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.[4] 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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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 That no hydrogen iodide is present in the reacting mixture is shown by the results of some unpublished experiments made by the late Prof.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

$$2\mathrm{ICl(g)} + \mathrm{H_2(g)} = \mathrm{I_2(g)} + 2\mathrm{HCl(g)}$$

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

$$-d(\mathrm{ICl})/dt = k(\mathrm{H_2})(\mathrm{ICl})$$
$$k = \frac{2 \times 2.303}{t(c_1 - 2c_2)} \log \frac{2c_2(1 - B)}{2c_2 - c_1B}$$

where c_1 and c_2 are the initial concentrations of ICl(g) and H_2(g), respectively, and B is the fraction of 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 ICl and 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.	t, min.	Moles per liter $c_1 \times 10^2$	$c_2 \times 10^2$	Fraction ICl reacted B	k
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
	15	2.24	3.43	.098	.208
240	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

$$\mathrm{H_2} + \mathrm{ICl} = \mathrm{HI} + \mathrm{HCl} \qquad \text{(slow)}$$
$$\mathrm{HI} + \mathrm{ICl} = \mathrm{HCl} + \mathrm{I_2} \qquad \text{(rapid)}$$

The deviation of the values of individual rate constants from the mean is appreciably greater than is usually found where a single mixture can be followed with time, yet no correlation between the deviations and the concentrations of reactants or products is evident.

It must be pointed out that iodine monochloride dissociates[1] somewhat (3% at 210°) into iodine and chlorine, and that a mechanism involving the possible reaction of hydrogen with chlorine must be considered. Inasmuch as the dissociation is greatly repressed as soon as some free iodine is formed, and since mixtures initially containing excess iodine gave sensibly the same results, such a mechanism does not seem likely. The direct reaction between hydrogen and iodine is very slow at 240° and below.[2]

When the average values of the specific reaction rate constants are plotted against $1/T$ a straight line results. The energy of activation for the assumed slow reaction is 33,900 cal.

[1] McMorris and Yost, THIS JOURNAL, **54**, 2247 (1932).

[2] Bodenstein, *Z. physik. Chem.*, **29**, 295 (1899).

CONTRIBUTION FROM
GATES CHEMICAL LABORATORY
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Specific Heat and Binding Conditions of Adsorbed Argon on Charcoal

BY HANS M. CASSEL

When a monoatomic gas is adsorbed at the surface of an elementary solid, the first adsorption layer represents a more or less perfect continuation of the crystal lattice. Accordingly, the "adatoms"[1] behave as being bound by certain centers of attraction around which they move similarly as the atoms of the adsorbent. But, due to the anisotropy of the situation, the oscillation perpendicular to the surface freezes in, if the temperature is enough decreased, whereas the degrees of freedom parallel to the surface, corresponding to weaker binding forces, remain still excited at much lower temperatures.

It depends on the size and shape of the potential box in which the adatom may be regarded as contained,[2] whether the movement is a two-dimensional translation or a two-dimensional harmonic oscillation. Accordingly, the specific heat of the adatoms, in the first case, has the value, R, remaining constant except at extremely low temperatures, and, in the second case, the value, $2R$, decreasing with decreasing temperature in analogy to the Debye function of the three-dimensional oscillator.

F. Simon and R. C. Swain[3] recently having measured the heat capacity of argon adsorbed on charcoal observed the rather constant value, R, between 80 and 60°K., but, at lower temperatures, a decrease leading to an almost imperceptible amount below 20°K. Thus, the experimental result agrees neither with the first nor with the second possibility explained above. Instead, the appearance of the sloping-down perfectly resembles the Debye function of a one-dimensional oscillator.

This view, indeed, is justified, since it is much more probable that an argon atom is adsorbed in the hollow edges or steps of the very cleavable material than on the smooth surfaces of the netplanes. Adatoms bound by two vicinal crystal planes, at low temperatures, are capable of only one-dimensional vibrations parallel to both surfaces. The specific heat measurements, therefore, back the suggestion that the majority of the argon atoms is adsorbed in this way.

[1] I. Langmuir, *J. Chem. Physics*, **1**, 3 (1933).

[2] The author is very much indebted to Dr. L. Pauling, Cal. Tech., for the calculation of the degeneracy temperature.

[3] F. Simon and R. C. Swain, *Z. physik. Chem.*, **B28**, 189 (1935).

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Areametric Analysis. A Useful Technique in Estimating Small Amounts of Heavy Precipitates

BY V. R. DAMERELL AND M. AXELROD

In attempting to measure small amounts (0.01 to 5 mg.) of lead sulfate in contact with sulfuric acid, the authors were able to develop a simple technique whereby compact circular (or square) piles of precipitate could be obtained, of reproducible dimensions, in the center of the flask bottom (see Fig. 1). The apparent areas of these "spots" (as viewed from above, and assuming them to be flat circles or squares) could be readily measured and compared to the areas produced by known amounts of precipitate. This method of analysis is new, according to the authors' best knowledge, and since it involves the measurement of an area, the term areametric analysis is proposed.

The method is generally applicable to heavy