ON THE ROLE OF THERMAL DISSOCIATION

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Abstract

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Academician of the Academy of Sciences of the Uzbek SSR **N. V. LAVROV**,
G. P. KHAUSTOVICH

ON THE ROLE OF THERMAL DISSOCIATION IN THE PROCESSES OF INTERACTION OF CARBON WITH CARBON DIOXIDE AND OXYGEN

In view of the fact that, on the basis of works ([1,2]), it has become possible to compare the rates of interaction of carbon with carbon dioxide and with oxygen over a wide temperature range, it is of interest to consider the question of the role of thermal dissociation in these processes.

As follows from the most general considerations, any gas, if thermal dissociation is taken into account, is a mixture of various reagents. Thus, for example, in the simplest case CO_2 dissociates into CO, O_2, and O. Therefore, all investigators have essentially obtained, including in works ([1,2]), rate constants for the reactions of carbon interaction with a complex gas mixture.

In the general case, it is necessary to investigate separately the rate of interaction of carbon with CO_2, O_2, and O. However, having only total data, one can make certain judgments about the degree of influence of each gaseous component on the rate of the whole process.

In work ([1]), an approximate equilibrium composition of carbon dioxide in the range 1000—3500°K is given, and it is shown that the product of the greatly reduced value of the rate constant of the reaction $C + O$ by the equilibrium concentration of atomic oxygen, i.e., the rate of the reaction $C + O$, in the indicated temperature range is substantially greater than the rate of the reaction $C + O_2$ and, all the more, the reaction $C + CO_2$, while the rate of the reaction $C + O_2$ is considerably greater than the rate of the reaction $C + CO_2$ in the range 1000—3500°K.

It follows from the foregoing that the entire process under the given conditions can be determined only by the equilibrium concentration of atomic oxygen, while

CO_2 and O_2 will be only its suppliers. This is well illustrated by the calculated data placed in Table 1, taken from work (^{1}).

In order to arrive at the same conclusions, there is no need to make any assumptions concerning the rate constant of the reaction $C + O$. It is sufficient to note that, when carbon interacts with CO_2, the supplied reagent contains CO_2, CO, O_2, and O, whereas in the case of the reaction $C + O_2$ it contains O_2 and O; that is, in studying the reaction $C + O_2$, we in effect separate the action of molecular and atomic oxygen from the action of CO_2 in the reaction $C + CO_2$. The only assumption here is the adoption of first order with respect to the gaseous reagent, but this assumption was already made when obtaining the rate constants of the reactions themselves. Table 1 gives a comparison of the rates of the reactions $C + O_2$ ($C + O_2 + O$) and $C + CO_2$ ($C + CO_2 + O_2 + O$). True, if the reaction rate is expressed in grams of carbon per unit time per unit surface area, then the rate data must be multiplied additionally by a factor of 2 (the ratio of the stoichiometric coefficients).

Consequently, over the entire temperature range considered, 1000—3500°K, the rate of the process of interaction of carbon with CO_2 is practically completely determined by the rate of interaction of carbon with molecular and atomic oxygen that appears as a result of the thermal dissociation of CO_2.

