

### Summary

1. Attention is called to previous investigations of gaseous explosive reactions carried out under constant volume conditions, where the effect of inert gases on the thermodynamic equilibrium was determined. The advantage of constant pressure methods over those of constant volume as applied to studies of the gaseous explosive reaction is pointed out and the possibility of realizing for this purpose a constant pressure bomb mentioned.

2. The application of constant pressure methods to the study of gaseous explosive reactions made possible by the use of a transparent constant pressure bomb, led to the discovery of an interesting kinetic relation connecting the rate of propagation of the zone of explosive reaction within the active gases, with the initial concentrations of those gases

$$s = k_1[A]^{n_1} [B]^{n_2} [C]^{n_3} \dots$$

3. By a method analogous to that followed in determining the effect of inert gases on the equilibrium constant  $K$ , the present paper records an attempt to determine their kinetic effect upon the expression given above. It is found that this effect on the  $\text{CO}-\text{O}_2$  reaction for the inert gases investigated, helium, argon, nitrogen and carbon dioxide, may be expressed as

$$s = k_1[A]^{n_1} [B]^{n_2} [C]^{n_3} \dots + \beta[G_1]$$

where  $[G_1]$  represents the initial concentration of the inert gas in the mixture.

4. An example of the utility of the constant pressure bomb for the study of the kinetics of the gaseous explosive reaction is offered in the results given in the present paper.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PURDUE UNIVERSITY]

## THE EQUILIBRIUM OF SILVER OXIDE AND SILVER CHLORIDE WITH AQUEOUS POTASSIUM CHLORIDE AND POTASSIUM HYDROXIDE

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Lewis and Randall,<sup>1</sup> in one of their calculations of the free energy of formation of water, have made use of Noyes and Kohr's<sup>2</sup> measurements on the equilibrium between silver oxide, silver chloride, potassium hydroxide, potassium chloride and water. They point out that it would be much simpler to use the dissociation of silver oxide into silver and oxygen, and the electromotive force of a silver-silver oxide electrode against the hydrogen electrode, but that the silver-silver oxide electrode is quite variable

<sup>1</sup> Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Company, New York, 1923, p. 482.

<sup>2</sup> Noyes and Kohr, *Z. physik. Chem.*, **42**, 336 (1902).

and leads to results quite different from those obtained by other sets of reactions. However, Noyes and Kohr's results are not very consistent and it seemed worth while to redetermine the equilibrium between silver oxide, silver chloride, potassium hydroxide, potassium chloride and water.

### Materials

Silver oxide was prepared (*a*) by precipitation at room temperature of dilute solutions of barium hydroxide and silver nitrate, (*b*) by heating precipitate (*a*) for several hours at 300°, (*c*) by precipitating from nearly boiling solutions of the above reagents, (*d*) by addition of silver nitrate to boiling sodium hydroxide solution and boiling the precipitate in excess sodium hydroxide solution and (*e*) by precipitation from the silver ammonia complex hydroxide by vacuum distillation of the ammonia. Preparation (*e*) was made to see if silver oxide so prepared showed evidence of greater stability than the samples precipitated in the more usual ways. On the contrary, as judged by the concentration ratio of chloride to hydroxide in equilibrium with it in presence of water and silver chloride, it behaved as if it were less stable, or more soluble, than the other four preparations, and for this reason little work was done with it.

The silver chloride was prepared by mixing moderately dilute solutions of silver nitrate and hydrochloric acid and washing thoroughly by decantation. The silver chloride was prepared and stored in a dark room, was kept in a moist condition and did not darken.

The water used was distilled and made free of carbon dioxide by prolonged passage of carbon dioxide-free air. The potassium chloride was a c. p. grade recrystallized and fused. The potassium hydroxide was sometimes made from electrolytically prepared potassium amalgam, and sometimes by precipitating c. p. potassium hydroxide with excess barium hydroxide, filtering and removing the excess barium hydroxide by addition of the required quantity of potassium sulfate as determined by analysis. The potassium sulfate was a recrystallized c. p. product. The sulfuric acid was standardized by titration with weighed quantities of recrystallized borax, using methyl yellow (dimethyl-amino-azobenzene) as indicator.<sup>3</sup> The hundredth normal silver sulfate solution was standardized against recrystallized fused potassium chloride by electrometric titration as described later.

### Procedure

Varying proportions of silver oxide and silver chloride were put into 250-cc. ground-glass-stoppered Pyrex Erlenmeyer flasks, the desired quantities of potassium hydroxide, potassium chloride and water added, and the samples were then rotated in a 25.00 ± 0.02° thermostat for periods varying from several hours to three days. The equilibrium was approached from both sides. No consistent differences were observed. Samples consisting of most of the liquid contents of the flasks were filtered from them, using filters made by sealing disks of alundum into Pyrex glass tubes. First portions of ten to twenty cubic centimeters were rejected to avoid error due to possible selective adsorption. The flasks and filters remained in the thermostat during the filtrations. Potassium hydroxide was determined by titration of the entire samples (about 200 cc.) with 0.5 *N* sulfuric acid, using phenolphthalein as indicator. The solution was then

