

tained by fusing a mixture having the composition<sup>10</sup>  $4\text{CaO}\cdot 2\text{MgO}\cdot \text{Al}_2\text{O}_3\cdot \text{Fe}_2\text{O}_3 + 2(\text{CaO}\cdot \text{MgO}\cdot \text{SiO}_2)$ . This mixture dusted completely owing to the formation of  $\gamma\text{-}2\text{CaO}\cdot \text{SiO}_2$ . Also a sample having the composition  $4\text{CaO}\cdot 2\text{MgO}\cdot \text{Al}_2\text{O}_3\cdot \text{Fe}_2\text{O}_3 + 2\text{MgO}\cdot \text{SiO}_2$  dusted completely after being fused.

### Summary

1. A study has been made of the system  $2\text{CaO}\cdot \text{SiO}_2\text{-MgO-}5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$ . A diagram is given showing the fields in which each of these compounds separates as primary phases.

2. No evidence was obtained to show that MgO formed solid solutions with either  $2\text{CaO}\cdot \text{SiO}_2$  or  $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$  or that MgO was capable of replacing CaO in these compounds.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY AT IOWA STATE COLLEGE]

## REACTIONS IN LIQUID HYDROGEN SULFIDE.

### IV. THIOHYDROLYSIS OF ESTERS

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RECEIVED MAY 14, 1928

PUBLISHED AUGUST 4, 1928

Esters are well known to hydrolyze in water solutions, forming the free acids and alcohols. In a similar way the esters of the thio-organic acids should thiohydrolyze in liquid hydrogen sulfide to give the free acids and the mercaptans.

Of the several methods that are used to measure the degree of hydrolysis of esters in water solutions the one that is most applicable in the case of the thiohydrolysis in liquid hydrogen sulfide is that based on the determination of the conductance of the solutions.<sup>2</sup> The degree of hydrolysis is determined by measuring the conductance of the hydrogen sulfide solutions of the pure acid, the thiohydrolyzed ester and of the solution of the ester saturated with the base or mercaptan. It has been found that the solution of the mercaptan in liquid hydrogen sulfide does not conduct the current. Therefore, the conductance of the ester solution saturated with the mercaptan will be due to the unhydrolyzed ester alone.

The thiohydrolysis may be calculated from the expression

$$h = \frac{\lambda e - \lambda}{\lambda a - \lambda}$$

where  $h$  is the fraction of the ester thiohydrolyzed,  $\lambda e$  is the equivalent

<sup>10</sup> W. C. Hansen and L. T. Brownmiller, *Am. J. Sci.*, **15**, 225 (1928).

<sup>1</sup> This paper is from a portion of the work presented by A. W. Ralston to the Graduate Faculty at Iowa State College in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

<sup>2</sup> Walker, *Z. physik. Chem.*, **4**, 333 (1889); Bredig, *ibid.*, **13**, 214-321 (1894); Noyes, Kato and Sosman, *THIS JOURNAL*, **32**, 159 (1910).

conductance of the solution of the ester at that dilution,  $\lambda a$  is the equivalent conductance of the pure acid at the same dilution,  $\lambda$  is the conductance of the ester at this same dilution but after the solution has been saturated with the mercaptan.

### Experimental

A number of the esters of thioacetic acid were prepared by the method Obermeyer<sup>3</sup> used for the preparation of methyl thioacetate. An alcoholic solution of lead acetate was added to an alcoholic solution of the mercaptan until no further precipitate of the lead mercaptide was formed. The lead mercaptide was filtered, washed with ether and dried in a vacuum desiccator. It was then treated with ice cold acetyl chloride, keeping the reaction flask immersed in an ice-salt mixture. After the reaction had completed itself, the excess of acetyl chloride was destroyed by water, the lead chloride was filtered out and the light oil distilled. The distillate was treated with calcium carbonate to remove any free acetic acid and then further purified by fractional distillation.

With the esters of higher molecular weight such as the *isobutyl*, the reaction took place much more slowly and it was necessary to reflux the mercaptide for several hours with acetyl chloride to obtain the ester.

