been developed by Bauer (21) on the basis of the corrections which must be applied to the diffusion of the entering reagent in order to account for the effects of precipitate formation. A complete treatment ought to take into account both the present results and the results of Bauer's work. Such a discussion becomes very cumbersome; moreover, the experimental results of Ammon and Ammon (22), who studied by means of indicators the diffusion of ammonia into a gel in which magnesium hydroxide rings were forming, may be interpreted

as showing that the disturbances produced by precipitate formation tend to smooth themselves out in such a way that the diffusion of entering reagent may be represented by equation (3) with a diffusion coefficient D_e larger than ^{that} characterising unhindered diffusion.

We may now test Ostwald's hypothesis and the consistency of our own assumptions by calculating values of the critical concentrations \bar{C}_e and \bar{C}_i from the values of k_1 and k_2 in Table III. As was mentioned earlier, the data in Table III are for bands of silver chromate; on the basis of Ostwald's ideas we should expect the critical condition for precipitation to be $[Ag^+]^2 [CrO_4^{2-}] > H$.

It is first necessary to calculate the diffusion coefficients D_e and D_i ; this we may do by a method first suggested by Morse and Pierce (17).

From the values of k_2 in sets 4 and 5 of Table III it appears that \bar{C}_i is the same in the two cases. Assuming that for the formation of each ring, some function of \bar{C}_e and \bar{C}_i is constant, \bar{C}_e is also the same for the two sets. Application of equation (3) leads to

$$\bar{C}_e = \frac{2 \times 1.0}{\sqrt{\pi}} \int_{\frac{1.465 \times 10^{-2}}{2\sqrt{D_e}}}^{\infty} e^{-\omega^2} d\omega =$$

$$\frac{2 \times 0.50}{\sqrt{\pi}} \int_0^{\infty} \frac{1.310 \times 10^{-2}}{2\sqrt{D_e}} e^{-\omega^2} d\omega \quad (8)$$

This relation is satisfied by a value of $D_e = 1.78 \times 10^{-5}$ $\text{cm}^2 \text{sec}^{-1}$. By use of this constant \bar{C}_e has been evaluated for each set of experiments listed in Table III, the values so obtained are there tabulated.

The calculation of D_i may now be carried out in the same way, using the values of \bar{C}_e and k_2 from sets 2 and 4 of Table III. Substituting in equation (5) and assuming $\bar{C}_e^2 \bar{C}_i = H = \text{const.}$ we obtain

$$\begin{aligned} (1.425 \times 10^{-2})^2 (3.33 \times 10^{-3}) \int_0^{\infty} \frac{2.79 \times 10^{-3}}{2\sqrt{D_i}} e^{-\omega^2} d\omega = \\ (1.031 \times 10^{-2})^2 (6.67 \times 10^{-3}) \int_0^{\infty} \frac{2.65 \times 10^{-3}}{2\sqrt{D_i}} e^{-\omega^2} d\omega \quad (9) \end{aligned}$$

which is satisfied by $D_i = 1.28 \times 10^{-5}$ $\text{cm}^2 \text{sec}^{-1}$. This compares favorably with the value 1.1×10^{-5} for potassium dichromate in water at 16°C as estimated from values in the International Critical Tables.

Using this constant the values of \bar{C}_i and of the product $H = \bar{C}_e^2 \bar{C}_i$ have been calculated and are listed in Table III. The value of H appears to be reasonably constant. Since the assumption of constancy of H was made only in evaluating D_i

from sets 2 and 4 it appears from the results for sets 1, 3 and 5 that the data are consistent with this assumption. A more complete test over a wider range of concentration of both entering and internal reagents would of course be desirable.

The mean value of H obtained is 2.88×10^{-7} moles³ litres⁻³. Hughes (20) has obtained the value 2×10^{-7} by direct experiments in which increasingly dilute solutions of silver nitrate were diffused into a 5 % gelatin gel containing dilute potassium chromate until no precipitate was observed to form. It will be noted that the value of H here calculated is about 10^6 times as great as the solubility product for silver chromate in water. If further experiments indicate that the constancy of H has a real significance it would be of interest in the study of supersaturation phenomena to evaluate H for other precipitates and to study the effect on H of such factors as light intensity, nature and concentration of the gel etc.

