The separation of the rare earths by the fractional precipitation of their hydroxides upon electrolysis of solutions of their salts at voltages considerably higher than the decomposition values of the salts is probably due to the action of the hydroxyl ions, concentrated near the cathode, upon earths of different basicities. The hydroxide of the weakest base will first tend to form, and if the deposition of this insoluble hydroxide upon the surface of the cathode be prevented, and if the electrolyte be rapidly stirred throughout the electrolysis, a progressive precipitation of the hydroxides of the earths, in the order of their basicities, will result.

Summary.

1. The decomposition voltages of several neutral, normal solutions of salts of the rare earths were determined. The values were found to lie close together and to be in the neighborhood of two volts.

2. Fractional electrolysis of a solution of the chlorides of the yttrium earths yielded rapid concentration of the colored earths in the earlier fractions, and of yttrium in the later fractions. A small amount of neodymium that was present appeared in the last fractions.

3. Fractional electrolysis, with a diaphragm, of a solution of the nitrates of these earths showed concentration of the earths similar to that obtained in the electrolysis of the chlorides. The rate of precipitation of the hydroxides of the rare earths from the nitrate solution was, however, four times as rapid as from the chloride solutions. No ammonium salts were present in the electrolyte at the close of the run.

4. Fractional electrolysis of a solution high in erbium, holmium, thulium and yttrium gave, in a series of six fractions, no appreciable separation of the first three earths one from another, but rapidly separated the three from yttrium.

5. In the fractional electrolysis of solutions of certain salts of the rare earths, the hydroxides of the earths are precipitated, under the conditions here described, in the order of the basicities of the earths. Rapid concentration of certain groups of earths is attained in short series of fractions.

The method is being further studied in this laboratory.

ITHACA, N. Y.

THE EQUILIBRIUM BETWEEN CARBON OXYSULFIDE, CARBON MONOXIDE AND SULFUR.

BY GILBERT N. LEWIS AND WILLIAM N. LACEY.

The reduction of sulfur dioxide to sulfur by carbon monoxide is a reaction of great technical, as well as scientific, importance. From the free energy of this reaction the free energy of formation of sulfur dioxide could be obtained immediately. Any attempt, however, to determine

the conditions of equilibrium in this reaction is complicated by the formation of carbon oxysulfide, whenever carbon monoxide and sulfur are heated together. Before attacking the former problem it is therefore necessary to determine the free energy of the latter reaction.
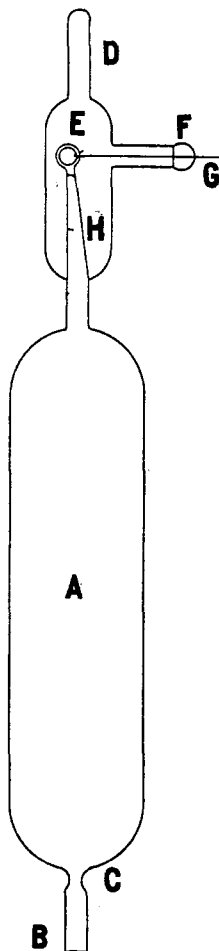
The reaction between carbon monoxide and sulfur to give carbon oxysulfide was shown by v. Than[1] to occur at a temperature corresponding to dull red heat. Later, Witzek[2] found evidence of a dissociation of the oxysulfide at as low a temperature as 300° C. This work seemed to indicate that the equilibrium $CO + S = COS$ might be attained within a reasonable time at moderately low temperatures.

Sulfur and carbon monoxide were heated together in a glass bomb of special design, shown in the accompanying figure. The special apparatus, D E F G H, having been sealed to the large tube A, the sulfur was placed in the latter before drawing down at C and joining to the tube B. The tube B was then attached to the vacuum pump and to the CO reservoir. After exhaustion, the bomb was filled with CO at a pressure a little below one atmosphere, the pressure and temperature were determined, and the tube B was drawn off at C. The bomb was then heated at the desired temperature long enough to insure the establishment of equilibrium and then cooled rapidly in a current of air. The end of the tube D was then cut off and it was joined to the vacuum pump and to the apparatus in which the gas was to be analyzed. After exhausting the chamber E, the platinum wire G and lead glass enamel F were heated to the softening point of the enamel. The wire G was then drawn out sufficiently to break the inner tube H where a file mark had previously been made. By this means the contents of the tube A could be brought directly into the analyzing apparatus without any contamination with air or rubber. This apparatus will doubtless prove convenient in many other experiments of a similar character.

