

has been recommended as a catalyzer for the oxidation of ammonia by Wortmann.

5. The example of silver taken as a catalyzer which does not form oxides and does not change its metallic individuality with rise of temperature demonstrated that near the fusing point the catalytic activity falls abruptly simultaneously with a change of the type of the reaction itself at the fusing point.

6. From this it becomes likely that in the process of decomposition of methyl alcohol by zinc the nature of the increasing activity may be explained by the formation of zinc oxide similarly to what had been demonstrated by us in the case of oxidation of ammonia by fused tin, where the increasing activity is related to the formation of tin oxide.

7. The formation of tin oxide in the process of decomposition of methyl alcohol is very probable, as Bone and Davies have demonstrated that its thermal decomposition takes place according to the equation  $\text{CH}_3\text{OH} \rightarrow \text{CH}_4 + \text{O}$ ,

and the reaction takes place according to the equation  $2\text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O}$ .

The formation of zinc oxide in proportion to water vapor is also quite evident, as in the case of  $\text{CH}_3\text{OCH}_3 \rightarrow \text{C}_2\text{H}_6 + \text{O}$ ; the formation of zinc oxide is inevitable.

8. The attempted decomposition of methyl alcohol vapor by zinc chips at 360–400° undertaken by us showed experimentally that zinc chips either are partially covered by zinc oxide on their surface or go over to it completely, depending on the quantity of methyl alcohol that has been passed and the time this has taken.

9. From the aforesaid, it is to be acknowledged that the conclusion of Steacie and Elkin that the surface of zinc is equally active and that in general the catalytic activity of a solid matter cannot be ascribed to a limited part of its surface, is baseless and results from an insufficient cleanliness of the experiment.

CHARKOW, RUSSIA

RECEIVED MARCH 15, 1935

## NOTES

### Thermocouples from 2 to 90° Absolute

BY J. ELSTON AHLBERG AND WALTER O. LUNDBERG

In the establishment of temperature scales, several methods are being employed. Due to the necessity of setting up an accurate temperature scale between 20 and 70°K. it was thought desirable to test mathematical equations relating the electromotive force of thermocouples to temperature. The general trend of the data given by Giaque and associates<sup>1,2</sup> for a copper-constantan thermocouple (ice reference junction) between 13 and 90° K. made it apparent that the following simple equation might accurately represent the results

$$E = A + BT^2 + CT^3 + DT^4$$

$E$  is the thermocouple voltage in microvolts,  $T$  is the absolute temperature,  $A$ ,  $B$ ,  $C$  and  $D$  are constants. The third law of thermodynamics requires that the term associated with the first

(1) Giaque, Buffington and Schulz, *THIS JOURNAL*, **49**, 2343 (1927).

(2) Giaque, Johnston and Kelley, *ibid.*, **49**, 2367 (1927).

power of temperature be equal to zero. Terms associated with powers of temperature higher than the fourth are assumed negligible.

Using the values by Giaque and associates<sup>1,2</sup> at 15, 20, 70 and 90°K. we find  $A = 6681.26$ ,  $B = -1.6547 \times 10^{-1}$ ,  $C = 5.5460 \times 10^{-4}$  and  $D = -9.878 \times 10^{-7}$ . The agreement between the data of Giaque and associates and the above equation is as follows: from 13 to 23°K. better than 0.008°; from 24 to 35°K. better than 0.05°; and from 40 to 90°K. better than 0.03°. The agreements are well within the limits of accuracy claimed by them. The agreements additionally indicate the validity of the temperature scale at the University of California and of the data used in its establishment.<sup>3</sup> Moreover, the average deviation of the temperature coefficients of voltage from the calculated values is but 0.3%.

At the Johns Hopkins University we have experimentally compared a copper-constantan ther-

(3) Onnes, Keesom and Associates, *Comm. Phys. Lab. Univ. Leiden*; Simon and Lange, *Z. Physik*, **15**, 312 (1923).

mocouple (ice reference junction) with a helium gas thermometer between 2 and 20°K. and with oxygen vapor pressures between 70 and 90°K. The average deviation of the thermocouple voltages from the above equation is less than 0.01%. The constants determined are  $A = 6039.9$ ,  $B = -1.5475 \times 10^{-1}$ ,  $C = 6.2064 \times 10^{-4}$  and  $D = -1.5652 \times 10^{-6}$ .