It will be seen that the values of \bar{C}_e calculated for the experiments of Morse and Pierce are approximately five to ten times as great as the values of \bar{C}_1 , so that in this respect at least the conditions are favorable for the present treatment. The fact that the ratio \bar{C}_1/C_1^0 is in all cases about 0.4, however, makes the apparent success of the calculations rather surprising. It should be worth while to attempt to obtain equally precise data for cases in which \bar{C}_e was more nearly equal to or less than \bar{C}_1 , and to investigate whether for this case equations (1) and (2) still hold.

The treatment here presented is of course far from complete. The assumption of the constancy of \bar{C}_1 , while it appears to be consistent with the data, seems somewhat arbitrary and should be derivable from a thorough treatment of the diffusion problem combined perhaps with the assumption that the condition for precipitation is $C_e^p C_1^q > H$.

An interesting relation which may have some bearing on this possibility can be derived in the following way: Let us assume that after the formation of the (n-1)'st ring that precipitation next occurs where the product $C_e^p C_1^q$ is a maximum with respect to x. But the value of x where precipitation occurs will be x_n , and C_e , C_1 will have the critical values \bar{C}_e , \bar{C}_1 . Then

$$\frac{\partial}{\partial x} (C_e^p C_1^q)_{x=x_n} = 0 \quad (10)$$

$$\text{or } p\bar{C}_1 \left(\frac{\partial C_e}{\partial x} \right)_{x=x_n} + q\bar{C}_e \left(\frac{\partial C_1}{\partial x} \right)_{x=x_n} = 0 \quad (11)$$

Differentiating equation (2) with respect to x and multiplying by x,

$$x \frac{\partial C_e}{\partial x} = - \frac{2C_0}{\sqrt{\pi}} e^{-\frac{x^2}{4De^2 t}} \frac{x}{2\sqrt{De^2 t}}$$

And from equation (1), at $x = x_n$ and $t = t_n$

$$x_n \left(\frac{\partial C_e}{\partial x} \right)_{x=x_n} = - \frac{2C_0}{\sqrt{\omega}} e^{-\frac{k_1^2}{4De^2}} \frac{k_1}{2\sqrt{De}} \quad (12)$$

Similarly differentiating equation 4, multiplying by $x - x_{n-1}$ and applying the condition $x = x_n$, $t = t_n$, we obtain by the use of equation (7),

$$(x_n - x_{n-1}) \left(\frac{\partial C_i}{\partial x} \right)_{x=x_n} = \frac{2C_i^0}{\sqrt{\pi}} e^{\frac{-k_2^2}{4D_1}} \frac{k_2}{2VD_1} \quad (13)$$

Substituting in (11) from (12) and (13) to eliminate $\frac{\partial C_e}{\partial x}$ and $\frac{\partial C_i}{\partial x}$ we obtain

$$1 - \frac{x_{n-1}}{x_n} = \frac{q \bar{C}_e C_i^0 e^{\frac{-k_2^2}{4D_1}} k_2 \sqrt{D_e}}{p \bar{C}_i C_e^0 e^{\frac{-k_1^2}{4D_e}} k_1 \sqrt{D_i}} \quad (14)$$

This is a more explicit form of the Schlessner relation (equation (2)). The term on the right hand side can be calculated for Morse and Pierce's experiments with the aid of the quantities tabulated in Table III, using $p = 2$ and $q = 1$. The calculated and observed values for $1 - \frac{x_{n-1}}{x_n}$ are listed in Table III and agree fairly well with one another. We may conclude that the hypothesis that ring formation occurs at a point where the product $C_e^p C_i^q$ is a maximum is not inconsistent with the more detailed assumptions made at the beginning of this treatment, and that it may be possible to derive the latter from the former.

Table III

C_e^0	$C_i^0 \times 10^3$	$k_1 \times 10^3$ cm sec $^{-\frac{1}{2}}$	$k_2 \times 10^3$ cm sec $^{-\frac{1}{2}}$	$\bar{C}_e \times 10^2$	$\bar{C}_i \times 10^3$	Experiments
2.0	6.67	1.665	2.66	1.058	2.68	3,4,5.
1.0	6.67	1.532	2.65	1.031	2.67	2,7,8.
0.50	6.67	1.377	2.61	1.058	2.63	18
1.0	3.33	1.465	2.79	1.425	1.40	{ 10,11,12,13 14,15,16
0.50	3.33	1.310	2.80	1.414	1.40	{ 19,20,21 22,23.