After the gas had been removed from A to the analyzing apparatus by a mercury pump, the volume of A was determined. It was usually about 100 cc.

[1] v. Than, *Lieb. Ann. Suppl.*, **5**, 236 (1867).

[2] Witzek, *J. Gasbeleuchtung*, **46**, 21 (1903); Abegg, *Handbuch der anorgan. Chemie,* III₂, p. 207.

The sulfur used was prepared from Kahlbaum's crystallized product by boiling it *in vacuo* to remove traces of CS_2. Enough sulfur was taken to provide an excess of liquid sulfur at the temperature of the reaction. The carbon monoxide was prepared from oxalic acid and concentrated sulfuric acid. The carbon dioxide and water were carefully removed with suitable absorption bulbs and the CO was drawn into a large glass container from which it could be transferred to the reaction bomb. All connections were of glass and the apparatus and generator were completely freed from air at the outset.

The reaction was carried on in a vapor bath of boiling diphenylamine at 302°. This substance carbonizes gradually, but this was found to have little, if any, effect upon the temperature of the vapor.

In the first experiments (Expts. 2 and 5 referred to below) the gas from the reaction bomb was pumped directly into a bulb containing concentrated alkali and allowed to stand for a sufficient time to absorb all the COS.[1] The absorption takes place according to the reaction

$$COS + 4OH^- = S^{--} + CO_3^{--} + 2H_2O.$$
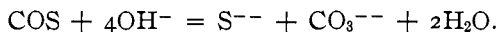
Into this absorption bulb an excess of hydrochloric acid and a known volume of a standard solution of iodine were allowed to enter. This was done in such a way that any H_2S set free by the acid would remain in the bulb and be later oxidized by the iodine. The whole solution was then withdrawn from the bulb and the excess iodine titrated against standard thiosulfate solution.

It was planned to determine the amount of CO in the gas left unabsorbed, by the ordinary methods of gas analysis, but the first experiments showed the amount of CO, remaining uncombined with sulfur, to be less than 1% of the initial CO. In order, therefore, to provide for a satisfactory determination of this gas it was necessary to adopt a different procedure. Therefore in the later experiments (Nos. 19, 20 and 22) the gas from the reaction bomb was drawn into a bulb immersed in liquid air and after a few minutes the uncondensed gas was drawn off. To avoid retention of CO in the solidified gases these were vaporized and once more solidified in liquid air. The total uncondensed gas was pumped into a separate reservoir over mercury and the gases which had been solidified were analyzed for COS as before. Owing to the fact that COS, as well as other substances like CS_2 and CO_2, which might have been expected to form during the reaction, exert very little vapor pressure at the temperature of liquid air, it was supposed that the total volume of uncondensed gas would represent the amount of CO left in the reaction. In order, however, to make a specific analysis for CO, after trying several unsuccessful methods, a method was adopted which has frequently been

[1] At ordinary temperatures any CS_2 which might have been formed in the reaction would not react appreciably with the alkali.

used for the determination of small amounts of CO in air.   The residual gas was mixed with a large volume of air and slowly drawn through a spiral containing iodine pentoxide at 150° and then into absorption bulbs containing KI dissolved in pure water.   The reaction is

$$I_2O_5 + 5CO = I_2 + 5CO_2,$$
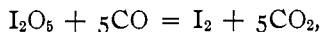
and experiments made with known quantities of pure CO gave excellent check analyses.

