

STUDY OF EQUILIBRIUM CARBONATE-BICARBONATE ELECTROLYTE IN PRESENCE OF POTASSIUM FORMATE

L. A. Matusevich and V. S. Bagotskii

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Carbon dioxide and water are formed as the result of complete electrochemical oxidation of organic substances in fuel cells. If alkaline solutions, with all their advantages, are used as the electrolytes, then the CO_2 liberated progressively carbonates them. Carbonation ultimately leads to conversion of the alkali into a mixture of carbonate and bicarbonate, in a state of equilibrium represented by the equation



The equilibrium depends on the reaction temperature and on the CO_2 partial pressure over the solution.

It has been reported [1, 2] that equilibrium carbonate-bicarbonate solutions can be used as electrolytes in fuel cells with organic fuel. The constancy of the electrolyte composition during continuous formation of CO_2 , in conjunction with the weakly alkaline reaction (presence of a certain amount of OH^- ions owing to hydrolysis of carbonate), makes this equilibrium electrolyte particularly attractive.

The efficiency of oxidation of organic substances may be improved by increase of the alkalinity of the system, i.e., by shift of the equilibrium (1) to the left. Such a shift occurs when the solution temperature is raised to near its boiling point. However, equilibrium (1) has not been studied in detail at high temperatures. It should also be taken into account that the equilibrium conditions in the carbonate-bicarbonate system may alter when an organic substance is present in solution.

This paper contains the results of an investigation of equilibrium in the system potassium carbonate-bicarbonate in relation to the temperature, total solution concentration, and amount of organic reducing agent (potassium formate) added to the system.

EXPERIMENTAL

The stainless-steel beaker 1, 500 ml in capacity (Fig. 1), placed in the oil thermostat 2, contained the electrolyte solution (KOH , K_2CO_3 , KHCO_3 , or mixture of K_2CO_3 and KHCO_3) of a definite total concentration (3, 4, or 5 g-eq/liter). Carbon dioxide was bubbled into the solution from a cylinder through the flask 3 containing water. The gas flow rate was about 0.2 liter/min. The beaker with the electrolyte was connected to the atmosphere through the reflux condenser 4. Equilibrium became established in 1-3 days, dependent on the solution concentration and temperature. Samples of solution for analysis were withdrawn through the sampling hole 5. Equilibrium was assumed to be established when the results of determinations of the solution composition remained constant for 24 h. The total concentration of the solution was maintained constant throughout the experiment by addition of distilled water as required. The determinations were performed at solution temperatures of 70, 80, 90, 95, 98, and 103°.

The curves in Fig. 2 represent variations of the carbonate and bicarbonate contents with time in a solution of total concentration 5 g-eq/liter at 70°. The figure shows that, regardless of the initial composition of the solution, when CO_2 was passed equilibrium became established between carbonate and bicarbonate in 24-40 h at the given temperature and CO_2 partial pressure.

The equilibrium established was independent of the route by which it was reached (whether it was approached from higher or lower temperatures, and whether the starting solution contained pure carbonate, bicarbonate, or a mixture of the two). Each temperature corresponded to a definite carbonate-bicarbonate ratio. Therefore it may be assumed that true equilibrium was attained in the experiments.

Carbonate and bicarbonate in the equilibrium solutions were determined by titration of samples by the Winkler method [3-5]. As the experiments were conducted at different temperatures and the solution

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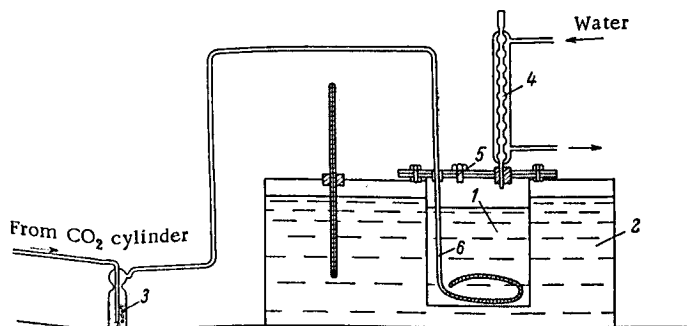


Fig. 1. Diagram of apparatus for equilibrium studies. 1) Cell; 2) thermostat; 3) absorption flask; 4) reflux condenser; 5) sampling hole; 6) bubbler.