$\frac{\bar{C}_i}{C_i^0}$	$\bar{C}_e \bar{C}_i \times 10^7$	$1 - \frac{x_{n-1}}{x_n}$ (Equ. 14)	$1 - \frac{x_{n-1}}{x_n}$ (Obs)	$K = \frac{x_n}{x_{n-1}}$ (Equ. 7)	$K = \frac{x_n}{x_{n-1}}$ (Obs)	Experiments
0.401	3.00	0.053	0.049	1.052	1.051	3,4,5.
0.400	2.84	0.062	0.058	1.062	1.062	2,7,8.
0.394	2.94	0.075	0.065	1.074	1.070	18
0.419	2.84	0.066	0.069	1.075	1.074	{ 10,11,12,13 14,15,16
0.420	2.80	0.081	0.088	1.096	1.096	{ 19,20,21 22,23.

Legend:

Units of C_e^0 , \bar{C}_e = moles AgNO_3 per litre.

Units of C_i^0 , \bar{C}_i = moles K_2CrO_4 per litre.

Mean value of $H = 2.88 \times 10^{-7}$ mole 3 litres $^{-3}$

Diffusion coefficients: $D_e = 1.78 \times 10^{-5}$ cm 2 sec $^{-1}$

$D_i = 1.28 \times 10^{-5}$ cm 2 sec $^{-1}$.

All experiments were run at $16.5 \pm 0.5^\circ\text{C}$.

Conclusion:

It has been possible by means of some perhaps rather arbitrary assumptions to carry out a treatment of the Liesegang phenomenon on the basis of Wilhelm Ostwald's supersaturation theory. This treatment can of course readily be extended to cases other than those involving supersaturation of crystalloidal solutions; for example the known examples of Liesegang ring formation involving periodic coagulation of colloids can no doubt be discussed in the same way.

The present treatment can hardly be regarded, however, as a fundamental one because of the ad hoc nature of the assumptions involved. A treatment based on a satisfactorily general postulational basis is yet to be carried out.

Part 4:

A Theory of the Chromatographic Adsorption of a Single Solute.

The technique of the so-called chromatographic adsorption method of analysis was originated by the Russian botanist M. Tswett (23) in 1906. He discovered that if a solution containing a mixture of colored solutes is allowed to run through a vertical glass tube packed with a suitable powdered adsorbing material, ~~that~~ a partial separation of the constituents of the solution takes place as shown by the occurrence of a series of colored bands of the various solutes, formed by adsorption on the powdered material. This series of colored bands is known as a "chromatogram". The separation can be further increased by a process known as "development of the chromatogram": there is poured through the column a suitable solvent which washes the colored bands down the tube at different rates, the lowest-lying bands moving the fastest. In this development process the segregation of the various solutes into individual bands becomes more complete; if the process is carried out in a sufficiently long tube with the use of a sufficiently large volume of solvent it is possible to effect complete separation of the initial constituents of the solution into a series of discrete bands separated by clear spaces of adsorbent.

The technique just outlined has become in recent years a very important method for the separation, purification and identification of small amounts of complex naturally occurring organic compounds; these developments have been described at length by Zechmeister and Cholnoky (24) to whose book the reader is referred for a more complete discussion.

Although the nature of the phenomenon seems to be qualitatively fairly well understood (24) there has been carried out so far no quantitative treatment by which even an approximate prediction could be made of the width or of the rate of "development" of the bands to be expected in a given chromatogram. The present treatment grew out of a desire to be able to make such predictions in order to decide on the basis of known adsorption isotherms whether or not a given adsorbent might be expected to be useful for carrying out the chromatographic separation of a given set of substances. It has not so far been possible to carry through a complete treatment; there will be presented here however a tentative theoretical discussion of the chromatography of a single substance; it is evident that this simpler problem must be solved before the much more complicated problem of the chromatography of mixtures can be successfully attacked.