When, however, this method was applied to the uncondensed gas from the reaction bomb, a very mysterious effect was observed.   The brown color of iodine appeared at first in the absorption bulbs but later disappeared and the spaces above the liquid were filled with white fumes. At first this phenomenon was attributed to COS and in later esperiments greater pains were taken to insure the efficiency of the liquid air condensation, but the same phenomenon persisted.   It evidently was due to some gas which could be formed from carbon, oxygen and sulfur and possessing an appreciable vapor pressure at the temperature of liquid air.   We were thus led to suspect the presence of a monosulfide of carbon, CS, which presumably would have a boiling point not much higher than that of CO. This suspicion was confirmed when we found that Baudrimont[1] had actually prepared this gas by heating CS_2 and CO together.   In our experiments there was evidence that an appreciable amount of CS_2 was formed, presumably from the reaction $2COS = CO_2 + CS_2$.   It seemed, therefore, highly probable that the gas CS was responsible for the difficulties in the analysis and steps were therefore taken to remove it from the CO.

From the mixture of CS and CO, the former gas should be removed by a hot metal like copper.   The mixture was, therefore, pumped into a glass tube, in the center of which a platinum wire was stretched, by means of a platinum spring, between platinum hooks sealed through the tube.   Before use the platinum wire was plated electrolytically with copper and after the introduction of the gas an electric current was sent through this copper plated wire, heating it to dull redness.   The copper appeared to react rapidly with the gas, becoming covered with a black coating of sulfide.   After this treatment the gas was mixed with air and the analysis for CO continued as before.   This procedure completely eliminated the bleaching of the iodine and the formation of the white fumes.

Owing to the very considerable experimental difficulties of manipulation and analysis, only a few of the numerous experiments which were made led to final results of value.   In fact, there was no single tube which was successfully analyzed for both COS and for CO, but owing to the complete similarity of the various experiments this fact need not diminish our confidence in the results which were ultimately obtained.   It may

[1] Baudrimont, *Compt. rend.*, **44**, 1000 (1857).

be added that a number of the experiments which are not included in our final summary furnish satisfactory checks of the results here given.

Table I summarizes the results of the five experiments upon which we may place complete reliance.

TABLE I (302°).

No. of expt....	2	5	19	20	22	Aver.
Time in hours..	189	72	120	120	100	
Mols CO (initial)........	0.005944	0.004375	0.004829	0.005279	0.004943	
Mols CO per mol CO (initial)........			0.00419	0.00407		0.00413
Mols COS per mol CO (initial)........	0.8181	0.8525			0.8185	0.8297

The equilibrium constant $K = [COS]/[CO]$ can be obtained from this table with an error apparently not exceeding a few per cent. Using the average values given above, $K = 0.830/0.00413 = 201$. Writing $S_{\lambda\mu}$ to represent liquid sulfur in its equilibrium condition, we may write for the reaction

$$S_{\lambda\mu} + CO(g) = COS(g), \Delta F_{575} = -R'T \ln K = -6070 \text{ calories} \quad (1)$$
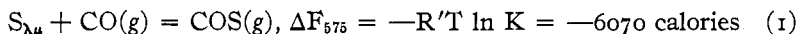
In order to obtain a similar equation involving sulfur in its standard state (rhombic), we may use the values of Lewis and Randall.[1] According to their Table I we may write for $S_{\lambda} = S_{\lambda\mu}$; $\Delta F_{575} = -44.5$. And, from their Equation 9, $S_R = S_{\lambda}$; $\Delta F_{575} = -294$. Adding these equations,

$$S_R + CO(g) = COS(g); \Delta F_{575} = -6410. \quad (2)$$

Unfortunately it is not possible, in the customary way, to calculate from this figure the value of ΔF at another temperature, owing to the very conflicting values of the heat of this reaction given by Thomsen and Berthelot. According to the former, the heat evolved in this reaction is 8030 cal., while according to the latter it is -6200 cal., a difference of over 14,000 cal. Both of these values are for rhombic sulfur at room temperature. For liquid sulfur at the temperature of our experiments these figures should be about 2000 cal. greater, according to the data given by Lewis and Randall, that is, approximately $+10000$ and -4000. We should expect the ratios of COS to CO to diminish with increasing temperature according to Thomsen, and to increase with increasing temperature according to Berthelot.

