A STUDY OF SEVERAL REACTIONS OF CARBON TETRA-CHLORIDE SYNTHESIS

COLIN G. FINK

Head of Division of Electrochemistry, Columbia University, New York City

AND

CHARLES F. BONILLA

Chemistry Department, College of the City of New York, New York City

INTRODUCTION

The manufacture of carbon tetrachloride, mainly for use as a grease solvent or as a fire extinguisher, is a relatively important industry. In 1925 the value of the output had reached the million dollar mark. Owing to its advantageous properties, the demand for carbon tetrachloride would undoubtedly increase if its price could be decreased. A glance at current prices shows carbon tetrachloride at about 6 cents per pound in drums and chlorine at below 2 cents in tank cars. There would seem to be much advantage in the discovery of a process of manufacture of carbon tetrachloride superior to the old carbon bisulfide chlorination process now in use.

The whole field of the chemistry of carbon tetrachloride is very dark, and what illuminated spots there are, are quite unattached. As will be recalled, the direct synthesis of carbon tetrachloride has not been successfully carried through, commercially. Theoretically there seems to be no reason why this synthesis does not take place readily. Recently both Bodenstein and Stock have been working on this subject, without obtaining results which were satisfactory either commercially or theoretically. The present study was instituted to investigate this field further and to attempt to help toward the clearing up of the situation.

The principal problems in our carbon tetrachloride research are the difficulty with which carbon tetrachloride forms and the difficulty with which its presence can be detected when at a low partial pressure in related gases. The difficulty of formation might be explained by steric hindrance (1). Practically all of the proposed schemes studied involve one reaction step which cannot at present be carried out practically, regardless of the free energy change. This is usually, but not always, the step in which the carbon tetrachloride is finally produced. Of course,

1135

the problem may be merely that of finding the proper catalysts, which no one has definitely discovered in spite of many trials. However, it also has the appearance of something more complicated, possibly the "false equilibrium" which Duhem describes (2) so thoroughly. This phenomenon seems to be found so far in the following reactions, proceeding from either side,

$$C + 2Cl_2 = CCl_4 \qquad (1)$$
$$2COCl_2 = (COCl_2)_2 \qquad (2)$$
$$2COCl_2 = CO_2 + CCl_4 \qquad (3)$$

and probably in

$$C_2Cl_6 + Cl_2 = 2CCl_4 \qquad (4)$$

Hood's explanation for the second reaction (3) is that the catalyst was poisoned by phosgene, but he did not investigate the phenomenon further.

Owing to the absence of simple and reliable methods for analysis of the small amounts of carbon tetrachloride that might be obtained in its formation reactions, the decomposition reactions have been studied much more widely, in fact, almost entirely. Arcs, sparks, visible and ultra-violet light, and heat with various catalysts have been some of the means employed. The principal reactions that we will consider are the following; they are gas phase or gas–solid interface reactions.

$$C + 2Cl_2 = CCl_4$$
$$C_2Cl_6 + Cl_2 = C_2Cl_4 + 2Cl_2 = 2CCl_4$$
$$2COCl_2 = CO_2 + CCl_4$$
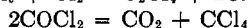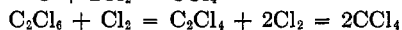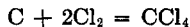
They may all proceed simultaneously, but something has been learned about their catalysts and reaction temperatures, so that each has been studied separately. It is very difficult to study their reaction rates quantitatively, and this has not been attempted by anyone as yet. These three reactions will be considered under separate headings.

In the present research pure and dehydrated chemicals were not used, as it was desired to study conditions that might be commercially obtained. Another item is that stopcocks were never greased, but were well ground and practically gas-tight, and the apparatus was run at slightly over atmospheric pressure. Any thermodynamic data taken from the literature and for which we have not given the source have been obtained from the International Critical Tables (4).

We have been working in what appears to be a very large field. Accordingly, it has not been possible to allow to any of the reactions investigated a sufficient amount of study to carry it to anything like a logical conclusion. However, we plan to continue study of these reactions, particularly the first and third mentioned above.

THE SPECIFIC HEAT OF CARBON TETRACHLORIDE VAPOR

No instance has been found in the literature of the direct determination of the molar specific heat at constant pressure of gaseous carbon tetrachloride. Capstick (4) determined the ratio of the specific heats as 1.13 at 20°C., which, on using Berthelot's relationship (5) for their difference,

$$C_p - C_v = R\left(1 + \frac{27}{16}\frac{pT_c^3}{p_cT^3}\right)$$

yields for the value of C_p, 17.7 calories per mole at 0.1 atmosphere. Applying the correction for pressure, as will be later outlined, to obtain the value at 1 atmosphere, the result is 18.4 calories. Owing to its magnitude with respect to R, C_p calculated from Capstick's data is probably inaccurate. Furthermore, we have no indication of the slope of the relationship between C_p and T. Therefore we decided to calculate C_p for the vapor at 1 atmosphere. For temperatures below the boiling point this condition would be merely hypothetical, but the results just as useful. We employed the following equation, which can be derived exactly by thermodynamics (6):

$$C_p(g) = C + \frac{dL}{dT} - \frac{L}{T} + T\left(\frac{dV}{dT}\right)_p\frac{dp}{dT} + B$$

C is the specific heat of the liquid under its saturated vapor, L is the heat of vaporization under saturation conditions, $\left(\dfrac{dV}{dT}\right)_p$ is for the vapor at the saturation pressure, and B is a term to convert C_p from the saturation pressure to 1 atmosphere. The value of B is determined as follows (6):

$$\left(\frac{dC_p}{dp}\right)_T = -T\left(\frac{d^2V}{dT^2}\right)_p \ ; \ B = T\int_1^p\frac{d^2V}{dT^2}\,dp$$

Since there are insufficient actual experimental data, Berthelot's equation of state was assumed to hold closely enough for the calculation of this correction term. Several simplifications were necessary to avoid tedious computations, involving mainly introduction of the perfect gas law for reduction of the smaller terms. The final result is:

$$B = -\left.\frac{6R^4T^4}{RT(R^2T^3 - ap) + 2abp^2}\right]_1^p$$

where a and b are the Berthelot constants, which in terms of the critical point data are given as

$$a = 16/3\ p_cV_c^2T_c \text{ and } b = V_c/4$$

The value of C was obtained from Hirn's and from Regnault's results (7), and is expressed by

$$C = 30.5 + 0.0209t + 0.000205t^2$$

giving calories per mole in terms of degrees Centigrade. L we obtained from the published data. dL/dT we calculated by passing a cubic equation in T through four selected values of L. By differentiation,

$$\frac{dL}{dT} = -59.17 + 0.316T - 0.000518T^2$$

To obtain $T(dV/dT)_p$, Berthelot's equation in the form

$$pV = RT\left(1 + \frac{9pT_c}{128p_cT}\left(1 - 6\frac{T_c}{T}\right)^2\right)$$

is differentiated, giving as the desired quantity

$$T\left(\frac{dV}{dT}\right)_p = \frac{RT}{p} + \frac{108RT_c^3}{128p_cT^2} = 0.082\left(\frac{T}{p} + \frac{3,245,200}{T^2}\right)$$

This quantity is in liters, for p in atmospheres. Owing to the complexity of the $p - T$ relationship as shown by the data of Young (4), dp/dT was not obtained directly, but was calculated by the Clapeyron-Clausius equation

$$\frac{dp}{dT} = \frac{L}{T(V_g - V_l)} = \frac{0.26794L/T}{\dfrac{1}{d_g} - \dfrac{1}{d_l}}$$

in atmospheres per degree Centigrade for carbon tetrachloride. The figures calculated by this equation agree very well with differences from Young's data. His density data were used. For the point at 20°C. the empirical equation, to be discussed later, was employed:

$$\log p_{mm.} = 7.8717 - \frac{1732}{T}$$

C_p was calculated up to 280°C., although it was expected that at the higher temperatures it might be unreliable. The critical temperature is 283°C. The results of the calculations are shown in table 1. The values of C_p have been plotted in figure 1. The straight line curve which we have drawn through the points appears to us to be the most probable locus of the true values. Its equation is:

$$C_p = 14.0 + 0.0233T$$

Certainly the accuracy cannot be high, owing mainly to uncertainties in dL/dT, C, and $(dV/dT)_p$, particularly at the two or three temperatures, but the graph is a useful indication, and is probably not in error by more

TABLE 1

Calculation of C_p of carbon tetrachloride(g) at 1 atmosphere

| t	dp/dT	$T\left(\dfrac{dV}{dT}\right)_p$	$-L/T$	dL/dT	$T\left(\dfrac{dV}{dT}\right)_p\dfrac{dp}{dT}$	C	B	$C_p(g)$
degrees C.	atmospheres per degree C.	liters	calories per degree C.	calories per degree C.	calories per degree C.	calories per degree C.	calories per degree C.	calories per degree C.
20	0.00557	196.6	−26.52	−11.07	26.70	30.97	0.68	20.8
80	0.03301	28.38	−20.12	−12.17	22.72	33.46	−0.04	23.9
120	0.0734	11.97	−16.53	−15.01	21.35	35.92	−0.71	25.0
160	0.1360	6.30	−13.53	−19.46	20.80	39.06	−1.64	25.2
200	0.2255	3.89	−10.64	−25.60	21.30	42.83	−2.86	25.0
240	0.351	2.64	−6.69	−33.42	22.50	47.30	−4.33	25.4
280	0.530	1.92	−2.91	−42.85	24.70	53.05	−6.34	25.6
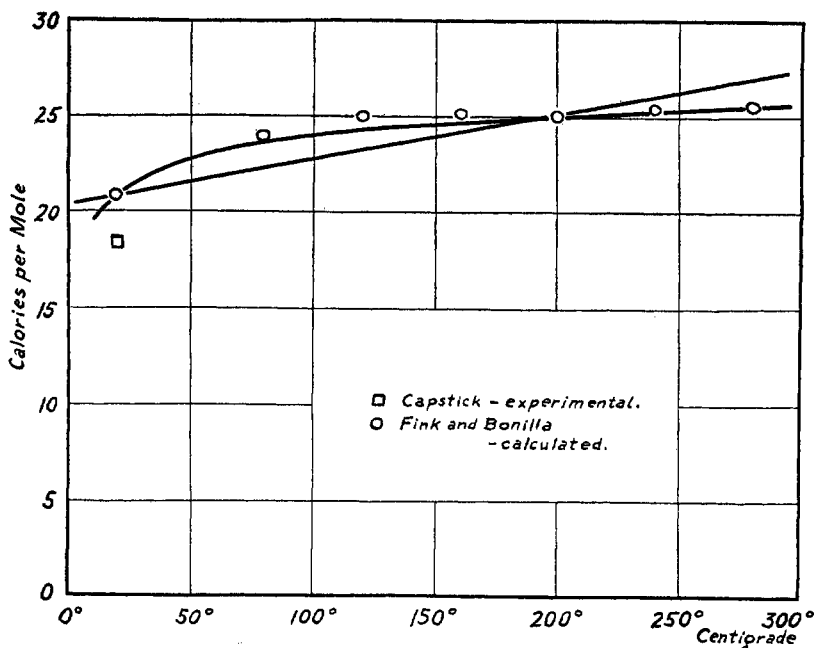
FIG. 1. C_p OF CARBON TETRACHLORIDE VAPOR AT 1 ATMOSPHERE