Let us consider a long column which contains M grams of adsorbent per centimeter of its length; we wish to calculate the distribution of adsorbed material in this column after a

volume v of a solution containing a solute at an initial concentration C_0 has been poured through it. We shall assume that the rates of adsorption and desorption are much greater than the rate of flow of solution past any point in the tube so that equilibrium between solution and adsorbed material is always maintained. Let the isotherm which represents the adsorption of the given solute on the given adsorbent be

$$q/m = f(c)$$

where q is the number of millimoles of solute adsorbed on m grams of adsorbent and in equilibrium with a solution whose concentration is c moles per liter. Then under equilibrium conditions at any point in the column where the concentration of solute in the liquid phase is c , there will be adsorbed Q millimoles of solute per centimeter length of the column, where

$$Q = M f(c) \quad (1)$$

Let the distance from the top of the column of adsorbent to any lower point in the column be x , and consider the changes in Q and c which occur at x when an element of volume dv of solution, whose concentration at x is c , passes through a thin cross-sectional layer of the column, of thickness dx , on which is adsorbed initially an amount $Q dx$ of solute. The number of millimoles of solute adsorbed on this layer will change by an amount $(\frac{\partial Q}{\partial c})_x dv dx$, and the concentration of the solution will change by an amount $(\frac{\partial c}{\partial x})_v dx$. The number of millimoles of solute contained in the volume dv of solution will therefore

change by an amount $(\frac{\partial c}{\partial x})_v dx dv$. But since matter is conserved, we have

$$(\frac{\partial Q}{\partial v})_x dx dv + (\frac{\partial c}{\partial x})_v dx dv = 0$$

Substituting for Q from equation (1) of this section, we obtain as the differential equation for the fundamental process occurring in the chromatographic adsorption of a single substance

$$M \frac{\partial}{\partial v} [f(c)]_x + (\frac{\partial c}{\partial x})_v = 0 \quad (2)$$

The general solution of this equation is

$$c = \phi \{ v - xM f'(c) \} \quad (3)$$

where ϕ is an arbitrary function and $f'(c)$ is the first derivative of $f(c)$. This equation will apply to either the process of formation of the chromatogram or the process of development. Different boundary conditions will, however, apply to the two cases.

Let the chromatogram be formed by pouring a volume v_1 of solution whose initial concentration is c_0 through the column. The appropriate boundary conditions are:

$$(1) \text{ When } v_1 = 0, f(c) = 0 \text{ for } x \geq 0. \quad (4)$$

$$(2) \text{ When } v_1 > 0, f(c) = f(c_0) \text{ at } x = 0. \quad (5)$$

$$(3) \quad v_1 c_0 = \int_0^{\infty} Q dx = \int_0^{\infty} M f(c) dx. \quad (6)$$

The last is a conservation condition.

The solution of the differential equation for this case has been found to be

$$\text{For } 0 \leq x \leq \frac{V_1}{M f'(c_0)}, f(c) = f(c_0); Q = M f(c_0)$$

$$\text{For } x > \frac{V_1}{M f'(c_0)}, f(c) = 0; Q = 0 \quad (7)$$

The discontinuous nature of this solution accounts in a satisfactory way for the sharpness of the bands produced in chromatographic experiments; the solution is also in accordance with the experimental observation that the intensity of color in the band is uniform ($Q = M f(c_0) = \text{constant}$).

The solution (7) was discovered in an indirect way: The problem was treated not by differential methods but by a method of finite differences. For simplicity an adsorption isotherm $q/m = Kc$ was assumed, and the column of adsorbent was considered as being made up of a succession of thin layers of thickness $\frac{1}{s}$. The volume V of solution of initial concentration c_0 was considered as being divided up into a number of small volumes V/m . The first of these elements of volume was now allowed to pass through the column of adsorbent step by step in such a way that equilibrium was reached with each layer before the element of volume passed on to the next layer. The amount of solute adsorbed and the change in concentration of solute in the element of volume was calculated for each step. The calculations were repeated for the similar passage of a second element of volume, taking into account the conditions imposed by the previous passage of the first. This process was continued until the whole volume V had been passed through the solution in this stepwise manner. The total amount of solute

q_{mn} adsorbed on the n 'th layer after the passage of the m 'th element of volume V/m could then be expressed as a series:

$$Q_{mn} = sq_{mn} = V\alpha c_0 \frac{1}{\left(1 + \frac{\alpha m}{s}\right)^n} \left\{ 1 + n \frac{\frac{m\alpha}{s}}{1 + \frac{m\alpha}{s}} + \frac{n(n+1)}{2!} \left[\frac{\frac{m\alpha}{s}}{1 + \frac{m\alpha}{s}} \right]^2 + \dots + \frac{n(n+1)\dots(n+m-2)}{(m-1)!} \left[\frac{\frac{m\alpha}{s}}{1 + \frac{m\alpha}{s}} \right]^{m-1} \right\}$$

