Proceedings of the Iowa Academy of Science

Volume 66 | Annual Issue Article 29

1959

Dissociation of Carbon Dioxide

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Abstract. An investigation of possible methods of dissociation of respiratory carbon dioxide to provide for recovery of oxygen indicates the most feasible methods to be a catalytic decomposition by chemisorption on reduced metals and photolysis of carbon dioxide by ultraviolet light. Reduction of carbon dioxide by iron, nickel, and cobalt gives 0 to 25 volumes per cent carbon monoxide at temperatures from 300 to 800° C.

In the race to carry man into space there is a need to create an atmosphere within the space ship which will contain an infinite supply of oxygen. Present breathing systems use an absorbent to remove carbon dioxide from respiratory gas, but this is good for only a few hours. Under normal conditions of breathing, man exhales about 16.3 percent oxygen and 4.5 percent carbon dioxide. The volume of carbon dioxide exhaled by man is 0.5 to 5 cu. ft. per hour, depending on the extent of his activity. Normal respiration of carbon dioxide is about 0.9 cu. ft. per hour.

A system, therefore, that would separate the carbon dioxide from oxygen and dissociate the carbon dioxide into carbon and oxygen would serve to reuse all available oxygen from this source. In this study the possibilities of dissociation of carbon dioxide are considered. Two important requirements of such a system are that it must function at a flow rate of about 3 cu. ft. per hour and be a light compact unit.

Carbon dioxide is a colorless, odorless gas with a density of 1.977 grams per liter at standard conditions. Solid carbon dioxide sublimes at −78.5° C. It can be liquefied only under pressure. The carbon dioxide molecule is relatively stable and does not easily dissociate into its components. Dissociation to any great extent is prohibited by the reversibility of the reaction $2CO_2 = 2CO + O_2$. The heat of formation of carbon dioxide from carbon and oxygen is exothermic and equal to approximately −94 kilocalories. When it is formed from carbon monoxide plus oxygen the heat of formation is −66.81 to −68.21 kilocalories (Mellor, 1947).

At high temperatures it is possible to dissociate carbon dioxide, the degree of dissociation being a function of temperature. Table 1

[1]This investigation was carried out at Pioneer-Central Division of Bendix Aviation Corporation under the Student Industrial Research Program which is in cooperation with St. Ambrose College. The author wishes to express appreciation to the following: Sister Mary Helene, Mr. E. M. Vaughn, Mr. D. M. Perry, Mr. M. Owen, and Mr. J. O'Brien.

gives the percentage of dissociation as calculated by Bjerrum (Quinn and Jones, 1936).

Table 1

Percentage of Dissociation of Co_2

°K	0.1 ATM	1 ATM	70 ATM	100 ATM
2000	4.35	2.05	0.96	0.445
2500	33.5	17.6	8.63	4.09
3000	77.1	54.8	32.2	16.9
3500	93.7	83.2	63.4	39.8
4000	97.9	93.9	83.4	63.8
4500	99.2	97.4	92.4	80.3
5000	99.6	98.7	96.1	89.0

Magnesium and aluminum will continue to burn in an atmosphere of carbon dioxide to form the metal oxide and carbon. This presents the possibility of reducing the carbon dioxide to the metal oxide and obtaining the oxygen from the oxide. Further investigation reveals that MgO and Al_2O_3 are not easily dissociated.

Certain metals will act as catalysts in the dissociation of carbon dioxide. A chemisorption or adsorption process in which a surface oxide is formed usually takes place. Nickel, cobalt, and iron can reduce carbon dioxide by this process. In a thermodynamic consideration the possible chemisorption reactions of carbon dioxide and reduced iron include the following (Kawakita, 1939):

$$Fe + CO_2 = FeO + CO$$
$$3FeO + CO_2 = Fe_3O_4 + CO$$
$$3Fe + 4CO_2 = Fe_3O_4 + 4CO$$

In investigating the chemisorption of carbon dioxide on nickel at 200° C, it has been reported that it is completely dissociated into three atoms (C, O, and O) (Kwan and Fugjita, 1953). These same three metals—Ni, Co, and Fe—are used as catalysts in the reformation reaction $2CO = CO_2 + C$. The oxides of these metals are used in the reduction of CO to CO_2 and C (Baukloh and Henke, 1942). This brings to mind the question of whether any carbon monoxide could actually be collected before a reformation of carbon dioxide takes place.

