the relation $A_{12} = \sqrt{A_{N_2} A_{CH_4}}$. In a later paper the theoretical conditions under which this can be true will be discussed.

Summary

1. Experimental data for three mixtures of nitrogen and methane have been obtained for the temperature range 0 to 200° and to pressures amounting to 200 or 300 atmospheres.

2. The equation of state for each mixture has been found to be the same in form as that applying to the pure gases.

3. The constants of the equations of state representing the mixtures were found to be linear functions of the constants of nitrogen and methane and compositions of the mixtures as follows: $A = (\sqrt{A_{N_2}} W_{N_2} + \sqrt{A_{CH_4}} W_{CH_4})^2$; $\beta = \beta_{N_2} W_{N_2} + \beta_{CH_4} W_{CH_4}$; $\alpha = \alpha_{N_2} W_{N_2} + \alpha_{CH_4} W_{CH_4}$; $l = l_{N_2} W_{N_2} + l_{CH_4} W_{CH_4}$.

4. The generalized equation of state based on the present results for a mixture of n gases would be written

$$p = \frac{\Sigma R_1 W_1 T}{v - \Sigma \beta_1 W_1 e^{-\frac{\Sigma \alpha_1 W_1}{v}}} - \frac{(\Sigma \sqrt{A_1} W_1)^2}{(v + \Sigma l_1 W_1)^2}.$$

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EQUILIBRIUM IN THE REACTIONS OF TIN WITH WATER VAPOR AND CARBON DIOXIDE

BY E. D. EASTMAN AND PRESTON ROBINSON

The reactions of metals and their oxides with water vapor, together with the corresponding reactions with carbon dioxide, offer an indirect method of study of the water–gas equilibrium. Conversely, the equilibrium data pertaining to the latter reaction may be used to test the consistency of results obtained in the systems involving the metals. A series of such inter-comparisons in the case of iron and its oxides[1] revealed a large difference between the directly and indirectly determined values of the water–gas equilibrium constant. In view of the close agreement of the two sets of indirect determinations with each other it appears probable that the directly obtained data are in error. It remains desirable, however, to test this conclusion by further experiments. With that object the work here described was undertaken.

The equilibria selected for study may be represented by the following equations

$$Sn(l) + 2H_2O(g) = SnO_2(s) + 2H_2; \quad K_1 = (H_2)/(H_2O) \tag{1}$$
$$Sn(l) + 2CO_2 = SnO_2(s) + 2CO; \quad K_2 = (CO)/(CO_2) \tag{2}$$

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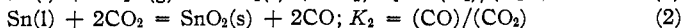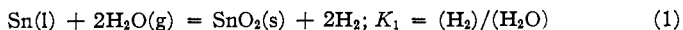
[1] Eastman and Evans, THIS JOURNAL, **46**, 888 (1924).

These equations may, of course, be combined to give that for the water–gas reaction, which will be written

$$H_2 + CO_2 = H_2O + CO; K_3 = (H_2O)(CO)/(H_2)(CO_2) = K_2/K_1 \qquad (3)$$
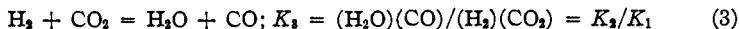
The systems shown in Equations 1 and 2 are well suited to the purpose stated. The gas phases at equilibrium in convenient temperature ranges contain readily measurable quantities of both constituents. The liquid tin is less subject to structural and surface differences than solid metals and may therefore be assumed to be nearly identical in character in the two systems. The stannic oxide necessary may be obtained (within the apparatus employed) by the reactions themselves, and should show little difference in-character as prepared by the two very similar methods. That it is stannic oxide rather than stannous that is formed in these reactions is known from the work of Fraenkel and Snipischski[2] and Maeda.[3] They proved that SnO is unstable at the temperatures obtaining in our experiments. Finally, there is no evidence of solution to any appreciable extent of the condensed phases in each other, a point which is important only because of the possibility that solid solutions, which are known to be involved in the previous tests,[1] may be less readily reproducible as to state than nearly pure phases.

Measurements in Reaction 1

Dynamic Method.—The first method employed for the determination of K_1 was of the dynamic type. In principle it consists in finding the proportion of water vapor in a stream of it mixed with hydrogen that is just sufficient to produce continued oxidation when passed over tin held at a constant high temperature, the pressure being atmospheric.