than 2 calories between 0°C. and 300°C. From the graph we find $C_{p,298} = 20.9$.

If it is desired to fit an equation more closely to the calculated points,

the following one may be used, which, plotted, gives the curve in figure 1, probably preferable for extrapolating:

$$C_p = 21.6 + 0.0073T - 1.4 \times 10^{25} \, T^{-10}$$

THERMODYNAMIC DATA FOR THE SUBSTANCES INVOLVED

C (graphite):

$C_p = -1.652 + 0.01676T - 0.00001727T^2 + 0.0^8994T^3 - 0.0^{11}263T^4$.

$C_{p,298} = 2.05$ calories per mole degree.

$S_{298} = 1.3$ calories per mole degree.

$C_p = 6.4 - 26,500/T^{3/2}$ (approximate, Fink and Bonilla).

Cl_2(g):

$C_p = 7.4 + 0.001T$; $C_{p,298} = 7.7$.

$S_{298} = 26.62$ calories per atom degree.

CCl_4:

ΔH_{293}(g) $= -25,430$ calories per mole.

ΔH_{298}(g) $= -25,430 + 5(20.9 - 15.4 - 2.05) = -25,410$.

S_{298}(l) $= 49.06$.

ΔS_{298}(l) of $CCl_4 = 49.06 - 4 \times 26.62 - 1.3 = -58.72$.

ΔH_{298} (vaporization) $= 7,700$; $p_{298} = 114.7$ mm.

ΔH_{298}(l) $= -25,410 - 7,700 = -33,110$.

ΔF°_{298}(l) $= -33,110 + 298 \times 58.72 = -15,610$.

ΔF°_{298}(g) $= -15,610 - RT(\ln 114.7 - \ln 760) = -14,490$ calories per mole at 1 atmosphere.

$C_p = 14.0 + 0.0233T$; $C_{p,298} = 20.9$.

$COCl_2$:

ΔH_{298}(g) $= -51,920$; ΔF°_{298}(g) $= -48,960$ (8).

$p_{298} = 1500$ mm.

ΔF°_{298}(l) $= -48,960 - RT(\ln 760 - \ln 1500) = -49,370$.

$C_{p,298}$(g) $= 13.3$ (by interpolation; see later).

CO_2(g) (9):

$\Delta H = -94,210 - 0.30T + 0.003T^2 - 0.0^6 1T^3$; $\Delta H_{298} = -94,280$.

$\Delta F = -94,210 + 0.30 \, T \ln T - 0.003T^2 + 0.0^7 5T^3 - 0.94T$.

$\Delta F^\circ_{298} = -94,010$.

$C_p = 7.40 + 0.0066T - 0.0000015T^2$.

$SiCl_4$:

ΔH_{298}(g) $= -142,650$; ΔH_{298}(l) $= -149,100$.

S_{298}(l) $= 56.43$; $p_{298} = 234.5$ mm.

ΔS_{298} (formation) $= 56.43 - 4 \times 26.62 - 4.54 = -54.59$.

ΔF°_{298}(l) $= -149,100 + 298 \times 54.59 = -132,800$.

ΔF°_{298}(g, 1 atmosphere) $= -132,800 - RT \ln\dfrac{234.5}{760} = -132,100$.

$C_{p,298}$(g) $= 20.9$ (1 atmosphere; assumed equal to CCl_4).

$SnCl_4$:

ΔH_{298}(g) $= -118,300$; ΔH_{298}(l) $= -127,360$.

S_{298}(l) $= 61.84$; $p_{298} = 24.02$ mm.

ΔS_{298}(l) (formation) $= 61.84 - 4 \times 26.62 - 12.50 = -57.14$.

ΔF°_{298}(l) $= -127,360 + 57.14 \times 298 = -110,420$.

ΔF°_{298}(g) $= -110,420 - RT \ln \dfrac{24.02}{760} = -108,300$.

$C_{p,298}$(g, 1 atmosphere) $= 20.9$.

AlCl$_3$:

$\Delta H_{298}(s) = -167,000; \Delta H_{298}(g, 1 \text{ atmosphere}) = -140,620 \ (10)$.

$S_{298}(s) = \frac{3}{2}R \ln 26.97 \times 35.455^3 - 3.76 = 37.97$ (see later).

$\Delta S_{298}(s)$ (formation) $= 37.97 - 3 \times 26.62 - 6.73 = -48.62$.

$\Delta F^{\circ}_{298}(s) = -167,000 + 298 \times 48.62 = -152,510$.

$p_{298} = 0.00025$ mm. (10); $C_p(s) = 6n = 24$ (assumed for 298).

$\Delta F^{\circ}_{298}(g, 1 \text{ atmosphere}) = -152,510 - RT \ln \dfrac{0.00025}{760} = -143,660$.

SiO$_2$ (quartz):

$\Delta H_{298} = -202,000 \ (4, 11); S_{298} = 9.81$ (see later).

$\Delta S_{298} = 9.81 - 4.54 - 2 \times 24.52 = -43.77; C_p = 10.7$.

$\Delta F^{\circ}_{298} = -202,000 + 298 \times 43.77 = -188,960$.

SnO$_2$ (amorphous):

$\Delta H_{298} = -137,800; \Delta F^{\circ}_{298} = -123,200 \ (12); C_p = 13.5$.

Al$_2$O$_3$ (amorphous):

$\Delta H_{298} = -384,000 \ (11); \Delta F^{\circ}_{298} = -356,600; C_p = 19.01$.

When not otherwise indicated, the source of data in this table is the International Critical Tables (4).

No data were found on the specific heat of phosgene gas. We will assume that the variation of $C_p(g)$ along the series methane–methyl chloride–methylene chloride–chloroform–carbon tetrachloride should be quite similar to that for the series carbon dioxide–phosgene–carbon tetrachloride, as would be expected to be approximately true. Since, furthermore, the values of $C_{p,298}$ are almost equal for carbon dioxide and for methane, those for phosgene and for methylene chloride should similarly be equal. C_p for the latter compound, however, was not available in the literature, and has therefore been obtained by interpolation, in figure 2. The result is 13.3.

No data were found on S for aluminum chloride or any similar compounds, so Latimer's approximation was used, since aluminum has at 298°C. almost reached the Dulong and Petit value.

Although sufficient C_p data are available, the entropy of quartz has apparently not been calculated. This we have done graphically, using the well-known relationship:

$$S_T = \int_0^T \frac{C_p}{T} \, dT$$

The graphical integration gives 9.81 as the entropy of quartz at 298°C.

THE CHLORINATION OF C$_2$Cl$_4$ AND OF C$_2$Cl$_6$

One of the reactions of which the reverse is found to occur in several of the methods of decomposition of carbon tetrachloride is:

$$C_2Cl_4 + 2Cl_2 = 2CCl_4$$

Lob (13) has shown it to occur in the action of a hot platinum filament on carbon tetrachloride vapor. The only study of the thermal reaction has been that due to Weiser and Wightman (13), also on the decomposition of carbon tetrachloride, and very much from a practical point of view. Some fairly helpful results can be calculated from their data if the assump-

tion is made that they approached the equilibrium, which seems likely.
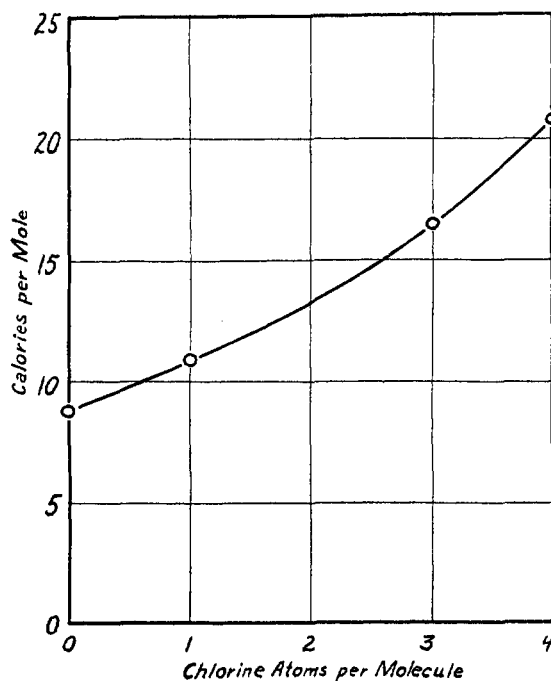However, it must be remembered that this may not be the theoretical

FIG. 2. C_p AT 298° K. AND 1 ATMOSPHERE FOR THE GASES CARBON DIOXIDE, METHANE, METHYL CHLORIDE, CHLOROFORM, AND CARBON TETRACHLORIDE