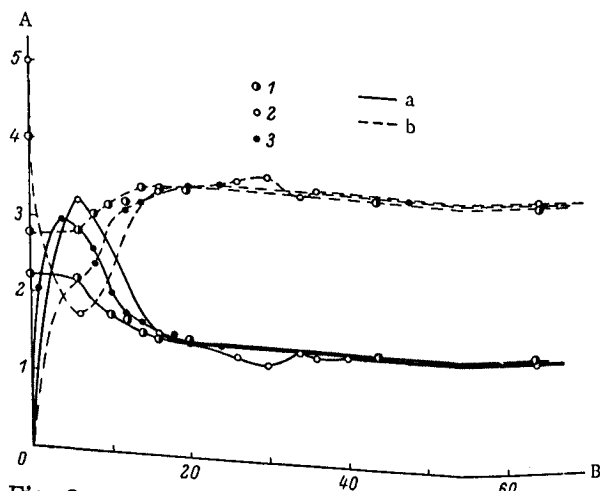


Fig. 2. Effect of the time of passage of CO_2 on the composition of an electrolyte of total concentration 5 g-eq/liter at 70° . A) Carbonate or bicarbonate concentration (g-eq/liter); B) time (hours). Original solution: 1) $\text{K}_2\text{CO}_3 + \text{KHCO}_3$, 2) KHCO_3 , 3) KOH . a) Potassium carbonate; b) potassium bicarbonate.

In addition to these experiments, the pH values of the pure solutions and solutions with 1.2 moles of potassium formate per liter were determined with the LPU-01 instrument with the aid of a glass electrode at 70, 80, 90, 95, and 98° .

DISCUSSION OF RESULTS

Figure 3 shows variations of the carbonate and bicarbonate contents of solutions with temperature (for solutions containing 3, 4, and 5 g-eq/liter).

The relative content of carbonate increases and that of bicarbonate decreases with rise of temperature from 70 to 103° . The patent [2] gives a similar curve for an equilibrium carbonate-bicarbonate solution with a total concentration of 2.5-2.6 g-eq/liter. The equilibrium carbonate ion concentration indicated by this curve is higher than was found in our determinations for a solution with 3 g-eq/liter. This may be attributed to the different partial pressures of CO_2 . Evidently the German investigators [2] must have used absorbents for CO_2 over the solution which are not mentioned in the publication, or passed an inactive gas through the solution.

It follows from Fig. 3a, b, and c, that the increase of the amount of carbonate in the solution with rise of temperature is more pronounced in solutions with lower total concentrations. Addition even of a

densities were unknown, the samples taken for analysis were weighed and weight corrections were applied in the subsequent calculations.

In addition to equilibrium in these carbonate-bicarbonate solutions, we studied equilibrium in the same solutions with additions of 0.6, 0.9, and 1.2 moles of potassium formate per liter. Potassium formate was prepared from analytical grade KOH and HCOOH of density 1.084 g/cm^3 . The potassium formate concentration was checked by the Jones method [6].

The equilibrium constants were calculated for all the solutions over the entire temperature range from the equilibrium molar concentrations of $\text{P}_{\text{CO}_2} = 1 \text{ atm}$ from the following formula:

$$K_e = \frac{c_{\text{KHCO}_3}^2}{c_{\text{K}_2\text{CO}_3}}$$

The heat ΔH of reaction (1) in the temperature range from 70 to 98° was estimated from the average slope of the plots of $\log K_c$ versus $1/T$. The results of the calculations are given in Table 1.

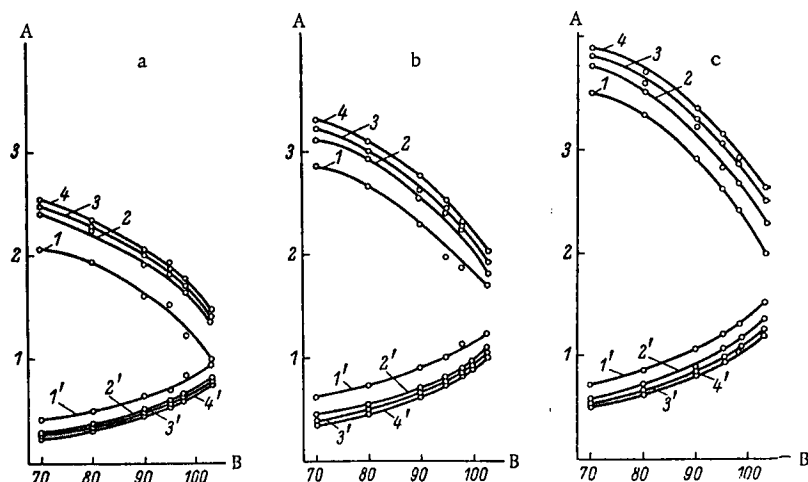


Fig. 3. Influence of temperature on the composition of the equilibrium electrolytes. A) Carbonate or bicarbonate concentration (M); B) temperature ($^{\circ}\text{C}$). Total solution concentration (g-eq/liter): a) 3; b) 4; c) 5. 1-4) Bicarbonate; 1'-4') carbonate. Potassium formate concentration (M): 1) 0, 2) 0.6, 3) 0.9, 4) 1.2.