In our application of this method the gas stream was obtained by passing hydrogen over distilled water in saturators immersed in a constant temperature bath. By changing the temperature of the thermostat the composition of the gas stream could be varied. The determination of its composition was made by measuring the temperature of the thermostat, the partial pressure of water vapor being taken as its vapor pressure at the measured temperature and that of hydrogen being obtained by subtraction of this value from the barometric pressure.

The tin, in the form of small drops, was contained in a long-necked bulb of silica glass held at nearly constant temperature in an electrically heated pot furnace. The neck of the flask projected from the furnace. It was fitted with an eyepiece of plane silica glass through which the tin in the bulb could be observed. On passing gas from the saturator through the flask it was readily determined from the appearance of the tin whether the gas was oxidizing or reducing in character. In an oxidizing atmosphere a white coating of oxide appeared on the tin; in reducing atmospheres this coating disappeared, or the tin remained bright. By successive settings of the thermostat it was possible to obtain a gas mixture of a composition such that slight variations in it would alternately oxidize the tin or reduce the oxide. This was taken as the composition of the mixture in equilibrium with the tin at the temperature of the interior of the flask. This

[2] Fraenkel and Snipischski, *Z. anorg. Chem.*, **125,** 235 (1922).

[3] Maeda, *Bull. Inst. Phys. Chem. Research (Tokyo)*, **2,** 350 (1923).

temperature was measured by a thermocouple. Details concerning the experiments follow.

The hydrogen was generated by electrolysis of sodium hydroxide solution. The tin was a commercial preparation purporting to be of high purity.

The saturator consisted of a series of glass tubes about 4 cm. in diameter placed horizontally in the thermostat and half filled with water. The hydrogen passed over but did not bubble through the water.

The temperature of the thermostat was measured with a Beckmann thermometer which was compared with a thermometer calibrated by the Bureau of Standards. The gas compositions calculated from the measured temperature of the thermostat and the barometric pressure were checked by analysis at the two extremes of the composition range employed. Agreement was found to be within 1% in each case.

The gases from the saturator entered the neck of the flask near its top, and were preheated in the neck by a Chromel wire heater wrapped around it. From the neck the gases entered the bulb of the flask, where they were in contact with the tin, and escaped through a capillary the tip of which was under water. After resettings of the thermostat, a long interval with all conditions constant was allowed to ensure uniformity of composition of gas and give ample time for reaction with the tin.

Illumination of the interior of the bulb was accomplished by inserting a silica glass tube through the asbestos packing of the furnace to the wall of the bulb (at an angle of about 30° with the neck of the flask) and placing a 500-watt lamp at the outer end. At high temperatures the visibility of the tin was greatly diminished. Much above 800° the thermal radiation within the flask was so intense as to prevent distinct observation of the state of the tin.

The temperature of the furnace was regulated by hand. The thermocouple employed for measuring the temperature of the flask was of platinum and platinum-rhodium. It was calibrated against the melting point of various salts by the method of Roberts.[4] It was inserted during measurements in a protecting tube sealed through the wall of the bulb and extending nearly to its bottom. E.m.f.'s were read on a portable potentiometer to 0.01 mv. Temperatures determined with it we consider to be correct to within 5°.

A sample series of observations is shown in the following tabulation.

TABLE I

TYPICAL OBSERVATIONS

Barometric press., mm.	E.m.f. of thermocouple, mv.	Thermostat temp., °C.	Condition of tin
759.8	5.65	89.90	·Reduced
753.6	5.65	90.20	Oxidized
752.7	5.60	90.00	Oxidized
749.7	5.65	89.95	Oxidized
751.6	5.68	89.85	Reduced
751.6	5.68	89.95	Oxidized
751.6	5.68	89.90	Reduced
754.0	5.69	90.05	Oxidized
751.6 ± 0.2	*5.68* ± 0.05	*89.92* ± 0.05	

The final (italicized) figures in each column are those chosen as representative of the equilibrium condition. Our estimate of the possible error in these values is also indicated. The vapor pressure of water