It seemed desirable, therefore, to attempt a determination of this equilibrium at some other temperature. A higher temperature seemed out of the question, since such evidence as we possessed regarding the

[1] THIS JOURNAL, **36**, 2468 (1914).

speed of the reaction indicated that at a temperature much higher than 300° it would be impossible to cool the reacting mixture with sufficient rapidity to prevent a shift of equilibrium. Experiments were therefore made at 260° with the same kind of apparatus in a thermostat of fused nitrates, the construction of which has been described by Lewis.[1] Unfortunately, owing to difficulties in the central power system, the thermostat was not entirely satisfactory and the experiments about to be described must be regarded as preliminary in character.

Table II shows the results of five experiments. The first three tubes were in the thermostat from 21 to 23 days, but in all three cases the temperature fluctuated very greatly at the beginning, and before the tubes were removed, constant temperature was maintained for only seven days in the first case, eight days in the second and five days in the third. But a later experiment showed that these intervals could hardly suffice for a complete establishment of equilibrium. With the possible exception, therefore, of the second experiment these three may be disregarded. The fifth experiment was in every way satisfactory and constant temperature was maintained for seventeen days. In the fourth constant temperature was maintained but the tube was left in the thermostat only five days. The large amount of CO left in this case shows conclusively that this length of time is insufficient for the establishment of equilibrium.

<div align="center">TABLE II (260°).</div>

No. of experiment	1	2	3	4	5
Time in days	22(7)	23(8)	21(5)	5	17
Mols CO (initial)	0.00534	0.00550	0.00508	0.00842	0.00789
Mols CO per mol CO (initial)	0.00118	0.00168	0.00097	0.0216	0.00171
Mols COS per mol CO (initial)	0.8015	0.6990		0.7725	0.7402

It is evident that with diminishing temperature the equilibrium is shifted in favor of CO. In the fifth experiment there can be little doubt that equilibrium was reached, and except that, for reasons which will be explained presently, the amount of COS found in this experiment may be 2% or 3% low, this experiment may be regarded as a sufficient basis for a provisional calculation of the equilibrium constant at this temperature. In this case $K_{533} = 0.74/0.0017 = 435$.

If now, by the van't Hoff equation, we use the two values of K to determine the heat of the reaction, we find —11000 instead of —4000 from Berthelot and +10000 from Thomsen. This indicates that Thomsen's value, at least, is erroneous. We must not, however, lay too much stress upon the value which we have obtained from the van't Hoff equation, used over a small range of temperature, with one equilibrium constant obtained from a single measurement. It seems therefore desirable to post-

[1] THIS JOURNAL, 28, 1380 (1906).

pone the calculation of the free energy of this reaction at standard temperature until we have more reliable calorimetric measurements. Such measurements are now being made in this laboratory.

It will have been noticed that a considerable part of the gas left in the tubes after heating was neither COS nor CO. Thus, at 302°, about 0.5% of the CO remained as such, and 83% was used in forming COS. Judging from the volume of the residual gas and from the amount of CO determined by analysis, the amount of CS was approximately equal to that of CO. This leaves 16% of the gas unaccounted for. This was assumed to be a mixture of approximately equal parts of CO_2 and CS_2. Each of the three reactions, $CO + S = COS$, $2COS = CO_2 + CS_2$ and $CS_2 = CS + S$, leads to no change in the number of mols of gas when the temperature is sufficiently low for the condensation of the sulfur, but not low enough to condense CS_2. In fact, the final volume of the reacting mixture was always 1–2% lower than that of the CO used. This was attributed to the fact that the resulting gases are less perfect than CO. It would have been desirable to analyze for CO_2 and CS_2, but this would have added almost insuperable difficulties to the already very difficult analytical procedure. It did seem worth while, however, to satisfy ourselves as to the general correctness of our assumption. In the last two experiments at the lower temperature that portion of the gas which was frozen out by liquid air was transferred to a tube immersed in liquid alcohol at a temperature of —80°. The gas was then pumped out from this cold chamber until the pressure was 0.5 mm. of mercury. This gas was analyzed as before for COS, and the liquid which remained was afterwards transferred to a small tube which was sealed off and weighed. This liquid was unquestionably CS_2. In Expt. 4 the weight of this liquid corresponded to 0.073 mols of CS_2 per mol of CO (initial). The boiling points of CS_2, COS and CO_2 are, respectively, 46°, —47.5° and —80°. The separation of COS from CS_2 could hardly be expected to be quantitative and it seemed probable that in the experiment just mentioned some of the CS_2 was pumped off. In Expt. 5, therefore, the gases were pumped off only until the pressure was about 1 mm. The amount of liquid left in this case corresponded to 0.155 mol CS_2 per mol CO (initial). In this case it is almost certain that some of the COS remained with the CS_2.