TABLE 2

The reaction $2CCl_4 = C_2Cl_4 + 2Cl_2$

(Calculated from Weiser and Wightman)

t (COR-RECTED)	$1/T$	C_2Cl_4	CCl_4	Cl_2	TOTAL MOLES	TOTAL VOLUME	$log_{10}K$	K_p	$\Delta F°$	ΔH
degrees C.		*moles*	*moles*	*moles*		*liters*				
750	0.000980	0.219	0.581	0.442	1.242	104	−2.91	0.00122	13,600	
850	0.000883	0.278	0.451	0.566	1.295	119	−2.42	0.00378	12,400	
900	0.000855	0.238	0.516	0.493	1.247	120	−2.74	0.00182	14,700	15,000
1025	0.000769	0.278	0.454	0.564	1.296	138	−2.51	0.00310	14,900	
1125	0.000714	0.351	0.297	0.572	1.220	140	−2.032	0.00928	13,000	

The number of moles given here is that obtained for a constant amount of carbon tetrachloride passed through the tube.

equilibrium; this will be discussed later. Weiser and Wightman's temperatures are for no gas flow, which we have approximately corrected to actual gas temperatures from data supplied by them. A further correction

was made: the carbon tetrachloride unaccounted for was portioned up between CCl_4 and C_2Cl_4 in ratio of the two vapor pressures, using Duhring's rule. Table 2 shows our calculated results. The values for log K were plotted against $1/T$ in figure 3, and $\Delta H'$ obtained from the slope. The only check on these figures is given by Berthelot's incomplete heat of combustion data (14) from which we may say that ΔH of formation of
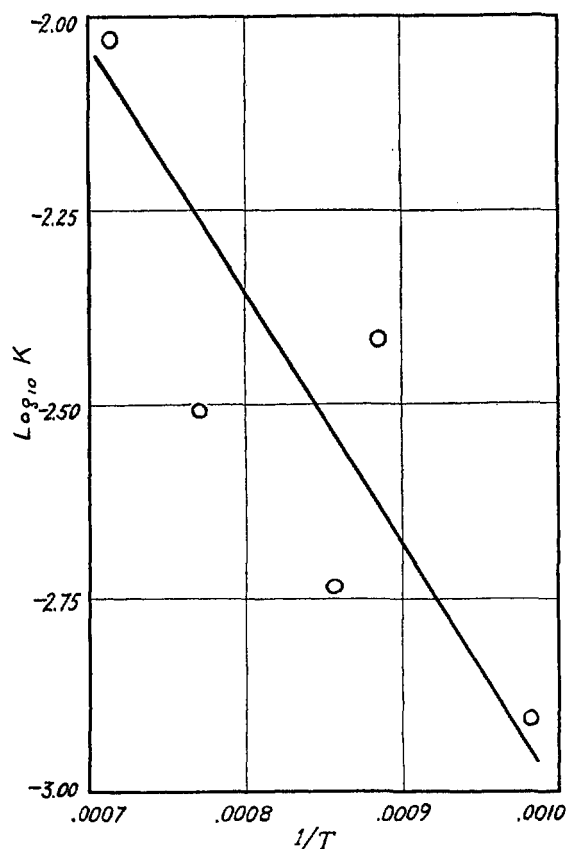

FIG. 3. EXTENT OF THE REACTION $C_2Cl_4 + 2Cl_2 \rightleftharpoons 2CCl_4$

$C_2Cl_4(g)$ will be greater than about $-40{,}000$ calories, so that ΔH for the decomposition of two moles of CCl_4 to C_2Cl_4 will be greater than 10,000 calories, compared with 15,000, the value from table 2. Therefore the chlorination of C_2Cl_4 to CCl_4 is thermodynamically quite possible, yet has never been accomplished empirically.

Weiser and Wightman found the gas reaction,

$$C_2Cl_4 + Cl_2 = C_2Cl_6$$
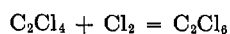
to occur, but at a slower rate than the C_2Cl_4 formation between the temperature limits they used.   At lower temperatures the velocity does not decrease as rapidly as may be expected, and it is appreciable at room temperature.   Recently (15) the reaction in solution, as affected by light, has also been studied.   Berthelot's figures on this reaction (16) are doubtless more accurate than his single heats of combustion, since the errors will cancel to some extent.   His data give $-54,000$ calories for the heat absorbed at room temperature.   From these two reactions we obtain the rough value of ΔH, 39,000 for

$$C_2Cl_6(g) + Cl_2 = 2CCl_4(g)$$
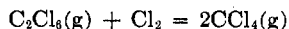
which is therefore endothermic, and favored by a temperature rise.   This reaction, too, has never been directly carried out.   The reverse action, however, has, and as early as 1839 Regnault (17) obtained C_2Cl_6 besides other substances in the following sequence with rising temperatures: C_2Cl_6, C_2Cl_4, C_2Cl_2, C_6Cl_6, C.

Except for carbon tetrachloride, the other carbon chlorides mentioned can all be produced consistently by the action of chlorine on carbon in a heated tube or in a carbon arc, as our own experiments and those of others have shown.   Bolton (18), for instance, obtained C_2Cl_6 and C_6Cl_6 in an arc.

From these considerations it is seen that the splitting and chlorination of the inter-carbon bond in C_2Cl_4 and in C_2Cl_6 is the operation which has not been directly carried out so far.   The problem seems to reduce itself to finding catalysts for these chlorinations, exothermic and endothermic, respectively, which will not simultaneously assist the decomposition to carbon and chlorine of the carbon tetrachloride formed.

Experimental

In an effort to duplicate Bolton's results and to determine simultaneously whether under any ordinary conditions carbon tetrachloride was produced, we constructed a Pyrex reaction chamber containing two axially perforated electrodes of carbon.   The arc was run under varying conditions of length, current, and chlorine flow rate, and the gas was admitted through both carbons.   Alternating current was used as well as direct.   Another apparatus was constructed, containing a graphite rod heated electrically to the desired temperature in a stream of chlorine.   In both of these setups mixtures of solid carbon chlorides, probably C_2Cl_6 and C_6Cl_6, were obtained on the walls and in the exit gas water condenser, but no carbon tetrachloride was obtained.   Soaking the electrodes and rods in solutions of metal salts (copper, iron, and nickel) did not seem to make any difference.   In the analysis for carbon tetrachloride the issuing gases were all completely condensed in a test tube by means of liquid air.   This test tube was then transferred to a beaker containing an ice–salt mixture.

The gas boiling off came out through the tube previously used as inlet, which was of small bore, about 20 cm. long, and for this last operation it was thermally insulated from convection currents by means of a larger concentric tube. By regulating the amounts of salt and ice we found that the desired rate of heating up could be obtained. With this simplified column it was found possible to detect easily about 0.1 cc. of carbon tetrachloride in several cubic centimeters of liquid chlorine.

THE CHLORINATION OF PHOSGENE

A great deal of work has been done by others on the chlorination of metal oxides by chlorine, by phosgene, or by mixtures of carbon monoxide and chlorine, and by carbon and chlorine, on a laboratory scale, at least. All of the oxides tried have been successfully chlorinated, so that it is safe to assume, in general, that any metal chloride can be readily produced by means of cheap chlorinating agents. Silicon dioxide is the most refractory oxide, and when treated with chlorine only, the temperature must approximate 1000°C. before appreciable interaction sets in. It is the only common oxide or anhydride that cannot be chlorinated by phosgene below 600°C.

Chlorinations can also be readily carried out by means of carbon tetrachloride vapor (19, 20), and we felt that some of these latter reactions might be reversed under attainable conditions, particularly the reaction involving silicon dioxide. Three of these reactions were studied by us, experimentally and theoretically. The free energy changes calculated for the reactions show why chlorination by carbon tetrachloride is so successful.

Pyrex glass bomb tubes were dried by heating overnight to more than 600°C. with a slow stream of carbon dioxide dried over magnesium perchlorate, $Mg(ClO_4)_2$, passing continually through the bombs. We then placed the bombs in an ice–salt freezing mixture and passed in and condensed the phosgene and added the metal chloride by means of a special funnel to prevent wetting the stem. Otherwise good seals were difficult. The bombs were then heated for a day at a time to successively higher temperatures. Before raising the temperature each time, the bombs were cooled and inspected for the production of any solid oxides. The following reactions were studied:

Reaction I

$$2COCl_2(g) + SiCl_4(g) = 2CCl_4(g) + SiO_2$$
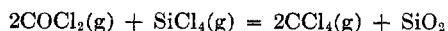
Approximately a dozen bombs were prepared with up to 4 cc. of each reactant as a liquid, in a total volume of 12 to 15 cc. Several were exposed for days to sunlight, others to a mercury vapor arc, and all were heated to
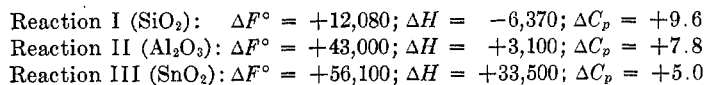
temperatures ranging up to 540°C. Two withstood this temperature and the large pressure involved without bursting. Traces of other chlorides, ferric chloride and aluminum chloride, had been added to two of the bombs to test for any catalytic action. In practically none of these tubes was there found any silicon dioxide deposited on the walls, or any other indication of reaction. Under the mercury arc a rather dense cloud always formed which would later disappear in a few hours or a day, even with the bomb at below 0°C. Quickly breaking the bomb after an exposure to the arc left only the merest amount of powder after the evaporation of the liquids. No corrosion of the glass by the phosgene was noticed, though some investigators (21) have been troubled by such an action on other types of glass.