Table 1

$T°$, K	K_{CO_2}	C_{CO_2}	$(KC)_{CO_2}$	K_{O_2}	C_{O_2}	$(KC)_{O_2}$	K_O	C_O	$(KC)_O$	$(KC)_O/(KC)_{CO_2}$	$(KC)_O/(KC)_{O_2}$	$(KC)_{O_2}/(KC)_{CO_2}$
1000	$6.55\cdot10^{-10}$	0.999	$6.54\cdot10^{-10}$	$4.22\cdot10^{-4}$	$8.0\cdot10^{-6}$	$3.38\cdot10^{-9}$	$1.26\cdot10^{5}$	$4.4\cdot10^{-13}$	$55\cdot10^{-8}$	$8.45\cdot10^{2}$	$1.64\cdot10^{2}$	5.15
1500	$1.04\cdot10^{-3}$	0.999	$1.04\cdot10^{-3}$	8.25	$1.84\cdot10^{-4}$	$1.51\cdot10^{-3}$	$2.5\cdot10^{6}$	$5.4\cdot10^{-8}$	$1.35\cdot10^{-1}$	$1.30\cdot10^{2}$	$1.22\cdot10^{2}$	1.07
2000	1.30	0.977	1.27	$7.86\cdot10^{2}$	$7.43\cdot10^{-3}$	5.84	$1.12\cdot10^{7}$	$5.6\cdot10^{-5}$	$6.26\cdot10^{2}$	$4.95\cdot10^{2}$	$1.07\cdot10^{2}$	4.60
2500	$9.25\cdot10$	0.815	$7.55\cdot10$	$1.43\cdot10^{4}$	$5.90\cdot10^{-2}$	$8.42\cdot10^{2}$	$2.76\cdot10^{7}$	$3.0\cdot10^{-3}$	$8.27\cdot10^{4}$	$1.10\cdot10^{3}$	$9.82\cdot10$	$1.10\cdot10$
3000	$1.64\cdot10^{3}$	0.436	$7.15\cdot10^{2}$	$9.45\cdot10^{4}$	$1.58\cdot10^{-1}$	$1.49\cdot10^{4}$	$5.0\cdot10^{7}$	$4.5\cdot10^{-2}$	$2.25\cdot10^{6}$	$3.15\cdot10^{3}$	$1.51\cdot10^{2}$	$2.08\cdot10$
3500	$1.25\cdot10^{4}$	0.131	$1.64\cdot10^{3}$	$3.86\cdot10^{5}$	$1.95\cdot10^{-1}$	$6.12\cdot10^{4}$	$7.75\cdot10^{7}$	$1.96\cdot10^{-1}$	$1.52\cdot10^{7}$	$9.29\cdot10^{3}$	$2.48\cdot10^{2}$	$3.72\cdot10$

K_{CO_2}, K_{O_2}, K_O—rate constants of the corresponding reactions (cm/sec); C_{CO_2}, C_{O_2}, C_O—equilibrium concentrations of CO_2, O_2, and O upon dissociation of CO_2.

However, simple calculations show that what was stated above is valid only under the condition that the rates of the reactions $C + CO_2$ and $C + O_2$ are proportional to the product of the reaction-rate constant and the concentration of the corresponding gaseous reactant.

As is known (^{3}, ^{4}), this condition is fulfilled either at low temperatures (the kinetic regime), or at sufficiently high temperatures, since in the general case the rate of interaction of carbon with a gaseous reactant (a spherical particle, first order with respect to the gaseous reactant (^{4})), if the supply of substance is sufficiently large, is equal to

$$K_s = \beta Ca,$$

where K_s is the specific rate of interaction of carbon with the gaseous reactant, β is the stoichiometric coefficient, C is the concentration of the gaseous reactant in the core of the flow, and a is the coefficient of reactive gas exchange.

At sufficiently low temperatures

$$a \sim S_{iK},$$

where S_i is the specific surface area of carbon, K is the reaction-rate constant; while at high temperatures $a \sim K$.

Thus, at sufficiently high temperatures, when for the reaction $C + \mathrm{CO}_2$ $a \sim K$, and at sufficiently low temperatures, when for the reaction $C + \mathrm{O}_2$ $a \sim S_{iK}$, the rate of the process of interaction of carbon with CO_2 is practically completely determined by the interaction of carbon with molecular and atomic oxygen obtained as a result of the thermal dissociation of CO_2. It would be entirely logical to assume that the whole process is determined by the interaction of carbon only with atomic oxygen, but for final judgments experimental data on the reaction $C + \mathrm{O}$ are necessary.

The conclusion that at high temperatures the process of interaction of carbon with CO_2 is determined by the equilibrium concentration of oxygen is quite natural, since the condition $a \sim K$ for the reaction $C + \mathrm{CO}_2$ is fulfilled at sufficiently high temperatures, $\sim$ 2200-2500°C, i.e., when CO_2 is already strongly dissociated. As for the second conclusion—that at sufficiently low temperatures (the kinetic regime for the reaction $C + \mathrm{O}_2$) the process of interaction of carbon with CO_2 is mainly determined by the equilibrium concentration of oxygen—it is, to some extent, unexpected. In the intermediate temperature range the role of the reaction $C + \mathrm{CO}_2$ increases substantially, since it occurs in a considerably larger mass of carbon than does the reaction $C + \mathrm{O}_2$.

It is interesting to note that the activation energy of the thermal dissociation of CO_2 is 87 kcal/mol (^{5}), i.e., it coincides with the activation energy of the reaction of reduction of carbon dioxide by carbon. From what has been set forth it follows that at low and high temperatures this coincidence is regular. In the intermediate temperature region, i.e., when the role of the reaction C + CO_2 is large, this can apparently be explained only by the fact that in this case as well the initial stage of CO_2 dissociation is determining.

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CITED LITERATURE

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