where $\alpha = \frac{KM}{V}$ and M and Q have their previous significance. Eliminating s by means of the expression $x = n \cdot \frac{1}{s}$ an expression was obtained for $Q_{m,n} = Q(V,x)$

$$Q(V,x) = \frac{KMc_0}{\left\{ 1 + \frac{m}{n} \frac{Kmx}{V} \right\}^n} \left[\left\{ 1 - \frac{\frac{m}{n} \frac{Kmx}{V}}{1 + \frac{m}{n} \frac{Kmx}{V}} \right\}^{-n} \text{ to } m \text{ terms} \right]$$

where the factor inside the square brackets is to be expanded by the binomial expansion, the first term being 1, and only the first m terms are to be retained. To obtain the solution to the problem it is then necessary to evaluate the limit of this expression as m and n tend to infinity, where n is now the number of layers of adsorbent from the top of the column to the point x . In order to reduce the problem to a limit in one parameter, the physically reasonable assumption is made that $\frac{m}{n} = \frac{V}{ax}$ where a is a constant. The result is

$$Q(x,V) = \lim_{m \rightarrow \infty} \frac{KMc_0}{\left(1 + \frac{KM}{a}\right)^{\frac{\max}{V}}} \left[\left\{ 1 - \frac{\frac{KM}{a}}{1 + \frac{KM}{a}} \right\}^{-\frac{\max}{V}} \text{ to } m \text{ terms} \right]$$

This limit has apparently never been evaluated and its evaluation appears to be very difficult. Arithmetical computation based on the expansion however showed that as m was given larger and larger values, ~~that~~ the solution approached the form

$$Q = KMc_0 \text{ for } 0 \leq x \leq \frac{V}{KM}$$

$$Q = 0 \text{ for } x > \frac{V}{KM}.$$

This indication, combined with the general solution given in equation 3, suggests that the solution for the given boundary conditions should be given by equations (7), and these are indeed found to provide a satisfactory solution.

We may now consider the case in which a band already formed is "developed" by passage through the column of a volume v_2 of some solvent not necessarily the same as the solvent used in forming the band. Let the adsorption isotherm for the "developing" solvent and the given adsorbent be, for the solute in question,

$$q/m = F(c) \quad (8)$$

We shall assume that the band was formed in accordance with equation (7), i.e. that up to some point $x = x_1$, $Q = Q_0 =$ constant, and beyond x_1 , $Q = 0$. We may also write

$$Q_0 = M f(c_0) = M F(c'_0) \quad (9)$$

where c_0' is the concentration of solute which would be in equilibrium with Q_0 in the new solvent, and is not necessarily equal to c_0 . The boundary conditions to be applied are as follows:

$$1) \text{ When } v_2 = 0, 0 \leq x \leq x_1, Q = Q_0 = M F(c_0') = \text{constant} \quad (10)$$

$$2) \text{ When } v_2 > 0, \text{ at } x = 0, Q = M F(c) = 0 \quad (11)$$

$$3) \text{ For all values of } v_2, \int_0^{\infty} M f(c) dx = \int_0^{\infty} Q_0 dx = \text{constant} \quad (12)$$

The solution of equation (2) for these conditions is

$$Q = 0 \text{ for } 0 < x < \frac{v_2}{M F'(c_0')} \text{ and for } x > x_1 + \frac{v_2}{M F'(c_0')} \\ Q = Q_0 \text{ for } \frac{v_2}{M F'(c_0')} < x < x_1 + \frac{v_2}{M F'(c_0')} \quad (13)$$

We reach the conclusion then that the band should remain sharp during the process of development and that its width should remain constant as it moves down the column. Experimentally the first conclusion is verified; the second holds only very approximately.