Reactions II and III

$$3COCl_2(g) + 2AlCl_3(g) = 3CCl_4(g) + Al_2O_3$$
$$2COCl_2(g) + SnCl_4(g) = 2CCl_4(g) + SnO_2$$
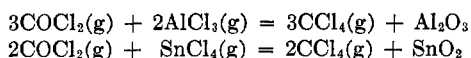
Two bombs with aluminum chloride and two with stannic chloride were prepared and treated similarly to those with silicon tetrachloride. Aluminum chloride was used because of its ready availability and stannic chloride because of its similarity to carbon tetrachloride. None of these bombs showed the formation of any oxide, which could have formed according to the above reactions. Even with C_2Cl_6 as an end product no oxides were formed; this reaction should have a greater tendency to occur, as we have already indicated.

Free energy calculations suggest the non-occurrence of the reactions to be due to lack of tendency toward the change rather than to lack of a catalyst. Calculations for 25°C. give the following results:

Reaction I (SiO_2): $\Delta F° = +12,080; \Delta H = -6,370; \Delta C_p = +9.6$
Reaction II (Al_2O_3): $\Delta F° = +43,000; \Delta H = +3,100; \Delta C_p = +7.8$
Reaction III (SnO_2): $\Delta F° = +56,100; \Delta H = +33,500; \Delta C_p = +5.0$

Because of the magnitude of the free energy change, reactions II and III are seen to be hopeless, but reaction I merits a little study. If the three chlorine-containing compounds are in their liquid forms, $\Delta F°$ becomes +11,360. The effect of increases in temperature and pressure were approximately calculated, assuming ΔC_p to remain constant over the range.

$$\left(\frac{dF}{dT}\right)_p = -S = -\int \frac{C_p}{T} dT = -C_p \ln T + A$$

$$\Delta F_{T_2} - \Delta F_{T_1} = -\int_{T_1}^{T_2} (C_p \ln T + A) dT = (-C_p T \ln T + (1-A)T) \Big]_{T_1}^{T_2}$$

$\Delta F°$ can be calculated closely enough for our purposes by knowing ΔH and assuming ΔC_p constant down to absolute zero. Knowing now $\Delta F°$ at two different temperatures, the value of $(1 - A)$, Lewis and Randall's I, can be calculated and

$$\Delta F°_T = -7860 - 5\ T \ln T + 95.1T$$

Thus $\Delta F°$ rapidly increases with temperature, decreasing the reaction tendency. For a pressure change

$$\Delta F_{p_a} = \Delta F_1^0 - RT \ln \frac{a_{CCl_4}^2}{a_{COCl_2}^2\ x a_{SiCl_4}}$$

where, approximately,

$$RT \ln a = \int_1^p V dp$$

for each substance. There is practically nothing in the literature on the gaseous molar volumes (or densities) of the substances involved, so only a rough calculation assuming $a = p$, or, in general, that the activity coefficients cancel, can be carried out. For the greatest yield with a given total pressure P of phosgene and silicon tetrachloride, the pressure of phosgene should be $2P/3$, as can be shown by setting

$$M = p_{COCl_2}^2\ x p_{SiCl_4};\ p_{COCl_2} + p_{SiCl_4} = P$$

and making dM/dp_{COCl_2} equal to zero. A final pressure of carbon tetrachloride of 1 atmosphere will be assumed, which in the bombs would have amounted to a deposit of silicon dioxide of about 25 mg. Therefore at a given temperature

$$\Delta F = RT \ln \tfrac{1}{2}p_{COCl_2}^3$$

and at 230°C., just above the critical temperatures of the substances involved, p_{COCl_2} amounts to 3700 atmospheres. The pressure actually would exceed this value, as can be seen from Dodge's reduced pressure versus compressibility curves (22). For the reaction between the liquids rather than the gases, and at 25°C., p is obtained as 740 atmospheres, so that if the reaction velocity is appreciable it would not be impossible to carry out the reaction under these conditions, but probably not commercially in spite of the small work of compression of the liquids.

The effect of the ultra-violet light from the mercury vapor arc lamp was obviously not merely catalytic, as the reaction reversed on removal of the light source, but the light also shifted the equilibrium. This is therefore another action that might be utilized.

THE DIRECT CHLORINATION OF CARBON

Our previously mentioned attempts to carry out the direct chlorination of carbon by chlorine to form carbon tetrachloride indicated that a catalyst was necessary. The reaction is decidedly exothermic and ΔF° of formation under standard conditions of gaseous carbon tetrachloride at 25°C. is $-14,500$.
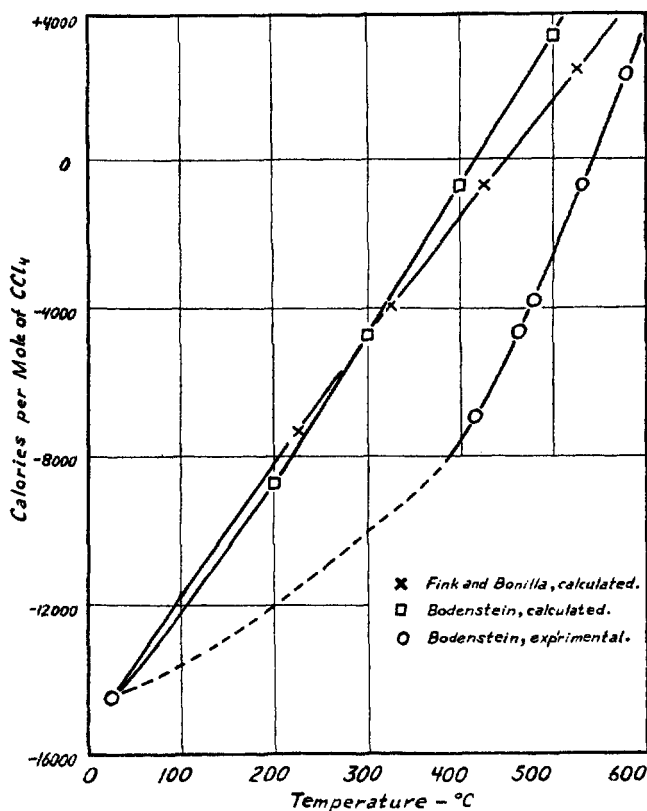
FIG. 4. EXTENT OF THE REACTION $CCl_4 \rightleftharpoons C + 2Cl_2$

After many fruitless attempts to find a catalyst, it was decided to attempt to reach equilibrium from the carbon tetrachloride side of the reaction:

$$C + 2Cl_2 = CCl_4$$
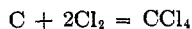
At this time Bodenstein's (23) work along this line appeared. His results are plotted in figure 4. They show that it is probably necessary to work at a temperature not over about 500°C. in order to synthesize carbon

tetrachloride. Needless to say, this equilibrium was reached by Bodenstein from only one side, and is not very near the thermodynamic or calculated equilibrium. The values for the curves, calculated from Bodenstein's data, are given in table 3. The Nernst heat theorem values (24) have also been plotted, though they involve the rough "chemical constants." We find by using the simpler relationship for $C_p(g)$ of carbon tetrachloride already obtained, and for carbon, the simpler of the expressions given:

$$\Delta H_T = \Delta H_0 + \Delta C_p dT = 21{,}160 + 7.2T - 0.01065T^2 + \frac{53{,}000}{T^{1/2}}$$

TABLE 3
Extent of the reaction $CCl_4 = C + 2Cl_2$
(Calculated from Bodenstein's results)

TEMPERATURE	CARBON TETRACHLORIDE DECOMPOSITION	$-\log_{10}K_p$	CHLORINE FRACTIONAL PRESSURE	$\Delta F°$
degrees C.	*per cent*			*calories per mole*
298	—	—	—	14490
417	4.06	2.18	0.078	6900
462	10.0	1.38	0.182	4650
477	13.9	1.10	0.244	3780
530	36.5	0.20	0.535	735
580	66.7	−0.506	0.800	−1790

on substituting the known value of ΔH_{298}. Since $\Delta F°_{298}$ is also known, the general free energy expression is obtained:

$$\Delta F_T° = 21{,}160 - 16.6T \log T + 0.01065T^2 + \frac{35{,}300}{T^{3/2}} + 8.66T$$

These signs of ΔH and ΔF are for the decomposition of carbon tetrachloride. Values of equilibrium partial pressure of chlorine for 1 atmosphere total pressure were plotted in figure 5. The results of the calculations are shown in table 4. The agreement with the rough heat theorem values is seen from the curve to be fairly close.

Stock (24) has recently succeeded in producing some carbon tetrachloride by the action of chlorine on activated charcoal between 400°C. and 600°C. at pressures between 1 and 4 atmospheres. His results were not very reproducible, but interesting. The maximum pressure of carbon tetrachloride that he obtained was at 400°C. and 4.1 atmospheres total pressure, and amounted to 0.29 atmosphere, certainly quite sizeable. Assuming the gas pressure quotient to hold constant over the pressure range, we can
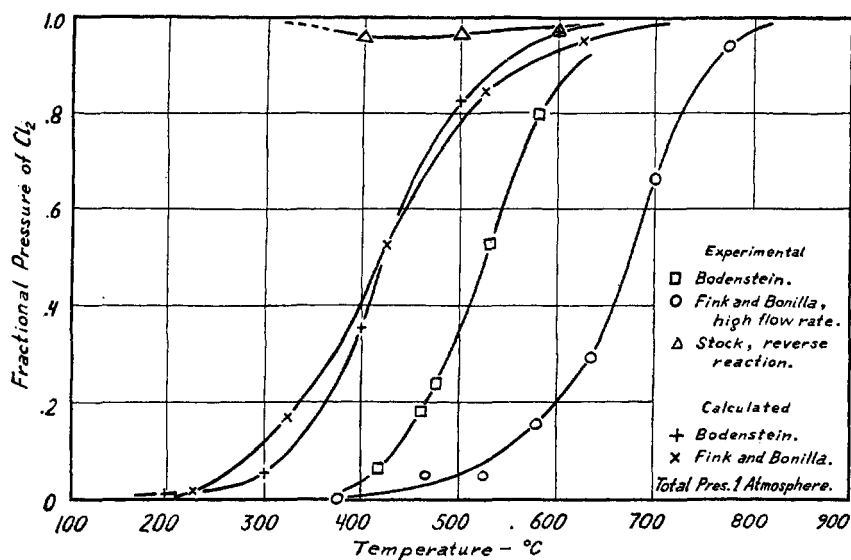
FIG. 5. FREE ENERGY CHANGE OF THE REACTION $C + 2Cl_2 \rightleftharpoons CCl_4$