4 Roberts, *Phys. Rev.*, **23,** 386 (1924).

at 89.92° was taken as 524.0, the error corresponding to the uncertainty in the temperature being about 1 mm. From this the value of K_1 is calculated to be 0.434 ± 0.004. The furnace temperature corresponding to 5.68 mv. is 655 ± 5°. The combined error in the temperature measurement and the constant itself should not exceed about 5% in individual determinations.
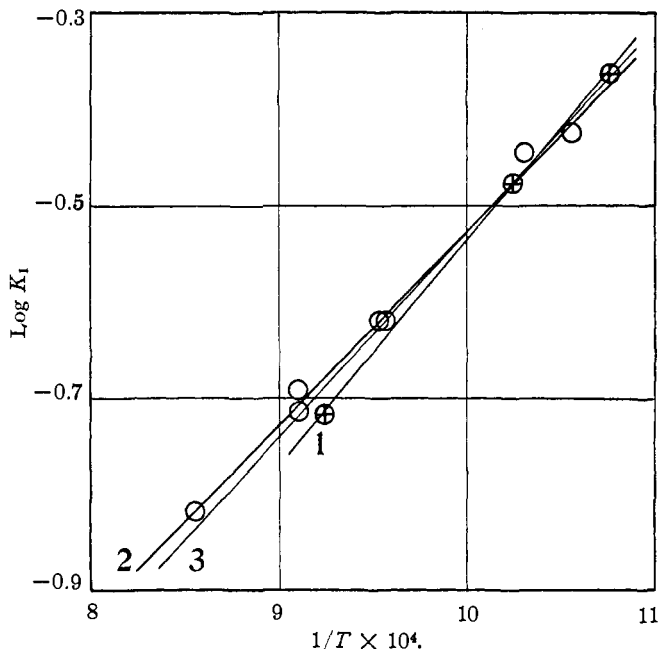

Fig. 1.—Equilibrium constant of reaction 1. Curve 1, Dynamic Method; Curve 2, Static Method; Curve 3, Best Values.

The final values obtained, each based on an extended series of observations similar to the preceding, are recorded in Table II and shown graphically in Curve 1 of Fig. 1.

TABLE II

EQUILIBRIUM CONSTANTS OF REACTION 1 FROM DYNAMIC MEASUREMENTS

t, °C.	655	703	809
K_1	0.434	0.333	0.191

Static Method.—Several considerations made it appear desirable to determine the value of K_1 by an independent method. The above modification of the dynamic method, while possessing many advantages and apparently free from large error, had never previously been used. Again, the coatings of stannic oxide produced in the reactions, while they were far from being merely surface films, did not contain large amounts, and the material need not be quite identical with "massive" samples. Fi-

nally, the values in Table II do not agree at all with the only previous measurements in this system, those of Wöhler and Balz.[5] For these reasons measurements were made also by the well-known method of Deville.

The principle of this method, it will be recalled, is to allow water vapor from a reservoir maintained at a constant and known temperature to react until equilibrium is reached with the metal kept at a known and constant high temperature in another portion of the apparatus, the course of the reaction being followed by observing the pressure. The partial pressure of water vapor at equilibrium is taken as the vapor pressure of water at the measured temperature of the thermostat, and the partial pressure of hydrogen obtained by difference.

In these experiments the temperature of the thermostat ranged from 50 to 70°. It was measured to 0.02° with a thermometer calibrated by the Bureau of Standards. The thermostat was constant to 0.05° or better.

The tin, about 5 g. in weight, was contained in a porcelain boat in a silica glass tube in a tubular resistance furnace. The section containing the boat was 2.5 cm. in diameter and 10 cm. long. A tube 1 cm. in diameter connected with the water reservoir and a capillary tube at the opposite end led to the manometer and pump. The tube was pumped out and baked before runs. To insure the presence of a considerable amount of oxide a stream of water vapor was pumped over the tin for fifteen minutes at about 800° before starting any of the runs, and for shorter intervals between several of the runs. Determination of the vapor pressure of water within the apparatus while the furnace was at 200° agreed to 0.3 mm., about the error in pressure measurement, with the standard values at the measured temperature of the thermostat. The tube leading from furnace to reservoir was bent at an angle of 90° and again at 45°, so there was no direct radiation reaching the surface of the water from the furnace.

The thermocouple was enclosed in a thin-walled protecting tube sealed into the reaction chamber in a position just over the tin in the boat. Measurements with it are of about the same accuracy as in the preceding. The current for the furnace was drawn from storage batteries and remained sensibly constant over long periods of time, requiring little regulation of the furnace temperature once it was suitably set.

Pressures were read on an open-end mercury manometer of 5 mm. bore, provided with a leveling bulb so that the mercury column could be adjusted to a position close to the capillary opening, eliminating dead space. The capillary connecting tubes and a 10cm. length of mercury in the manometer were heated electrically to prevent condensation of water vapor. The temperature of the heated portion of mercury was

⁵ Wöhler and Balz, Z. Elektrochem., 27, 406 (1921).

approximately measured by means of thermocouples, and density corrections made. The barometer and steel scale of the manometer were calibrated by comparison with a standard meter, with the aid of a cathetometer. Correction for capillarity was also made.