An attempt has been made to test experimentally the relations (7) and (13). It has proved difficult however to carry out chromatographic adsorption experiments in a quantitative and reproduceable way. It is apparently not easy to make the solutions flow evenly through the adsorbent: in some cases most of the flow occurs adjacent to the wall of the tube which confines the adsorbent; when this does not occur flow is more rapid through the center than through the outer sections of the column. Either of these effects causes the bands to be wider than they should be according to equation (7) and to increase in width as development proceeds, because the effective number of grams of adsorbent per unit length of the column is

decreased below the value which it would have if effective contact were made between the solution and the entire surface of the adsorbent in the column, and varies moreover from one region in the column to another. "Channeling" of the column also occurs and leads to the same result. It should also be borne in mind that equations (7) and (13) were derived on the basis of an assumption that equilibrium between solution and adsorbed material is always maintained. If this condition is not fulfilled, i.e. if the rates of adsorption and desorption are not much more rapid than the flow of liquid through the tube, then the band formed will be wider than it should be according to equations (7) and will increase in width as development proceeds. Furthermore in this treatment the effects of diffusion, which will also tend to widen the band, have been neglected. It should not occasion surprise then if equations (7) and (13) do not agree precisely with the results of experiment.

Nevertheless a few experimental results have been obtained ^{rough} in agreement with the relations given here. For instance the band formed on pouring 20 cc. of a solution of picric acid in alcohol through a column of alumina was 2.0 mm. wide; the width predicted on the basis of adsorption measurements was 1.8 mm. In other cases however the observed width of the band has differed from the predicted width by as much as a factor of two; "channeling" of the adsorbent was observed to occur in some of these cases and may have been responsible for the discrepancy. According to equation (13), the distance the band

moves down the tube during development should be directly proportional to the volume of developing solvent. This has been found to be approximately true (within 10%) in an experiment in which eosin bands on alumina were developed by washing with water and in an experiment in which fluorescein bands on alumina were developed by washing with benzene. The experiments which have been done so far on the chromatography of single substances are so inconclusive that no detailed data will be presented here. A satisfactory experimental test of equations (7) and (13) has yet to be made. The treatment presented here appears however to have sufficient significance to enable one to decide from measured adsorption isotherms whether a given adsorbent may be expected to be useful for effecting the separation of a given set of substances.

It has not yet been found possible to develop a quantitative treatment for the chromatography of a solution containing two or more solutes. The principal difficulty lies in the fact that when adsorption occurs from a solution containing several solutes the amount of a given solute adsorbed is a function of the concentrations of all the solutes in the solution. It appears moreover that no general rules are known for predicting the form of this function in terms of the adsorption isotherms of solutions of the individual solutes (25). It is usually true, however, that the solutes with the stronger adsorbing tendency displace from the adsorbent those with a weaker adsorbing tendency. If a chromatogram is prepared

from a solution of two solutes, the first of which tends to adsorb very strongly on the adsorbent while the second has only a moderate tendency to adsorb, the formation of an adsorption band by the first solute will be practically uninfluenced by the presence of the second solute; the latter will however be forced to adsorb below the former, so that a partial separation of the substances will take place when the chromatogram is first formed. The width of each of the bands should be given approximately by equation (7), appropriately modified to take into account the displaced origin of the second band. There will probably be between the two bands a region where both substances are adsorbed to some extent. On development of this band system, however, there will eventually occur separation into bands in each of which the concentration of one adsorbed solute is uniform, as may readily be seen by carrying out a qualitative discussion of the development of an initially non-uniform band of a single solute on the basis of the results of our previous treatment.

Summary:

A treatment of the chromatographic adsorption of a single solute has led to results by means of which a rough prediction of the width of the adsorption band and of the rate of its migration during development can be made in terms of the adsorption isotherm of the solute.

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Summary of Results

- Part 1(a) Measurement of the rate of the iodine-catalysed exchange of radioactive arsenic between arsenious and arsenic acids indicates that the kinetics of the reaction are the same remote from equilibrium as they are at equilibrium.
- 1(b) No exchange of radioactive phosphorus between phosphorous and phosphoric acids was found to occur in either alkaline or acid solution.
- 1(c) Rapid and complete exchange of radioactive bromine was found to occur thermally between bromine and stannic bromides, and photochemically between bromine and trichlorobrom methane in carbon tetrachloride solutions. No measureable exchange was observed to occur thermally between bromine and ethylene bromide or trichlorobrom methane in carbon tetrachloride.
- Part 2 The reaction between gaseous PF_3 and chlorine in glass vessels is almost completely heterogeneous and has at 0°C a negative temperature coefficient.
- Part 3 An approximate theoretical treatment of the process of the formation of Liesegang rings has been developed on the basis of simple assumptions.
- Part 4 A theoretical treatment of the chromatography of a single solute has lead to equations by means of which rough predictions can be made regarding the width of the band formed from a given volume of solution and the rate at which the band will be developed by a given solvent.