TABLE 4

Theoretical extent of the reaction $CCl_4 = C + 2Cl_2$

TEMPERATURE	$\Delta F°$	$-\log_{10}K_p$	K_p	CHLORINE FRAC-TIONAL PRESSURE
Absolute	*calories per mole*			
500	7342	3.20	0.00063	0.0248
600	3955	1.437	0.0364	0.1735
700	725	0.226	0.594	0.529
800	−2426	0.661	4.58	0.846
900	−5359	−1.300	19.95	0.954

TABLE 5

The reaction $C + 2Cl_2 = CCl_4$

(Calculated from Stock's experiments)

TEMPERATURE	TOTAL BOMB PRESSURE	PARTIAL CHLORINE PRESSURE	PARTIAL CARBON TETRACHLORIDE PRESSURE	PRESSURE QUOTIENT K_p	PARTIAL CARBON TETRACHLORIDE PRESSURE AT 1 ATMOSPHERE TOTAL PRESSURE
degrees C.	*atmospheres*	*atmospheres*	*atmospheres*		*atmospheres*
400	2.5	2.12	0.204	0.0453	0.0416
500	1.65	1.56	0.088	0.0365	0.034
600	1.65	1.58	0.065	0.027	0.0256

calculate that the partial pressure of carbon tetrachloride will equal that of chlorine at a total pressure of about 40 atmospheres. Stock's maximum yields of carbon tetrachloride do seem to indicate a limit of reaction. We have made the appropriate calculations from them, and give the results in table 5. These values we have also plotted in figure 5, and the combination of theoretical and experimental curves for the equilibrium is strikingly similar to the curves given by Duhem (2).

Experimental

We decided to use the decomposition reaction to find a catalyst for the reaction of synthesis, knowing that the same catalyst should theoretically catalyze both opposing reactions. An apparatus was set up in which carbon tetrachloride vapor was produced by boiling the liquid in a graduated flask. The vapor passed through a Pyrex combustion tube in an electric heater. The tube contained a thermocouple hot junction, and in it were placed in different runs the various materials to be tested for catalytic effect. The gases next traversed a gas sampling tube maintained at about 80°C. to prevent condensation of the carbon tetrachloride, and from there were removed by a water jet suction pump in which the pressure was regulated by an air admission valve. A run was ended when the conditions of temperature and flow rate had remained constant for about 30 minutes, which corresponds to a large volume of carbon tetrachloride vapor, as the average flow rate was about 2 cc. of liquid carbon tetrachloride per minute. An excess of strong potassium iodide solution was admitted to the sampling tube, the liquid shaken about, poured out, the tube rinsed with alcohol, and solution and rinsings titrated with standard sodium thiosulfate solution and starch indicator, for free iodine. The partial pressure of chlorine was calculated, knowing the volume of the sampling tube (300 cc.) and the temperature at which it had been held. The carbon tetrachloride pressure was obtained by difference, for which purpose a manometer was connected to the system.

In order to obtain correct results with the above scheme it is necessary that chlorine and carbon should be the only decomposition products of the carbon tetrachloride. With some of the substances tested as catalysts solid and liquid products such as C_2Cl_6, C_2Cl_4, C_6Cl_6, etc., were produced in varying quantities. Many wood charcoals and silicon dioxide were among this class of substances. Ordinary granulated animal charcoal of 88 per cent ash was the best catalyst for the total decomposition, even when present in only small amounts, and no liquid or solid products of carbon tetrachloride decomposition ever condensed when the animal charcoal was used. Runs were made between 300°C. and 800°C. The results have been plotted alongside Bodenstein's curve in figure 4. The total time that the carbon tetrachloride vapor remained in the heated

portion of the tube we calculate to have been about 2 seconds, excluding the adsorption by the charcoal.   Furthermore, at this high flow rate it is probable that the vapor did not reach the temperature indicated, as the charcoal was never packed tightly and the granules were coarse.   The animal charcoal was therefore a very effective catalyst for this reaction, and undoubtedly more active than the charcoal Bodenstein used, though it is difficult to determine how much his reaction rates were affected by diffusion velocity.   When chlorine was passed through the heated tube at various temperatures and rates, there was, however, no noticeable carbon tetrachloride formation, using the same system of freezing and redistilling the outcoming gases as previously described under the C_2Cl_4 and C_2Cl_6 reactions.

Since pressure aids the formation of carbon tetrachloride by direct synthesis, according to Le Chatelier's principle, an iron bomb was prepared and filled with a mixture of several brands of active charcoals, including the animal charcoal already used.   Liquid chlorine was condensed in the bomb, which was then closed and heated for 60 hours in a sand bath at approximately 170°C.   Upon opening, a mixture of solid and liquid chlorides of carbon was found, as well as iron and lead chlorides (the latter from the lead gaskets), but no carbon tetrachloride could be detected.

Thus it is seen that the direct chlorination of carbon by chlorine to form carbon tetrachloride is a reaction that is quite particular as to its catalyst. Stock seems to have struck a charcoal that serves the purpose, though apparently not specially well, but none of the substances we have tested seem to have any value along this line, including a very porous graphite prepared at 4000°C.

It is not impossible, of course, to explain by the catalyst poisoning theory why these two reactions should not reach the calculated equilibrium. It is merely necessary to assume that Bodenstein's catalyst was poisoned by the chlorine which was formed, but not by carbon tetrachloride, whereas Stock's catalyst was affected in exactly the reverse manner.   More work along this line will undoubtedly clear up the situation, and show whether some simple assumption is correct, or whether there are complications or an entirely different phenomenon.

THE REACTION $2COCl_2 = CCl_4 + CO_2$

From the thermodynamic data already given, we find for the above reaction $\Delta F^\circ_{298} = -9580$ calories and $\Delta H_{298} = -15,870$ calories.   Therefore, there is a decreasing tendency for the left-to-right reaction at higher temperatures, assuming ΔC_p to remain small.   At about 500°C., however, the carbon tetrachloride equilibrium pressure ought yet to be appreciable and readily determinable, as well as that of carbon dioxide.   Stock and Wustrow (25) have calculated several points on the theoretical equilibrium

curve, by the use of the heat theorem. We have calculated the position of the equilibrium over a broader band of temperatures, using the thermodynamic data we give above. We have assumed that phosgene has a value of C_p which approximates the average of the values for carbon dioxide and carbon tetrachloride. Therefore ΔC_p will remain small, and will be assumed constant at $+3.2$, the figure based on our data for 25°C. These data yield:

$$\Delta F° = -16{,}824 - 7.375T \log T + 42.5T$$

Starting with this equation, the values for $\Delta F°$, log K, and fractional phosgene pressure have been calculated and are given in table 6.

The formation of phosgene from carbon monoxide and chlorine has been thoroughly studied and commercial-sized plants built for its manufacture (26). Therefore phosgene could undoubtedly be a practical source of

TABLE 6

Calculated equilibrium for the reaction $2COCl_2 = CCl_4 + CO_2$

TEMPERATURE	$1/T$	$\Delta F°$	$-\log_{10}K_p$	PHOSGENE FRACTIONAL PRESSURE
degrees C.	*Absolute*	*calories*		
162	0.0023	−6784	−3.41	0.019
203	0.0021	−5984	−2.745	0.041
267	0.00185	−4754	−1.92	0.098
352	0.0016	−3144	−1.10	0.220
496	0.0013	−494	−0.140	0.460

carbon tetrachloride, or rather, simply an intermediate product, if a suitable catalyst were found. Quantitative studies of reactions involving phosgene have been made frequently, and for widely varying conditions (27, 28). But seldom have other reactions than $COCl_2 = CO + Cl_2$ and its intermediate steps been investigated, and no carbon tetrachloride has apparently ever appeared when its presence was not desired, or expected. The formation of carbon tetrachloride from phosgene has been reported only by Stock (21, 25), and in very small amounts. The static method he used does not lend itself to accurate results, owing to the small volumes of carbon tetrachloride produced, although it has an important advantage in permitting of long reaction periods. Accordingly, we investigated the decomposition of phosgene by the dynamic method. We decided to attempt to carry out the reaction at as low temperatures as possible, by the use of suitable catalysts if they could be found, to eliminate the multiplicity of other reaction products than carbon dioxide and carbon tetrachloride, such as carbon monoxide, chlorine, hexachloroethane, etc., which complicate the analysis and the interpretation of results.