Comparisons of the above sets of experimental data, and of other thermocouples, show, to a first approximation, that the differences in voltages of two different thermocouples are proportional to their average voltage. The limitations of this last rule can be estimated from the two sets of constants given in this report.

The data discussed suggest that only four isolated comparisons of voltage and temperature are necessary in the calibration of thermocouples for use below 90°K.<sup>4</sup> However, when time and equipment are available, direct experimental calibration of thermocouples is to be preferred to the method suggested in this report.

(4) At temperatures lower than 20°K. the temperature coefficient of voltage of thermocouples becomes very small making it advisable to resort to other methods for temperature measurement.

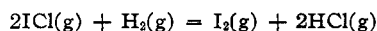
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RECEIVED JULY 16, 1935

### The Thermal Reaction between Gaseous Iodine Monochloride and Hydrogen

BY W. D. BONNER, W. L. GORE AND DON M. YOST

It has been found that at about 200° and above, gaseous iodine monochloride and hydrogen react slowly to form hydrogen chloride and iodine. That no hydrogen iodide is present in the reacting mixture is shown by the results of some unpublished experiments made by the late Prof. H. P. Ramsperger, who found that iodine monochloride and hydrogen iodide react very rapidly to form iodine and hydrogen chloride. A simple free energy calculation shows that this reaction goes practically to completion. The main reaction between iodine monochloride and hydrogen is then



Inasmuch as no pressure change accompanies the reaction, the compositions of the reacting mixtures were determined iodimetrically. Weighed quantities of best quality liquid chlorine and solid iodine in small breakable capsules were placed in 100-cc. bulbs. The bulbs were evacuated

and then filled to the desired pressure with hydrogen which had been carefully freed from oxygen and water vapor. After sealing off, the bulbs were shaken to break the capsules and were then immersed in a thermostat filled with molten Crisco. At suitable time intervals a bulb was removed from the thermostat, and the reaction was stopped by cooling the bulb rapidly in an air blast. Independent experiments had shown that no detectable reaction takes place below 100°. The cooled bulbs were opened under a solution of potassium iodide and the resulting iodine titrated with 0.1 *N* thiosulfate.

The best constants were obtained when the rate equation was assumed to be

$$-\frac{d(\text{ICl})}{dt} = k(\text{H}_2)(\text{ICl})$$

$$k = \frac{2 \times 2.303}{t(c_1 - 2c_2)} \log \frac{2c_2(1 - B)}{2c_2 - c_1B}$$

where  $c_1$  and  $c_2$  are the initial concentrations of  $\text{ICl}(\text{g})$  and  $\text{H}_2(\text{g})$ , respectively, and  $B$  is the fraction of  $\text{ICl}$  consumed in time  $t$ . At 205°,  $k = 0.031 \pm 0.006$ ; at 230°,  $k = 0.17 \pm 0.06$ ; and at 240°,  $k = 0.35 \pm 0.06$ . The concentrations of  $\text{ICl}$  and  $\text{H}_2$  are here expressed in moles per liter, and the time is given in minutes. Experiments in which the bulbs were filled with powdered Pyrex glass yielded, within the errors indicated, the same values for the specific rate constants. Representative results of the experiments are presented in Table I.

TABLE I  
RESULTS OF REACTION RATE EXPERIMENTS

Temp., °C.	<i>t</i> , min.	Moles per liter		Fraction ICl reacted <i>B</i>	<i>k</i>
		$c_1 \times 10^2$	$c_2 \times 10^2$		
205	360	3.12	3.19	0.329	0.033
	360	4.43	3.19	.199	.021
	60	2.20	3.15	.0674	.038
230	120	3.09	3.42	.402	.139
	60	2.53	3.43	.376	.248
	60	2.04	3.43	.202	.113
	31	1.49	3.43	.131	.138
	31	2.66	3.45	.113	.116
	30	2.68	3.13	.155	.180
240	15	2.24	3.43	.098	.208
	85	2.41	3.44	.466	.322
	50	1.38	1.94	.241	.298
	48	2.13	2.73	.375	.414
	39	1.68	1.94	.188	.284
	31	1.62	3.44	.350	.420

The mechanism suggested by these results is the following, which is put forward as a purely tentative one