Propositions

1. The mechanism suggested by a number of authors^{*} to explain the anodic deposition of PbO_2 from a rapidly stirred nitric acid solution of plumbous ion involves the sweeping of plumbous ions, by means of stirring, to the anode, where they can be oxidized. It is here proposed that this mechanism is not a reasonable one.

^{*}Nichols, Ind. Eng. Chem., Anal. Ed. 3, 384 (1931);
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2. A spherical bubble in a dielectric liquid will not remain spherical under the influence of a homogeneous electric field.
3. The solution of the diffusion equation suggested by Eversole and Doughty^{*} is invalid.

^{*}J. Phys. Chem. 39, 289 (1935); J. Phys. Chem. 41
663 (1937).

4. The critical temperatures and volumes computed for the vapors of ionic salts by Lorenz and Herz^{*} on the basis of empirical equations are of doubtful significance.

^{*}Z. anorg. Chem. 138, 330 (1924); Landolt-Börnstein
Tabellen, Erg. 1, p. 159.

5. For a crystalline normal hydrocarbon, the sum of the entropy changes occurring on fusion and in transitions below the melting point is a linear function of the number

of carbon atoms in the chain.

6. The effect of pressure on the specific rate of a chemical reaction is well expressed by the equation

$$RT \frac{\partial \ln k}{\partial P} = A(1 - BP)$$

where A and B are constants independent of the temperature T and the pressure P. Since BP is not negligible compared with unity over the pressure range usually investigated, it would appear that the neglect of compressibilities in the theoretical treatment by Evans and Polanyi* is not justified.

*Trans. Faraday Soc. 31, 875 (1935); 32, 1333 (1936).

7. The so-called quantum mechanical theory of the formation of Liesegang Rings or periodic precipitates is of doubtful validity despite the opinions of

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8. The observed relation* between the distances of successive Liesegang rings from the origin of the ring system

$$\left(\frac{X_n}{X_n - 1} = \text{const.} \right)$$

can be accounted for on the basis of simple assumptions.

*C. A. Schleussner, Koll. Z. 31, 347; 34, 338 (1924)

K. Jablczynski, Koll. Z. 40, 22 (1926)

9. The sharpness, extent, and rate of "development" of the bands produced in chromatographic adsorption experiments can be accounted for in a semi-quantitative way on the basis of the assumptions that diffusion is negligibly slow and that equilibrium between solution and adsorbent is reached very rapidly compared to the velocity of flow of solution through the adsorbent.
10. It is certainly true, ~~that~~ if n and r are positive integers, ~~that~~

$$\sum_{i=0}^n i(i+1)(i+2) \dots (i+r-1) =$$

$$\frac{n(n+1)(n+2) \dots (n+r)}{r+1}$$

and it is reasonable to suppose that

$$\lim_{m \rightarrow \infty} \frac{1}{(1+\delta)^{-m\beta}} \left[\left\{ 1 - \frac{\delta}{1+\delta} \right\}^{-m\beta} \right. \left. \begin{array}{l} \text{expanded by the} \\ \text{binomial expansion} \\ \text{to } m \text{ terms} \end{array} \right]$$

$$= 1 \text{ for } \beta < \frac{1}{\delta}$$

$$\text{but } = 0 \text{ for } \beta > \frac{1}{\delta}$$

11. Onsager's theory of liquid dielectrics can be modified to give results for the dielectric constants of polar liquids which, though they do not agree quantitatively with experiment, are fairly self-consistent and deviate from experiment in a way which can be qualitatively accounted for

on the basis of intermolecular interactions.

12. A simple graphical method can be used to facilitate the interpretation, by means of Langmuir's adsorption theory, of the rate of a heterogeneous gas reaction.
13. In calculating the concentrations of reacting ions at any point in a titration, it is usually advisable to use approximate methods. These methods unfortunately become inaccurate in the vicinity of the equivalence point. By means of simple criteria it may be decided in simple cases (such as the titration of chloride with silver ion, or the titration of weak acids with strong bases) how close to the equivalence point the approximations usually made can be applied to obtain results of any desired accuracy. These criteria have pedagogic and practical value.