In some of the experiments the pressure was still slowly changing when the observations were discontinued, though the approach to equilibrium was always close. In these cases a small extrapolation to the final equilibrium condition was made by each of two methods. In the first, entirely empirical, the total pressure or its logarithm was plotted against the reciprocal of the time of observation and the series extrapolated to zero. The second method has a semi-theoretical basis. In the vicinity of the equilibrium conditions the rate of change of pressure may no doubt be assumed to be proportional to the distance from equilibrium, that is, to $p_0 - p$, where p is the pressure at a given time and p_0 the equilibrium pressure. If this is true it follows that a plot of log $(p_0 - p)$ against the time should be linear. Selecting by trial values of p_0 such that this is fulfilled gives the desired limiting figure. These two methods of extrapolation agreed well.

The directly observed quantities and final calculated results are shown in Table III, and the points corresponding are also plotted in Curve 2 of Fig. 1.

TABLE III

EQUILIBRIUM DATA IN REACTION 1, STATIC METHOD

Thermostat temp., °C.	Vapor press. of H₂O, mm. of Hg at 0°	Total equilib. press., mm. Hg at 0°	Time of run, hours	Furnace temp. °C.	K_1
50.94	96.4	119.5	4.0	773	0.240
50.94	96.4	119.5	2.0	771	.240
62.76	169.0	229.8	9.0	698	.359
62.75	169.0	233.0	14.0	658	.377
69.30	226.3	272.4	3.3	826	.203
69.30	226.3	270.0	2.0	826	.193
69.25	225.8	260.1	1.0	896	.152

As shown in Fig. 1, the results of the static and dynamic methods agree very closely at the lower temperatures, but show some tendency to diverge. At the highest temperature of the range common to both sets the deviation is some 9%. This amount is not greater than the estimated possible combined error of the measurements. We assume, therefore, that both sets are essentially correct.

To determine "best values" of K_1, Curve 3 of Fig. 1, which gives some weight to both series of results, has been drawn. From it the figures of Table IV have been taken. We are unable to ascribe any meaning to the figures published by Wöhler and Balz[5] and have omitted them from consideration.

TABLE IV

BEST VALUES OF EQUILIBRIUM CONSTANT OF REACTION 1

Temperature, °C.	650	700	750	800	850	900
$K_1 = (H_2)/(H_2O)$	0.456	0.340	0.266	0.213	0.174	0.144

Measurements in Reaction 2

The dynamic method described above is readily adaptable to the carbon system and was employed virtually unchanged in principle. In this case mixtures of carbon dioxide and carbon monoxide of known composition are passed through the reaction flask, the temperature of the furnace being raised or lowered to produce reduction or oxidation.

The same tin in the same flask and furnace with the same thermocouple were used in Reaction 2 as in Reaction 1. Gas mixtures of the desired composition were prepared by addition of carbon dioxide from calcium carbonate and hydrochloric acid to the mixture of carbon monoxide and carbon dioxide obtained by heating oxalic acid with sulfuric acid. These gases were stored in aspirator bottles, using sodium bicarbonate solution as the confining liquid in order to reduce variations in the composition of the gas due to the changes in solubility of carbon dioxide caused by temperature and pressure changes. Before entering the reaction flask the gas stream was passed over calcium chloride. At the beginning and end of each run samples of gas from the aspirator were analyzed by absorption of carbon dioxide in sodium hydroxide and carbon monoxide in acid cuprous chloride solutions, the average of the closely agreeing results being taken as the equilibrium ratio corresponding to the temperature finally established in the furnace.

A typical series of observations with a ratio $(CO)/(CO_2) = 0.326$ is as follows.

E.m.f. of thermocouple, mv.	5.20	5.80	5.40	5.60	5.52	5.58	5.55
Condition of tin	ox.	red.	ox.	red.	ox.	red.	ox.

From these observations 5.56 mv., corresponding to 645°, was taken as the temperature of equilibrium of the solids with this gas mixture.

A summary of final results is contained in Table V and plotted in Fig. 2 (Curve 1).

TABLE V

EQUILIBRIUM CONSTANTS OF REACTION 2

Temperature, °C.	645	666	681	704	772	815
$K_2 (CO)/(CO_2)$	0.326	0.312	0.304	0.295	0.270	0.255

Our results are lower by some 20% than the figures for K_2 chosen by Maeda[3] from observations of gas compositions obtained on streaming carbon monoxide or carbon dioxide at low velocities over the solid phases at various temperatures. His smoothed results are shown in Curve 2 of Fig. 2. This method as applied by him does not approach in accuracy the one used by us. It may be said, however, that within the rather wide limits of error his work agrees with ours.