TABLE 1. Effect of Potassium Formate Concentration on ΔH of the Equilibrium Electrolyte

Potassium formate concentration (M)	Heat effect ΔH and solution concentration (g-eq/liter)		
	3	4	5
0	-13.5	-11.0	-10.0
0.6	-13.0	-10.5	-10.0
0.9	-12.5	-11.0	-10.0
1.2	-13.0	-11.5	-11.0

small amount of potassium formate (0.6 mole/liter) to the equilibrium solution shifts the equilibrium curve 1 sharply in the direction of a higher bicarbonate content and a correspondingly lower carbonate content in the system (curves 2, 2'). Further increase of the potassium formate concentration shifts the equilibrium curves in the same direction (curves 3, 3' and 4, 4'). This relationship holds over the entire range of temperatures and electrolyte concentrations. However, the general character of the curves remains unchanged, i.e., the carbonate and bicarbonate branches of curve 1 move almost parallel, downward and upward along the ordinate respectively.

In Fig. 4 the logarithm of the equilibrium constant of reaction (1) is plotted as a function of the reciprocal absolute temperature. The curves for a given solution concentration are almost parallel, i.e., have the same slope. The curves for equilibrium solutions without potassium formate show some deviation. This may possibly be attributed to the somewhat lower accuracy in determinations of equilibrium carbonate and bicarbonate concentration in a solution in presence of the organic fuel (titration difficulties).

Examination of the plots of $\log K_c$ versus $1/T$ shows that they are fairly close together for the more concentrated solutions and differ from the curves for solutions containing 3 g-eq/liter. The slope of the curves decreases with increase of the total solution concentration.

The heats of reaction (1), given in Table 1, were calculated from the average slope of the $\log K_c$ versus $1/T$ curves. It may be concluded from these data that within the limits of experimental error the heat of reaction (1) is independent of extraneous organic substances added to the solution, and is determined only by the total concentration of carbonate and bicarbonate.

The results of determinations of the pH of all the solutions are given in Table 2. This table shows that the solution pH increases somewhat with increase of the total concentration. The influence of the total concentration on pH diminishes with rise of temperature. Addition of potassium formate to carbonate-bicarbonate solutions produces only a slight decrease of pH (on the average, by 0.05 pH unit).

CONCLUSIONS

Equilibrium in the system $\text{K}_2\text{CO}_3 + \text{KHCO}_3 + \text{H}_2\text{O}$ in a current of CO_2 in presence and in absence of potassium formate was studied. It was found that the total solution concentration does not have a strong

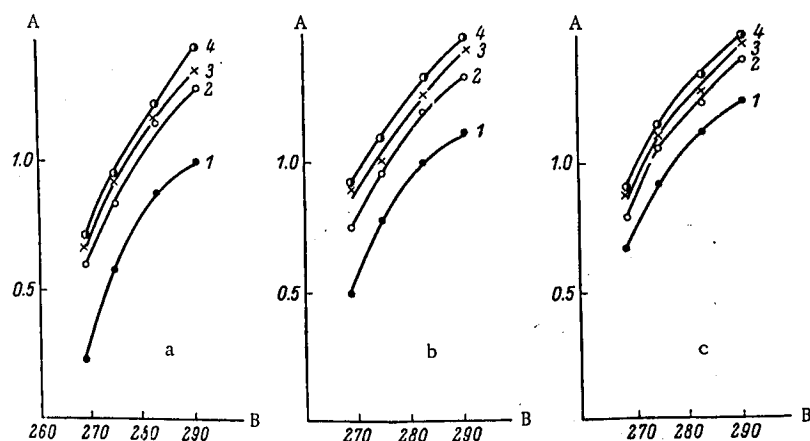


Fig. 4. Effect of temperature on the equilibrium constant of reaction (1). A) Logarithm of the equilibrium constant ($\log K_c$); B) reciprocal temperature $(1/T) \cdot 10^5$ ($1/^\circ\text{K}$). Potassium formate content (M): 1) 0, 2) 0.6, 3) 0.9, 4) 1.2. Total solution concentration, $^c\text{K}_2\text{CO}_3 + ^c\text{KHCO}_3$ (g-eq/liter): a) 3; b) 4; c) 5.

TABLE 2. Effect of Temperature on pH of Equilibrium Electrolytes

Solution concentration (g-eq/liter)	pH at temperature ($^\circ\text{C}$)				
	70	80	90	95	98
3	8.45	8.60	8.90	8.95	0.10
3*	8.45	8.55	8.80	8.90	9.05
4	8.65	8.80	9.00	9.10	9.15
4*	8.60	8.75	8.85	9.05	9.10
5	8.80	8.85	9.00	9.15	9.25
5*	8.75	8.80	8.95	9.05	9.15

* The same solutions with addition of 1.2 mole of potassium formate per liter.

influence on the OH^- ion concentration, especially at 90° and higher temperatures.

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