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Equilibration of CO_2 with CO and O_2 in Electric Discharge

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Equilibration of CO_2 decomposition, $2CO_2 \rightleftharpoons 2CO+O_2$, has been observed in electric discharge over a range of total pressures 10 to 50 Torr. The equilibrium conversion of CO_2 to CO decreased with increasing total pressure.

Carbon dioxide decomposes into CO and O_2 in electric discharge. Recently we happened to find out that this discharge reaction is reversible:

$$2CO_2 \rightleftharpoons 2CO + O_2. \qquad (1)$$

This reversibility provides a rare example of chemical equilibrium in radiation chemistry[1)] although there are numerous examples of thermal and photochemical equilibrium reactions. One might concern with this discharge reaction in relation to the production of synthetically useful CO or the excitation of a laser medium CO_2. For the former purpose the higher degree of CO_2 dissociation is required whereas the opposite is desirable for the latter. Here we report our measurements of the equilibrium positions for discharge reaction (1) under various discharge conditions.

Reaction (1), either forward or backward, was conducted using pure CO_2 or a stoichiometric mixture 2CO + O_2 in a closed circulating system equipped with Al dishcarge electrodes (6 cm apart) and a Hg-filled volume adjuster. The volume

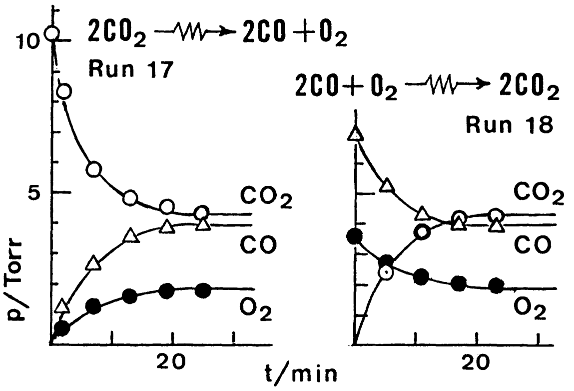

Fig. 1. Establishment of the chemical equilibrium of reaction (1) in electric discharge. Partial pressure vs. discharge time.

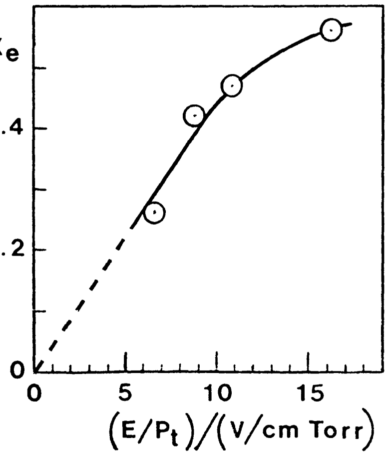

Fig. 2. Equilibrium conversion of CO_2 to CO.

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Table 1. Equilibrium Quantities under various Discharge Conditions

Run pair		5-8	9-10	11-12	13-14	15-16	17-18
Total pressure	P_t/Torr	50	30	20	10	30	10
Discharge voltage	U/V	1980	1580	1310	980	1440	930
Discharge current	I/mA	6.7	7.5	7.8	8.0	11.7	12.2
X_e		0.26	0.42	0.47	0.56	0.39	0.57
10^3K/atm		0.30	1.14	1.46	1.88	0.96	2.22

Xe = $1-[P(CO_2)_{eq}/P(CO_2)_{init}]$, the equilibrium conversion of CO_2 to CO in the forward reaction (1).

$K = P(CO)^2_{eq}P(O_2)_{eq}/P(CO_2)^2_{eq}$.

adjuster allowed the reaction to proceed at a constant pressure. The high voltage for electric discharge was supplied through a neon-sign transformer. The reaction was followed by gas chromatography.

Figure 1 shows typical reaction profiles for both the forward (run 17) and backward (run 18) sides conducted at a total pressure of 10 Torr (1 Torr = 133.322 Pa). Obviously both runs smoothly proceeded with a gradually decreasing rate and eventually ceased with identical gas compositions. We can thus conclude that reaction (1) is reversible under electric discharge, and the equilibrium conditions are easily established. Five more pairs of discharge runs were conducted similarly from both CO_2 synthesis and decomposition sides at various total pressures (P_t) or discharge currents (I). Table 1 lists the results obtained. The quantity K defined by the equilibrium partial pressure $P(\delta)_{eq}$ of gaseous species δ as

$$K = P(CO)^2_{eq}P(O_2)_{eq}/P(CO_2)^2_{eq} \qquad (2)$$

fell in a range of 10^{-3} - 10^{-4} atm (1 atm = 101325 Pa), in stark contrast of the practically irreversible 10^{-90} atm i.e., the equilibrium constant expected when reaction (1) is driven thermally at room temperature.[2)]

The per-cm discharge voltage U/6 divided by the total pressure, i.e., $U/6P_t$ E/P_t, is a familiar parameter in discharge chemistry, and is considered to increase with increasing electron temperature (T_e). Figure 2 shows a plot of X_e against E/P_t for the four run pairs of the left side in Table 1: the values of discharge current I are nearly identical for these runs. Apparently X_e increases with increasing E/P_t, and seems to level off eventually in high E/P_t regions.

References

1) S. C. Lind, "Radiation Chemistry of Gases," Reinhold, New York (1961), Chap. 6-8. According to this book, the radiochemical equilibrium has been determined under α-ray irradiation for several reactions including $2H_2+O_2 \rightleftharpoons 2H_2O$ and $3H_2+N_2 \rightleftharpoons 2NH_3$.
2) "Kagaku Benran (Kiso Hen)," revised 3rd ed, ed by the Chemical Society of Japan, Maruzen, Tokyo (1984), p. II-334.

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