Comparison of our data with the average values obtained by Fraenkel and Snipischski[2] (Table 4a of their paper) is also made in Fig. 2. The

curvature shown in the plot (Curve 3) of their results is probably indicative of some error in their work. However, between 775 and 925° the mean slope of their curve is nearly the same as ours (extrapolated above 825°) and points from the two curves agree within 6%, well within the combined error. Below 775° the curves deviate, differing by 16% at 650°. It should also be mentioned that at about 950° a sharp change in slope shows in Fraenkel and Snipischski's curve. At the higher temperatures, not shown in the figure, their results either correspond to different solid phases or are seriously in error.
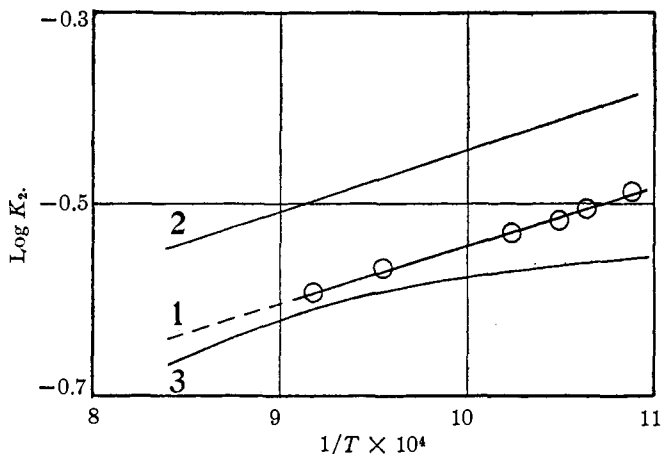

Fig. 2.—Equilibrium constant of reaction 2. Curve 1, Eastman and Robinson; Curve 2, Maeda; Curve 3, Fraenkel and Snipischski.

Our experiments permitted much greater precision than was attained either by Fraenkel and Snipischski or Maeda. We consider it justifiable to take points from Curve 1 of Fig. 2 as most representative of the equilibrium in this reaction. Table VI has been compiled in this way.

TABLE VI

BEST VALUES OF THE EQUILIBRIUM CONSTANT OF REACTION 2

Temperature, °C.	650	700	750	800	850	900
$K_2 = (CO)/(CO_2)$	0.321	0.296	0.277	0.260	0.245	0.232

The Water–Gas Equilibrium Constant

In calculating the water–gas constant the values of K_1 and K_2 determined under precisely similar conditions by our dynamic method will alone be utilized. These figures for K_2 have already been given in Table VI. Similar values for K_1, taken from Curve 1 of Fig. 1, are listed in the second column of Table VII. The calculated values of K_3 corresponding to these two sets are given in the third column of the table. Columns four, five and six, giving for comparison similar calculations from two equilibria in

the iron system, and the directly determined values, are taken from the paper of Eastman and Evans.[1]

TABLE VII

VALUES OF THE EQUILIBRIUM CONSTANT OF THE WATER–GAS REACTION

Temp., °C.	K_1	K_3 from K_2/K_1	K_3 from FeO:Fe	K_3 from FeO:Fe$_3$O$_4$	K_3 direct measurement
650	0.455	0.707	...	..	...
700	.336	0.882	0.862	0.86	0.581
750	.257	1.078	1.062	1.04	.733
800	.201	1.294	1.280	1.24	.892

The new data support the previous conclusion that the directly determined values are in error.

Summary

Indirect determinations of the water–gas equilibrium constant have been made from studies of the reaction of water vapor and of carbon dioxide with tin at temperatures between 650 and 800°. The results agree with previous indirect determinations and differ largely from the direct.

The data used in the calculation of the water–gas constant were obtained by a modification of the dynamic method of determination, in which the oxidizing or reducing effect of the gas stream is observed visibly. This method would appear to permit convenient and accurate measurements in other similar systems.

In confirmation of the method used, determinations by the static scheme due to Deville were made in the reaction of tin with water vapor. The latter measurements extend as high as 875°. They substantiate the results by the dynamic method.

From the various data considered, best values of the equilibrium constants of the two reactions above, at 50° intervals between 650 and 900°, have been tabulated.

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