<sup>3</sup> Kolthoff, *THIS JOURNAL*, **43**, 1447 (1926).

carefully evaporated to small bulk and titrated electrometrically with 0.01 *N* silver sulfate solution, using a silver-silver chloride electrode and connecting to a saturated potassium sulfate-mercurous sulfate-mercury electrode. Standardizations of the silver sulfate were made by titrating weighed quantities of potassium chloride mixed with amounts of potassium sulfate comparable with those encountered in the analyses. While steady potentials were obtained only slowly, and the titrations were tedious, the end-points were definite, the standardizations were reproducible and since the samples were practically identical in composition and concentration with the solutions titrated during standardization, systematic errors in the analyses are not to be expected,

TABLE I  
EQUILIBRIUM RATIOS OF CHLORIDE AND HYDROXIDE

Sample no.	Prepn. Ag <sub>2</sub> O	Concn. of OH <sup>-</sup> , mole/kg. water	Concn. of Cl <sup>-</sup> , mole/kg. water	Concn. ratio, Cl <sup>-</sup> /OH <sup>-</sup>	Activity ratio
1	a	0.0939	0.000852	0.00907	
2	a	.0978	.000875	.00895	
3	b	.1072	.000944	.00881	
4	b	.1065	.000945	.00887	
5	b	.1054	.000942	.00894	
6	b	.1011	.000925	.00915	
7	c	.1098	.000981	.00893	
8	c	.1130	.000999	.00884	
9	c	.1035	.000961	.00929	
10	c	.0997	.000921	.00924	
11	d	.1112	.000986	.00887	
12	d	.1065	.000996	.00935	
13	d	.1038	.000973	.00937	
Average for solutions approx. 0.1 molal				.00905	0.00892
14	a	.0529	.000471	.00889	
15	a	.0542	.000483	.00891	
16	b	.0520	.000465	.00894	
17	b	.0531	.000481	.00906	
18	c	.0536	.000485	.00905	
Average for solutions approx. 0.05 molal				.00897	.00897
Final weighted mean				.00903	.00893
Mean of Noyes and Kohr's results				.00937	.00930

The activity ratios were calculated by multiplying the corresponding concentration ratios by  $\gamma_{\text{KCl}}^2/\gamma_{\text{KOH}}^2$ , where  $\gamma$  is chosen to correspond to the *total* ion concentration.<sup>4</sup>

It may be noted that while individual samples are variable, the samples prepared in different ways do not differ significantly from one another, and while the general average is somewhat below the values of Noyes and

<sup>4</sup> Ref. 1, p. 362. The individual ion activity coefficients, p. 382, have been derived in the same way, but the values have been so rounded that the difference in activity coefficients of Cl<sup>-</sup> and of OH<sup>-</sup> in 0.1 molal solution have been exaggerated from barely over 1 to 2%.

Kohr, they probably agree within the limits of error, considering the individual variability, which is characteristic of the results both of Noyes and Kohr, and of the author. While the difference of the equilibrium ratio from that of Noyes and Kohr does not justify a recalculation of the free energy of water based in part on this equilibrium, it may be noted that the free energy calculated from the above results agrees with that obtained by other methods somewhat better than that calculated from the results of Noyes and Kohr.

### Summary

The equilibrium of  $\text{AgCl}$ ,  $\text{Ag}_2\text{O}$ ,  $\text{KOH}$ ,  $\text{KCl}$  and  $\text{H}_2\text{O}$ , previously studied by Noyes and Kohr, has been redetermined, using  $\text{Ag}_2\text{O}$  prepared in a variety of ways, and determining the chloride by electrometric titration. While the individual values are somewhat variable, the method of preparation has no significant effect on the equilibrium ratio of chloride and hydroxide. Within experimental error the equilibrium ratio is the same in 0.05 molal solution as in 0.1 molal solution.

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## A HIGHLY ACCURATE METHOD FOR THE ANALYSIS OF UREA

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There are many problems in physical and colloid chemistry which require for their experimental solution the use of a reference substance capable of analysis to a high degree of accuracy. Such a reference substance must also be chemically inert and a non-conductor of electricity. These problems include methods of indirect analysis, determination of solvation by the method of ultrafiltration<sup>1</sup> and the determination of the hydration of the ions by measurement of the displacement of the reference substance during electrolysis, as suggested by Nernst in 1900. In Washburn's<sup>2</sup> well-known work on this latter subject, only one substance, raffinose, was considered to possess the requisite properties and it is subject to the drawback that a highly sensitive polarimeter of a type not generally accessible is required to estimate it.

The high molecular weight of raffinose is also a disadvantage. The decimolar solution contains more than 50 g. to the liter, a quantity sufficient to cause considerable increase in the viscosity of the solution and consequently to affect the migration velocities of the ions. Also, it is

<sup>1</sup> McBain and Jenkins, *J. Chem. Soc.*, 121, 2325 (1922).

<sup>2</sup> Washburn, *THIS JOURNAL*, 31, 322 (1909); Washburn and Millard, *ibid.*, 37, 694 (1915).