Starting with pure phosgene, the reaction products to be expected at the low temperatures at which carbon tetrachloride will not decompose are carbon dioxide and carbon tetrachloride in equal concentrations and carbon monoxide and chlorine, the formation of which is to be minimized, also in equal concentrations. From the methods mentioned by Olsen (29) for the determination of phosgene, we found the precipitation with aniline most convenient. Chlorine was first removed by means of antimony trisulfide, then phosgene and carbon dioxide by a water solution saturated with aniline and about half saturated with strontium hydroxide. We found that under these conditions phosgene did not hydrolyze and precipitate any strontium carbonate, to interfere with the carbon dioxide determination. Also, the diphenylurea precipitate obtained by the action of phosgene on the aniline was not soluble in the strontium hydroxide solution, though it does dissolve in stronger alkaline solutions. The carbon monoxide and carbon tetrachloride present in the gas mixture were not determined directly. In the apparatus used, phosgene as a gas leaves a cylinder through a needle valve. The rate is measured by a flowmeter containing sulfuric acid, a correction for pressure being applied, for accurate results, from the reading of a special manometer. The phosgene then passes through the reaction tube which contains any catalyst being tested, and is heated electrically. A three-way cock permits the issuing gases to follow a by-pass and be finally exhausted by a water jet suction pump. When the conditions have remained constant a sufficient time, depending on the flow rate and on the age of the catalyst, the cock is turned to permit the gases to enter the absorption train. Liebig bulbs contain the antimony trisulfide and a bubble bottle holds the aniline–strontium hydroxide solution. By regulating line and air admission cocks the pressure in the system can be maintained at slightly above atmospheric. This is to prevent, practically, the entrance of air, which would oxidize phosgene to carbon dioxide, besides introducing a small amount of carbon dioxide otherwise. Perfectly dry antimony trisulfide, the chlorine absorbent, never absorbed any phosgene, nor gave other trouble. The aniline–strontium hydroxide solution was kept and handled entirely like a standard caustic solution, and never touched the air after being prepared. It was kept in a dark bottle to prevent discoloration. In preparing the absorption train flask the train was first filled with pure nitrogen, then the solution admitted. After a run the solution and precipitates were blown back by nitrogen through the gas inlet tube and into a Gooch crucible fitted with an air-tight stopper. After thorough washing with water the crucible was dried to constant weight at 75°C.—24 hours in an electric oven was sufficient—and weighed. The diphenylurea was then leached out by alcohol in a Soxhlet extractor. The crucible was again washed with water and dried at 75°C., the difference in weight being

taken as diphenylurea. Now the strontium carbonate was leached out with dilute hydrochloric acid and the crucible washed and dried as before, giving strontium carbonate by difference. The weight of chlorine absorbed was given directly by the gain in weight of the antimony trisulfide tube, as the displaced sulfur remains in the tube. The phosgene used contained some carbon monoxide as impurity. No carbon dioxide and merely the slightest trace of chlorine were found in it, by a blank run. The excess pressure of the cylinder over that of pure phosgene was approximately 5 per cent at the beginning and decreased as more of the gas was used. No hydrogen chloride was found in the phosgene, no test for hydrogen sulfide being obtained after passing over antimony trisulfide.

Experimental

With this apparatus numerous runs were made at 500°C. with the heating tube empty and with different varieties of carbon in it. Animal charcoal gave a substantial decomposition to chlorine and carbon monoxide and gave no carbon dioxide, so it was not used again. Wood charcoals gave little, if any, chlorine, but also practically no carbon dioxide. A very adsorbent and highly activated variety of alkaline black ash charcoal was used in many runs, both alone, and impregnated with solutions of metal salts and then outgassed at a high temperature. Nickel sulfate, copper sulfate, cobalt sulfate, ferric sulfate, and chromium sulfate were used. All of the runs gave the same result, no carbon dioxide, nor, presumably, any carbon tetrachloride. The weights of strontium carbonate obtained averaged about 1.0 mg., and decreased as experimental technique improved. These small weights were probably due to slight infiltration of air. In these runs very little decomposition of the phosgene to carbon monoxide and chlorine occurred, on account of the reaction's sensitivity for a catalyst. Flow rates were as small as 2 cc. per minute, and the heated volume of the tube about 25 cc. The aniline–strontium hydroxide solution was saturated with strontium carbonate, as carbon dioxide-free water was not used in its preparation. All washings were, however, with distilled and recently boiled water, to minimize the solubility of the carbonate.

For its possible interest, a previously used method of analysis will be mentioned, which was perfectly satisfactory for this gas mixture, but is not very sensitive. The issuing gases were passed through gas sampling tubes until at least ten volumes had passed, and then were treated quickly with strong sodium hydroxide solution in a Hempel pipette and gas burette. Simultaneously, a volume of nitrogen was admitted, sufficient to retain the carbon tetrachloride present in the gaseous state. The remaining nitrogen, carbon tetrachloride, and carbon monoxide were passed into

another pipette containing some thin paraffin oil saturated with air, and the carbon tetrachloride dissolved quantitatively. The carbon monoxide is lastly determined as usual by means of cuprous chloride. Thus we have determined the volumes of carbon monoxide, of carbon tetrachloride, and of the total gas mixture (that of the sampling tube), sufficient data to calculate the pressure quotient. Phosgene, obtained by difference, constitutes ordinarily the largest part of the total volume, so that little error is introduced in that way. If the gases after the caustic treatment are to be retained over a liquid, mercury should be used, as carbon tetrachloride vapor assumed at 1 atmosphere and 25°C. is soluble in about eight times its volume of water. This method, besides being very rapid, has the advantage that the carbon tetrachloride can be directly recovered afterward.

TABLE 7

Gas absorption by light paraffin oil, at room temperature

RUN NO.	CONDITION OF AIR	CONDITION OF OIL	INITIAL VOLUME	FINAL VOLUME	CALCU-LATED FINAL VOLUME
			cc.	*cc.*	*cc.*
1	Pure, dry	Saturated with air	88.0	88.0	——
2	Pure, dry	Free of air	92.15	92.1	——
3	Saturated with water	Saturated with air	64.6	64.6	——
4	About 50 per cent carbon monoxide	Saturated with air	24.1	24.1	——
5	Saturated with water and carbon tetrachloride	Saturated with air	88.8	76.0	75.95
6	Saturated with water and carbon tetrachloride	That used in No. 5	96.9	82.9	82.88

The oil we used was a standard light paraffin lubricating oil of the following physical properties: density at 27°C., 0.877; flash point, 196°C. (385°F.); fire point, 229°C. (445°F.), both by the Cleveland open cup tester. We found that 15 minutes of gas–oil contact time with frequent shaking was sufficient for equilibrium. In table 7 are given our tests to establish the utility of the method. Run 1 shows that the oil has no appreciable vapor pressure at room temperature; runs 2, 3 and 4 that air, water, and carbon monoxide are practically insoluble in it; and runs 5 and 6 that carbon tetrachloride vapor in small quantities is practically completely dissolved from air. Stock has already shown that concentrated potassium hydroxide solution can effectively dissolve phosgene and carbon dioxide without hydrolyzing carbon tetrachloride appreciably, nor dissolving it.

THE REACTION $CO_2 + CCl_4 = 2COCl_2$
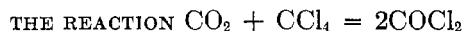
The reverse reaction of the one just discussed, or the formation of phosgene from carbon dioxide and carbon tetrachloride, was next taken up, to attempt to reach the equilibrium experimentally from that side, and to improve on the few and rather unreproducible data of Stock (21).

The apparatus we constructed is shown in figure 6. Carbon dioxide evaporates in the cylinder A and escapes through a needle valve into the system. The flow rate is measured by the oil-filled flowmeter B. The manometer C gives the gage pressure within the saturator D, which contains carbon tetrachloride and is surrounded by a water bath (F) to increase the heat capacity and minimize temperature fluctuations. When lower than room temperatures are desired, running water is employed to cool the saturator. Its temperature is given by the thermometer E. The gases then pass through a bubble bottle containing anhydrous magnesium perchlorate. Next they enter the reaction tube H, which is
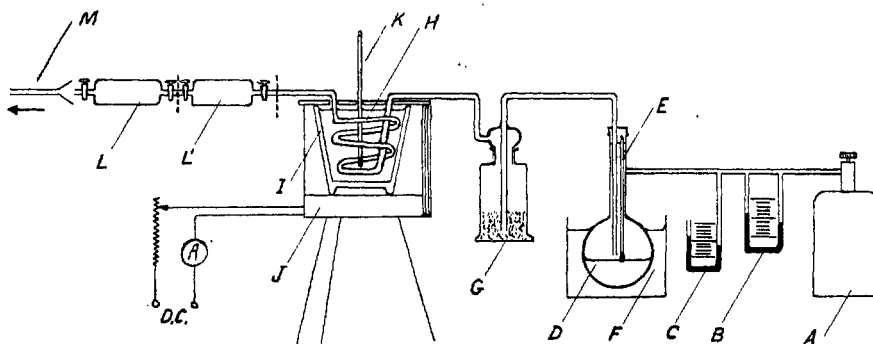

FIG. 6. SET-UP FOR THE FORMATION OF PHOSGENE

heated by the electric heater J. A fused nitrate bath is contained in the iron pot I. The issuing gases fill and traverse the gas sampling tubes L and L′, and the issuing phosgene is destroyed by a water jet suction pump.

The carbon dioxide practically saturated itself with carbon tetrachloride. This can be shown to be true by a brief calculation, knowing a figure for evaporation rate of carbon tetrachloride. The variables will be:

p' = carbon tetrachloride saturation pressure, in atmospheres.

p = actual carbon tetrachloride pressure, in atmospheres.

P = pressure of carbon tetrachloride and carbon dioxide, in atmospheres.

K = rate of evaporation of carbon tetrachloride, in moles per second × cm².

A = Effective liquid area, in cm².

Q = moles per second carbon dioxide flow.

$(p'-p)/p' = S$ = fraction of unsaturation.

The result is:

$$\ln S = \frac{-KA(P-p)}{Qp'}$$

Using $K = 6 \times 10^{-6}$, calculated from available data (30), we get $\ln S = -6.2$, or S is 0.2 per cent for our average conditions. As the temperature changes, K and p' should vary somewhat similarly, so that this value of S should hold over the range of room temperatures.

The pressure p' was calculated from the relationship

$$\log p' = 7.8717 - 1732/T$$

which we obtained by plotting data for p' of carbon tetrachloride between 0°C. and 50°C. (4, 30). The best curve through the points plotted as log p' against $1/T$ is this straight line, and the deviations are quite small. This equation gives the pressure of the liquid in contact with only the pure vapor. Owing to the added carbon dioxide pressure, the change in carbon tetrachloride vapor pressure is given by:

$$(\mathrm{d}p'/\mathrm{d}P)_T = V_1/v_g$$

At 30°C. $\mathrm{d}p'/\mathrm{d}P$ thus amounts to 0.00065, and Dp' is 0.33 per cent of p'. This error is in the opposite direction from that previously calculated for lack of saturation of the carbon dioxide with carbon tetrachloride, and both will be neglected. At the low pressures of 1/6 atmosphere it was assumed that carbon tetrachloride vapor obeys the gas laws closely enough in these calculations.