Carbon dioxide will dissociate into carbon monoxide and oxygen when it is passed over the reduced metal oxide of the heavy metals, chromium, molybdenum, and tungsten. When carbon dioxide is fed over MoO_2, with alumina as a carrier, at the rate of 10 volumes of carbon dioxide per volume of catalyst per hour at about 500° C. and at atmospheric pressure, 24-30 volumes percent carbon monoxide was reported. The reaction was believed to be:

$$CO_2 + MoO_2 \longrightarrow CO + MoO_3 \text{ (Holder, 1950)}$$

In an investigation of chemisorption on oxide catalysts of the spinel type which included copper ferrite, copper chromite, and zinc chromite, it was concluded the carbon dioxide is chemisorbed with partial disassociation into two particles, presumably carbon monoxide and oxygen atoms (Kwan and Fugjita, 1953).

Decomposition to a small extent is reported with the use of a radio frequency arc, the yield of dissociation products being on the order of 0.24 to 3.4 x 10^{-3} moles per electron volt, (G values of 0.024 — 0.34). A three megacycle electric discharge in a flow system at 30 to 150 mm. pressure, 0.4 to 11 cc/sec (S.T.P.) flow rate, and 80-180 milliamperes current was used. The main products were carbon monoxide and oxygen (Wilde, *et al.*, 1957). Nitrogen dioxide has been described as an inhibitor in the dissociation of carbon dioxide by ionizing radiation. Using radon as a source the yield of the dissociation products of gaseous carbon dioxide increased to a G Value of 9 or 10. Irradiation produces about 0.1 percent decomposition of primarily dissociated carbon dioxide. As little as 0.5 percent nitrogen dioxide is sufficient to stop the back reaction (Harteck and Dones, 1955). The yield of carbon monoxide and oxygen by this system is too little for practical use.

Ultraviolet light is reported to decompose carbon dioxide when the gas is confined over mercury. Three percent decomposition is reported at 1 atm. and 46 percent at 36 mm. Mercuric oxide and carbon monoxide have also been reported as products of this decomposition. Mercury atoms excited by resonance radiation of λ1849A but not those excited by λ 2537A have been shown to readily decompose carbon dioxide (Cline and Forbs, 1939). Studies have also been made using xenon (1470A) resonance lamps as ultraviolet sources for the photolysis of carbon dioxide (Dacy and Hodgins, 1950).

In attempting a stepwise decomposition of carbon dioxide, gaseous carbon dioxide was passed through a tube containing various mixtures of a metal (nickel, cobalt, or iron) and a carrier (alumina or pumice). The following conditions were used: 20-25 gram samples, 300-800° C., and a flow rate of 100-300 cc. per hour. The method consisted simply of connecting a cylinder of pure carbon dioxide to a metal tube (0.4 cm. diameter and 80 cm. long) which ran through a Burrell electric furnace. The issuing gas was collected in a gas sampling tube and analyzed in a Beckman gas chromatograph using a molecular sieve column. This column separates oxygen, nitrogen, and carbon monoxide, but does not show carbon dioxide. The approximate percentages of carbon monoxide in the gaseous mixtures were determined from a graph prepared by running pure carbon monoxide at varying pressures to obtain the peak height for the different concentrations. The peak height was plotted against percentage. The yield of carbon monoxide varied from zero to twenty-

Table 2

Reduction of Carbon Dioxide

Substance in Tube	Temperature °C	Percent CO
Iron Aluminum Tube	300-400	25
50% Iron 50% Alumina	500-800	14
50% Iron 50% Pumice	500-600	14
30% Cobalt 70% Pumice	400-600	4
30% Cobalt 70% Pumice	700-800	8
50% Cobalt 50% Alumina	500	2
30% Nickel 70% Alumina	600	16
30% Nickel 70% Alumina	700	10
70% Nickel 30% Alumina	600-700	1
50% Nickel 50% Alumina	700	10
Nickel	800	—
Nickel	500-800	—
Alumina	700	1

five percent as shown in Table 2. The remainder, with the exception of traces of air, was assumed to be carbon dioxide. Spectrographic analysis of the metal and carrier after the reaction with the carbon dioxide shows no trace of carbon. This indicates that the carbon dioxide has been separated into carbon monoxide and oxygen, the oxygen uniting with the metal to form a metal oxide. This investigation is not complete, and further study is being done on the possibility of obtaining oxygen. This method, however, at present does not appear practical for the purpose at hand. A complete system which would provide for recovery of oxygen would possibly include high temperatures and a large amount of equipment. An apparatus has been set up, and dissociation by ultraviolet light is being investigated.

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