It seems pretty certain, therefore, that of the 20% of gas which was not CS, CO and COS, approximately one-half is CS_2. Presumably the other half is CO_2, and if so we can estimate roughly the equilibrium constant for the reaction $2COS = CO_2 + CS_2$ as

$$K_{533} = [CO_2][CS_2]/[COS]^2 = 0.10 \times 0.10/(0.79)^2 = 0.016.$$

A calculation of the measurements at the higher temperatures, based upon similar assumptions, gives

$$K_{575} = 0.08 \times 0.08/(0.83)^2 = 0.009.$$

Now, these constants could be calculated from our value of the free energy in the reaction $CO + S = COS$, and the equation given by Koref[1] for the dissociation of CS_2 as a function of the temperature, together with the free energy tables given by Lewis and Randall.[2] This calculation, which we shall not reproduce here, would lead to the conclusion that at the temperature of our experiments CO_2 and CS_2 would be present in larger amounts than COS. Koref used a heat of dissociation of CS_2 calculated from his own equilibrium measurements and this value would be largely affected by small errors in the degree of dissociation. That such errors were probable is evident from the fact that Koref made no allowance for the formation of CS, nor for such other substances as may be formed by heating CS_2.[3]

We may note, in passing, that the reaction $2COS = CO_2 + CS_2$ appears to be much more rapid than the reaction $CO + S = COS$ at the temperatures of our experiments.

Finally, although CS was not directly determined in any of our experiments, we may give an approximate estimate of the equilibrium constant in the reaction $CS_2 = CS + S_{\lambda\mu}$. Taking the amount of CS as equal to that of CO, we have $K_{575} = [CS]/[CS_2] = 0.004/0.08 = 0.05$.

Until more reliable calorimetric measurements are available we shall not attempt to reduce any of these results to standard temperature.

Summary.

When carbon monoxide and sulfur are heated together at $250°$ to $300°$ C., carbon oxysulfide, carbon dioxide, carbon disulfide and carbon monosulfide are formed by the reactions:

$$CO + S = COS;$$
$$2COS = CO_2 + CS_2;$$
$$CS_2 = CS + S.$$
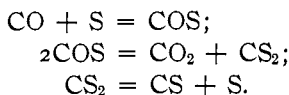
The equilibrium in the first reaction was determined at $302°$ and less reliably at $260°$. Approximate values were obtained for the equilibrium constants of the other two reactions.

BERKELEY, CAL.

THE POTENTIAL OF THE RUBIDIUM ELECTRODE.
BY GILBERT N. LEWIS AND WILLIAM L. ARGO.

The method used by Lewis and Kraus, and Lewis and Keyes for the determination of the electrode potential of sodium,[4] potassium[5] and

[1] Z. anorg. Chem., **66**, 73 (1910).

[2] THIS JOURNAL, **36**, 2468 (1914); and **37**, 458 (1915).

[3] See Arctowski, Z. anorg. Chem., **8**, 314 (1895).

[4] THIS JOURNAL, **32**, 1460 (1910).

[5] Ibid., **34**, 119 (1912).