In the apparatus, the Pyrex helix had a heated volume of 75 cc., and the bath was a eutectic mixture of sodium nitrate and potassium nitrate. This method of heating gives much greater uniformity of temperature than is obtained in a tube in an ordinary electric heater. One side of the pot we thermally insulated better than the other, so that a gentle convection current was obtained. The gases were dried by magnesium perchlorate to prevent carbon tetrachloride hydrolysis and hydrogen chloride formation, which would be included as phosgene in the analytical method finally adopted.

Since the gas mixture after reaction will be entirely composed of carbon tetrachloride, carbon dioxide, and phosgene if there is no chlorine present, only two data are necessary for the analysis, besides this fact. We decided that greatest accuracy would be attained by using: (a) the ratio of moles of phosgene to carbon dioxide in the gases after the reaction, and (b) the ratio of moles of carbon tetrachloride to carbon dioxide before the reaction. (a) can be determined by the usual analytical methods, and (b) from the saturator temperature and pressure. Thus, starting

with gas sampling tubes filled with nitrogen it is not necessary to displace the foreign gas completely before the correct result can be obtained. In the chemical analysis standardized solutions of sodium hydroxide, sulfuric acid, and silver nitrate were used. For 50 cc. of the caustic solution the sulfuric acid titre to the phenolphthalein end point was known. After a run, that volume of the caustic was admitted to the sampling tube by a pipette, the tube shaken thoroughly, but not long enough to hydrolyze carbon tetrachloride, and the solution and rinsings were titrated to the same phenolphthalein end point. The decrease in cubic centimeters of sulfuric acid solution required, calculated to moles of the acid, is equal to 1/2 the number of moles of carbon dioxide absorbed plus 3/2 the number of phosgene moles absorbed. The solution was then made to the correct acidity and the moles of phosgene absorbed determined by a Mohr's titration for chloride.

The relationship used in determining the pressure quotient from the data:

$$\frac{p_{CCl_4}}{P - p_{CCl_4}} = \frac{(CCl_4)}{(CO_2)} = R; \quad \frac{(COCl_2')}{(CO_2')} = Q$$

gives

$$K_p = \frac{R}{Q^2} + \frac{R-1}{2Q}$$

of which the latter term may be negligible. The unprimed gas concentrations are for before the reaction; the primed ones are for the gas mixture after reaction.

Experimental

Runs were made with this apparatus at 283°, 314°, 344° and 354°C., both with and without charcoals of different varieties in the tube. The carbon dioxide flow rate was varied between 0.5 and 3.0 cc. per minute. Some runs had to continue for as long as ten hours to yield a sufficient gas sample. In general, the charcoals showed no action, the reaction occurring principally on the Pyrex walls, apparently. We analyzed both gas sampling tubes, each time, and the agreement in the value of Q was generally good, if the conditions had remained uniform, showing that progressive catalyst poisoning was not occurring. New glass and very old glass (Pyrex) both seemed to be active catalytically.

For data by the dynamic method at a lower temperature, a different tube was used—the same one that had been utilized in the attempts to convert phosgene to carbon tetrachloride. It had seen much service, and had crystallized spots, or devitrified, on its inner surface. With otherwise the same apparatus, several runs were made at 250°C.

Many of these runs, in both set-ups, gave low phosgene yields, compared to the rest. These non-equilibrium results were obtained in a quite irregular order, in general, and were not reproducible. In magnitude they extended to perhaps five or ten times the minimum $K(CO_2 \times CCl_4/(COCl_2)^2)$ which was, however, fairly reproducible. The runs in which the maximum phosgene formation was obtained at a given temperature amounted to about one-half the total number, and were relatively fewer at the lower temperatures. It was obvious that the condition of the surface was very important in determining its catalytic effect.

TABLE 8

Experimental results for $CO_2 + CCl_4 = 2COCl_2$

TEMPERA-TURE	RUN NO.	$1/K$	WEIGHTED AVERAGE $1/K$	$+\log K$	$1/T$	Q	R
degrees C.							
354	1	331	316	−2.500	0.001595	0.0293	0.303
354	2	305				0.0316	0.310
344	3	450				0.0243	0.277
344	4	456				0.0244	0.284
344	5	394				0.0259	0.278
344	6	437	435	−2.638	0.001620	0.0236	0.252
344	7	437				0.0232	0.244
344	8	411				0.0135	0.0819
344	9	432				0.0120	0.0683
344	10	451				0.0121	0.0721
314	11	1,212				0.0130	0.214
314	12	1,116	1,280	−3.080	0.001704	0.0137	0.214
314	13	1,365				0.0128	0.229
314	14	1,313				0.0131	0.230
283	15	4,900	4,900	−3.690	0.001799	0.00595	0.175
250	16	16,600	17,100	−4.233	0.001911	0.00388	0.253
250	17	17,600				0.00378	0.255
198	18	458,000	452,000	−5.655	0.002120	0.00073	0.244
198	19	442,000				0.00074	0.242

For temperatures below 250°C. the dynamic method was dropped, as the reaction velocity becomes too slow. Two 2-liter Pyrex flasks were thoroughly dried by heating to almost the softening point for an hour and at the same time passing in a stream of dried carbon dioxide. At least one hundred volumes of carbon dioxide were passed through, insuring the removal of air. Then, weighed quantities of carbon tetrachloride in long thin tubes closed at the bottom were introduced and the flasks sealed off, as quickly as possible. They were placed in a constant temperature oven at 198°C. One was removed at the end of 5 days, and the other at 14 days. The same method for the calculation of K was used as for the

dynamic method runs, except that R was calculated from the known volume of carbon dioxide and the weight of carbon tetrachloride. Also, in determining Q it was unnecessary to analyze for carbon dioxide, so distilled water was used to decompose the small amount of phosgene formed and absorb the hydrogen chloride. Thus it was unnecessary to eliminate
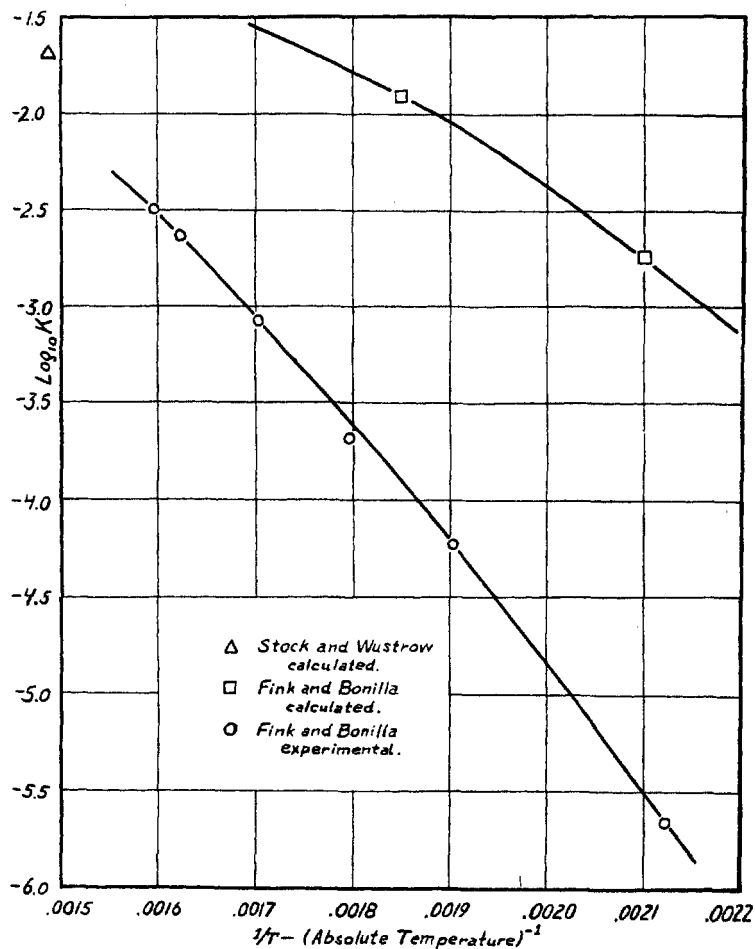

FIG. 7. EXTENT OF THE REACTION $CO_2 + CCl_4 \rightleftharpoons 2COCl_2$

carbon dioxide before proceeding with the Mohr's titration; instead, neutralization with calcium hydroxide was required. The two bulbs gave almost equal values of K, so that an equilibrium was obtained.

The results obtained by all of these methods are given in table 8. In all of these phosgene formation runs no chlorine was ever noticed, by smell or by the iodide–starch test, owing undoubtedly to the fact that no catalyst

for its formation was present. So the reaction was not complicated by the decomposition of carbon tetrachloride or that of phosgene to carbon monoxide and chlorine. Undoubtedly phosgene was formed in every case, as it could be detected by its distinctive smell even in the lowest concentrations. No hydrogen chloride was ever noticed after a run was well started.

The results have been plotted in figure 7, and approach the theoretical curve as the temperature rises. It is noticed that the point at 283°C. does not quite fall on the curve with the rest. This was the lowest temperature at which the first heating coil was used, and probably the corresponding equilibrium was not reached, owing to diminished speed of reaction, that was reached at the higher temperatures. It was practically impossible to operate at flow rates small enough to reach equilibrium at below 300°C. for this first coil, or at below 250°C. for the old tube. Five-tenths of 1 cc. of carbon dioxide per minute was the lowest rate found feasible.

The fact that a different tube, in the case of the point at 250°C. and an entirely new method at 198°C., gave points on a smooth curve that is almost straight seems to bolster up the possibility that a real metastable or false equilibrium is reached in this reaction, which similarly may be true for other reactions; $C + 2Cl_2 = CCl_4$ has already been considered, and $2COCl_2 = (COCl_2)_2$ has been mentioned.