TABLE I  
THIOHYDROLYSIS OF ESTERS

Mol. vol., l.	$\lambda e \times 10^3$	$\lambda a \times 10^3$	$\lambda \times 10^3$	$h$	Mol. vol., l.	$\lambda e \times 10^3$	$\lambda a \times 10^3$	$\lambda \times 10^3$	$h$
Methyl Thioacetate					2.5	0.089	0.580	0.020	12.3
50	0.110	1.450	0.004	7.33	2	.085	.578	.020	11.7
20	.065	.917	.004	6.68	1.33	.075	.569	.020	10.0
10	.035	.690	.004	4.52	1	.074	.565	.020	9.95
5	.021	.614	.004	2.80	<i>Isopropyl</i> Thioacetate				
3.33	.018	.591	.004	2.38	10	.229	.690	.024	30.8
2.5	.016	.580	.004	2.08	5	.146	.614	.024	20.5
2	.011	.578	.004	1.22	3.33	.129	.591	.023	18.7
Ethyl Thioacetate					2.5	.122	.580	.020	18.2
50	.180	1.450	.008	12.55	2	.118	.578	.016	18.2
20	.106	0.917	.008	10.80	1.33	.113	.569	.011	18.2
10	.076	.690	.007	10.10	1	.111	.565	.011	18.1
5	.059	.614	.007	8.56	<i>n-Butyl</i> Thioacetate				
3.33	.050	.591	.007	7.36	10	.48	.690	.034	68.0
2.5	.044	.580	.006	6.62	5	.395	.614	.025	56.7
2	.037	.578	.006	5.24	3.33	.331	.591	.016	54.8
<i>n-Propyl</i> Thioacetate					2.5	.327	.580	.012	55.5
20	.52	.917	.025	55.5	2	.313	.578	.010	53.3
10	.35	.690	.020	49.3					
5	.122	.614	.020	17.2					
3.33	.096	.591	.020	13.3					

<sup>3</sup> Obermeyer, *Ber.*, 20, 292 (1887).

The esters of thioacetic acid that were made by this method and used had the following boiling points: methyl 95–96°, ethyl 115–116°, propyl 135–137°, *isopropyl* 122–123°, normal butyl 134–135° and phenyl 110–111° at 8 mm.

The conductances were determined in cells similar to those described and used by Quam and Wilkinson.<sup>4</sup> The cell constants were determined with 0.02 *N* potassium chloride at 25°. No correction was made for the change in the cell constant due to the fact that the cells were then used at –77°. Since the thiohydrolysis is calculated from a ratio this correction will be the same in both the numerator and the denominator and will be eliminated in the calculation.

The concentrations were determined by adding from a weight buret known weights of the ester to definite volumes of liquid hydrogen sulfide. The preceding tables give the data obtained and the percentage of hydrolysis calculated from them. The phenyl thioacetate was found to show no conductance when dissolved in liquid hydrogen sulfide.

### Conclusions

1. Esters of thioacetic acid are shown to be thiohydrolyzed in liquid hydrogen sulfide. The degree of thiohydrolysis increases with the molecular weight of the ester.

2. The amount of thiohydrolysis of these esters in liquid hydrogen sulfide even at –77° is several times the value for the hydrolysis of esters of similar oxygen acids in water at room temperature.

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[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY, HARVARD UNIVERSITY]

## THE ATOMIC WEIGHT OF CESIUM

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RECEIVED MAY 24, 1928

PUBLISHED AUGUST 4, 1928

### Introduction

A redetermination of the atomic weight of cesium was undertaken on account of the difference in this value as found by chemical and physical methods. The modern value of 132.81 is based primarily upon the work of Richards and Archibald.<sup>2</sup> Earlier atomic weight determinations are adequately treated by Clarke.<sup>3</sup>

<sup>4</sup> Quam and Wilkinson, *THIS JOURNAL*, **47**, 989 (1925).

<sup>1</sup> The research here reported was completed under the direction of Professor Richards but the manuscript was written after his death. The junior author is responsible for the conclusions drawn and any opinions expressed.

<sup>2</sup> Richards and Archibald, *Proc. Am. Acad.*, **38**, 443 (1903).

<sup>3</sup> F. W. Clarke, "The Constants of Nature," Part V, "A Recalculation of the Atomic Weights," 4th ed., 1920, Nat. Acad. of Sciences, Washington, D. C.