The constant volume small bomb results of Stock (21) are naturally not of the same degree of accuracy as these based on the dynamic method. Stock could only produce a few hundredths of a cubic centimeter of phosgene in a bomb. For the production of carbon tetrachloride by the reverse of the reaction now being considered he has fairly good checks in two runs (31) at 400°C. and two at 500°C. The values of $(COCl_2)^2/(CO_2) \times (CCl_4)$ we obtain from his data are $\log^{-1} 2.77$ at 500°C. and $\log^{-1} 3.77$ at 400°C. These points bear out the false equilibrium theory, but were not plotted in figure 7 because the curves now shown would be dwarfed.

We believe that we have really reached an equilibrium. It may be the end of a fast reaction, with another slow one occurring simultaneously, which will eventually lead the system to the theoretical equilibrium. It is not possible at present to tell whether such a slower reaction exists, but from our data and those of Bodenstein and of Stock it is apparent that such a slower reaction must indeed be slow, compared to the observed one. This statement also holds for the other previously mentioned "false equilibria." In table 9 are given data for runs at 344°C. at higher flow rates than the minimum ones used. The pressure quotient obtained is plotted in figure 8 against the carbon dioxide flowmeter reading, which is practically proportional to the carbon dioxide mass flow at the low flow rates

used. It is seen that extrapolation to zero flow rate along the simple curve gives practically the same value for the extent of reaction as that obtained at the lowest flow rate that was actually used. In carrying out the extrapolation it should be remembered that at zero flow rate the curve should approach the pressure quotient axis normally. For simplicity we did not

TABLE 9

Effect of flow rate variations on the extent of reaction of $CO_2 + CCl_4 = 2COCl_2$ *at* $344°C.$

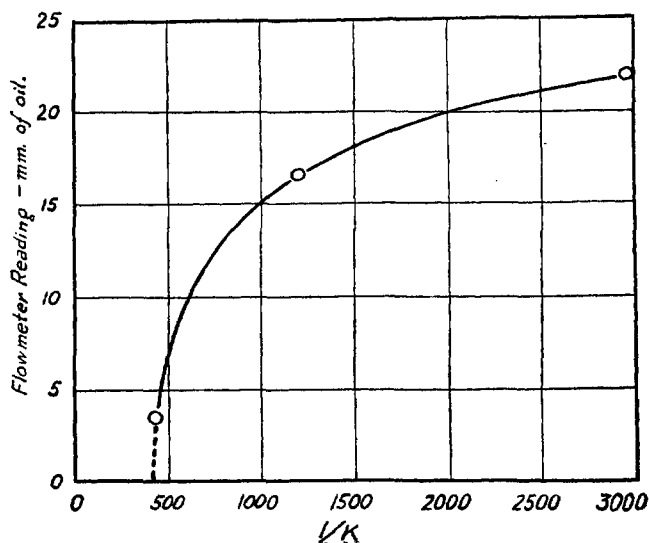| RUN NO.	FLOWMETER	$1/K$	WEIGHTED AVERAGE $1/K$	$\log K$	Q	R
	$mm.$					
3 to 10	3.4		435	−2.638	0.024	0.26
20	22.0	3,080	} 2,960	−3.472 {	0.00885	0.244
21	22.0	2,840			0.00920	0.244
22	16.5	1,090	} 1,200	−3.080 {	0.01446	0.234
23	16.5	1,490			0.01259	0.241

FIG. 8. EFFECT OF FLOW RATE ON THE REACTION $CO_2 + CCl_4 \rightleftharpoons 2COCl_2$ AT 344°C.

apply this slight correction for finite reaction time, owing to its small magnitude under the conditions and to the additional amount of data that would have been required at the various temperatures. We do not feel that these data are sufficiently accurate to merit calculation of the velocity constant, etc.

A careful consideration of the experimental facts seems to point more strongly to the existence of a false equilibrium of unknown mechanism

than to a simple catalyst poisoning, as advocated by Bancroft (31), for false equilibria in bomb reactions.   Bancroft does not mention the dynamic method.   The principle argument for catalytic surface poisoning in this reaction is given by the consideration that over a rather broad range of gas phase compositions, between the two false equilibrium curves, the forward and reverse reaction velocities are equal, or almost equal if a slight drift towards the true equilibrium exists.   It is hard to conceive of this being so unless the two velocities are each zero, or almost so, and the simplest explanation for this would be a poisoned catalyst, unable to allow either forward or reverse reaction to proceed.

In support of some other mechanism as causing the false equilibria let us consider the possible explanations according to the poisoned catalyst theory.   False equilibrium might be expected, owing to one of the following phenomena: (1) any one or more of the reactants being strongly and reversibly adsorbed by the catalytic surface (excluding others); (2) any reactant or outside substance being strongly and irreversibly adsorbed, forming a compound of very low dissociation pressure, deactivating the surface.   According to the first possibility the reaction velocity would decrease rapidly but smoothly as the pressure of the strongly adsorbed substance increased.   However, the composition of the gas phase in equilibrium with the catalyst could not vary, according to the principles of thermodynamics, or, to be more accurate, the equilibrium pressure-constant calculated for the gas phase cannot depend on the nature of the catalyst surface.   Our value of the pressure quotient therefore does not depend on the reversible absorption of one of the reactants, assuming equilibrium to have been practically reached.   Furthermore, if the reaction velocity in one direction were decreased by stronger adsorption of the product, that in the opposite direction with the same catalyst would be increased, and none of the reactions have been found to take place as readily as this would indicate.   For instance, the same tube that was utilized for the reaction $CO_2 + CCl_4 = 2COCl_2$ at 250°C. gave no indication whatsoever of the reverse reaction, as has already been mentioned. The second above possible explanation obviously cannot be true in this case, in which the extent of reaction was never found to vary consistently with the age of the catalyst, or length of the run.

To supply somewhat of a check on the results, runs 8 to 10 were performed, in which the relative amounts of the gases in the issuing equilibrium mixture were varied by cooling the carbon tetrachloride evaporator. Compared to runs 3 to 7, at the same temperature and flow rate, the equilibrium phosgene concentration has decreased to about one-half and the carbon tetrachloride concentration to about one-fourth of the values for the previous runs.   The pressure quotient K is seen to remain the same, in fact the average K's for the two groups of runs are so similar that the

agreement is partly fortuitous, as can be told from the magnitude of the individual deviations.

A third possible explanation of the results obtained is that one of the products, say phosgene, might reversibly combine with the solid catalyst to form a solid compound, of appreciable dissociation pressure, that has no catalytic properties. There would, from the phase rule, be only one equilibrium pressure of phosgene at any temperature, if both solid phases were present. Therefore it would not be possible to produce the poison phosgene, say, at a pressure higher than this pressure for equilibrium with the poisoned catalyst, and one would be measuring the dissociation pressure of this poisoned catalyst rather than the gas reaction equilibrium. This state of affairs would also give the same false equilibrium with the streaming method as with bomb reactions. However, this is probably not the explanation in this case, as many factors oppose it. In the first place, the same catalyst could not cause each of two opposing reactions to take place, separately, even to a slight extent, as Stock has succeeded in doing for the forward and reverse reactions of $CO_2 + CCl_4 = 2COCl_2$. In the second place, the calculated K would vary as the initial ratio R were varied, whereas runs 8 to 10 show no variation. Finally, if such a poisoned catalyst compound is formed, a little reasoning will show that a smooth curve of flow rate (or time of reaction) against K or fraction decomposed would not be obtained; there would be a discontinuity at the flow rate at which the time of reaction were just sufficient for the reaction to have proceeded to the point where the phosgene pressure produced equaled the poisoning phosgene pressure. Figure 8 seems to indicate that this is not so, although obviously there are not enough points to make the argument strong.

SUMMARY

We have investigated several little-known reactions by which carbon tetrachloride might be commercially produced. With this purpose in mind we have coördinated the previous work in this field and carried out similar and other experiments of our own.

We have concluded that a number of these reactions, generally chlorinations of carbon compounds or of carbon itself, and other related reactions, differ inherently in the manner in which they occur, from those between carbon and oxygen, sulfur, or even hydrogen. A great deal of further work is necessary to clear up the subject.

A detailed summary follows:

Theoretical calculations

1. A series of new thermodynamic data has been calculated from available data. The results include C_p of carbon tetrachloride vapor at 1 at-

mosphere from 0°C. to 300°C., S_{298} of silicon dioxide (quartz), $C_{p,298}$ of phosgene at 1 atmosphere, and $\Delta F°_{298}$ of formation of silicon tetrachloride (g), stannic chloride (g), aluminum chloride (g), and silicon dioxide (quartz).

2. The equilibrium constant for the reaction $2CCl_4 = C_2Cl_4 + 2Cl_2$ was calculated from experimental data of Weiser and Wightman.

3. A convenient and accurate method was developed for obtaining the equilibrium constant of the reaction, $CO_2 + CCl_4 = 2COCl_2$, involving saturating carbon dioxide with carbon tetrachloride at a known temperature and analyzing the equilibrium mixture for $(COCl_2)/(CO_2)$ ratio.

Experimental work

4. It was shown theoretically and supported experimentally that it is not possible to carry out appreciably the reaction $COCl_2 + 2MeCl = CCl_4 + Me_2O$, where Me is an equivalent of a metal. Ultra-violet light was shown to displace the equilibrium, in one case, towards the right.

5. Ordinary animal charcoal was found to be a good catalyst for the reaction $CCl_4 = C + 2Cl_2$, but experimental confirmation could not be obtained of the reverse reaction.

6. The reaction $2COCl_2 = CO_2 + CCl_4$ was attempted in both directions and the reverse reaction quantitatively studied, and indications were obtained of the existence of an undetermined factor which prevents the reaching of the theoretical equilibrium.

7. A new method for the volumetric analysis of carbon tetrachloride mixed with other gases was developed, tested and found satisfactory. Also, a method for the continuous absorption of chlorine, phosgene and carbon dioxide and determination of their proportions was devised and found satisfactory.

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