

SHORT
COMMUNICATIONS

Carbon Disproportionation and Fractionation in the Carbon–Water–Gas System

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Carbon is an ubiquitous and active participant in the diversity of reactions proceeding at the Earth's surface and in its interiors [1–5]. The wide application of thermodynamic simulations in Earth sciences during the past three decades provided a deeper insight into the processes that are related to physicochemical interactions in the water–rock–gas–organic matter system, a fundamental system of the Earth's crust [3, 6, 7].

One of the most important results in this field was formulation [1] and further development [4] of the concept of the hydrolytic disproportionation of organic matter (HDOM). Hydrolytic disproportionation is the process of the chemical interaction of organic matter (OM) with water. Water oxidizes OM and acts in this process as both an oxidizer and a reducer, and this process produces organic components with variable oxidation states of carbon en route to the complete thermodynamic equilibrium with the final products of the reactions: CH₄, CO₂, and C_(sol). The origin of significant amounts of organic acids is the fundamental idea of the HDOM concept. According to [1], disproportionation proceeds in such a way that oxidation reactions in the C–O–H system are counterbalanced by reduction reactions in terms of the carbon state.

In spite of the undeniable progress in the application of thermodynamic simulation to the study of physicochemical interaction processes in the water–carbon system, some issues pertaining to the detailed understanding of these interactions remain poorly understood as of yet. These are, first of all, (i) the physicochemical relations persistently occurring during carbon fractionation between organic matter (solid or liquid), an aqueous solution, and a gas mixture; and (ii) the stages of the these interactions in the water–carbon system. This publication proposes answers to these questions for the C–Cl–Na–O–H–e system. The research was conducted

with the application of the SELECTROR program complex (for the Windows operation system).

In order to clarify the effect of the modes in which carbon occurs on its interaction with water, we examined a system closed with respect to the atmosphere at a temperature of 25°C and a pressure of 1 bar, with the most stable mode of carbon occurrence assumed to be graphite ($\Delta G_{f298}^0 = 0$) and with chemically active amorphous carbon; ($\Delta G_{f298}^0 = +18.8$ kJ/mol) [8].

First we examined a model for the complete thermodynamic equilibrium. The comparison of the plots in Fig. 1 clearly demonstrates the effect of the mode of carbon occurrence on its solubility. Amorphous carbon can be completely dissolved in both acid and alkaline solutions. The solubility of graphite depends on the pH of a solution and increases only at alkaline pH.

As a further development of the HDOM concept, we determined the following pervasively occurring feature of the redox process in the carbon–aqueous solution–gas system. Carbon with the zero oxidation state (solid carbon and CH₃COOH) is distributed in equal mole fractions between two groups of species: dependent components with carbon oxidation states of +4 and –4. However, this balance pertains only to the carbon–aqueous solution–gas system as a whole. Because of this, when interactions are considered within the framework of this system, the distribution of carbon with oxidation states of +4 and –4 between phases should be taken into account. Carbon with the oxidation state of –4, in the form of methane, should enrich the gas phase, whereas carbon with the oxidation state of +4 should preferably accumulate in the aqueous solution. As a result, the aqueous solution and the gas phase become enriched in carbonate and in methane, respectively. The fractionation of carbon between these phases controls, for example, the release of marsh gas.

[†]Deceased.

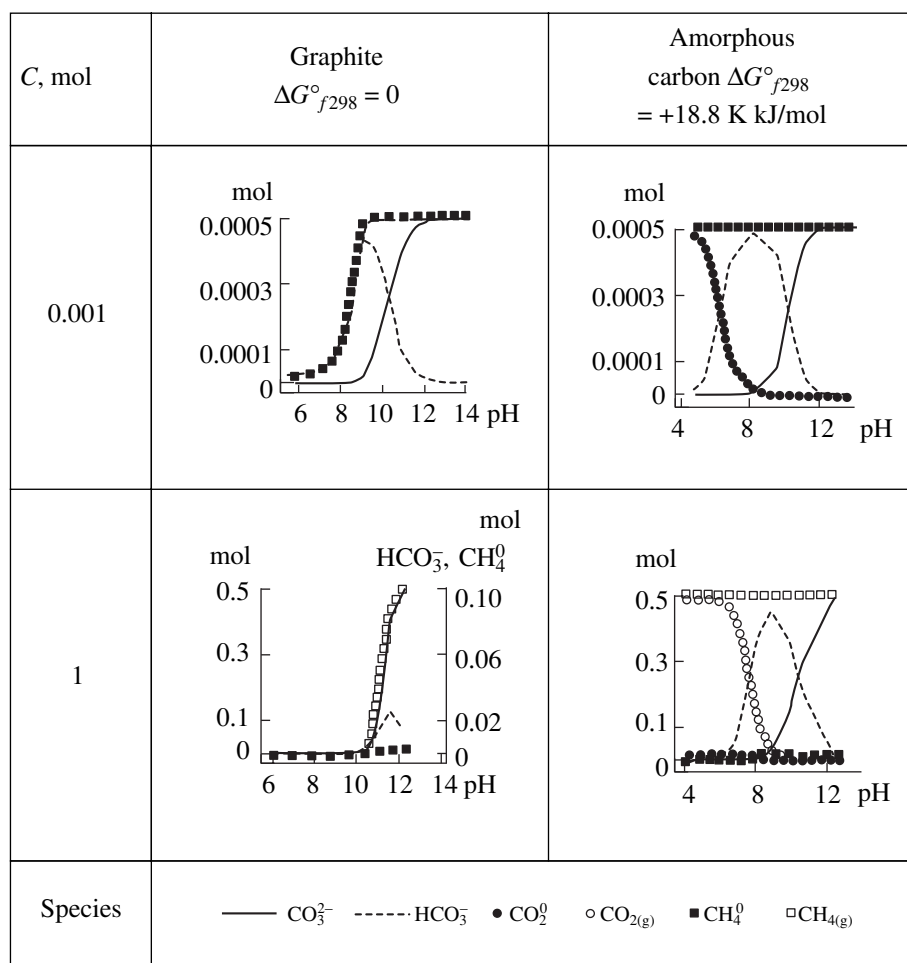


Fig. 1. Solubility of graphite and amorphous carbon in the system C–Cl–Na–O–H–e as a function of the pH of the aqueous solution ($T = 25^\circ\text{C}$, $P = 1 \text{ bar}$).

There is a certain limiting value for the content of carbon in the carbon–aqueous solution–gas system. Below this limit at a given temperature and pressure, no gas phase can be produced, and all carbon with the oxidation states of +4 and –4 remains retained in the aqueous solution (Fig. 1).

The Achilles heel of the minimization algorithm utilized in [1 and elsewhere] is that it does not allow the researcher to simultaneously calculate the complete or metastable equilibria in aqueous solution–gas systems in which the appearance or disappearance of the gas phase or aqueous solution is not specified by the starting conditions of the model but is determined by the solution itself. As can be seen from the results obtained for interactions between amorphous carbon and graphite with water, this disadvantage of the technique cannot be regarded as an insignificant defect of the calculation algorithms, because the appearance or disappearance of a gas phase is one of the major factors of the fractionation of dependent components in the water–gas system.

In order to account for the gas phase, Karpov et al. [9] put forth the concept of a two-stage interaction of

carbon-bearing compounds with water. Redox reactions are known to be slower than ion reactions not associated with changes in the valences of the participating elements [10]. This led us to propose a three-stage scheme for the process of carbon interaction with water. The first stage involves the formation of carbon acids, mostly acetic acid; the second stage is marked by the attainment of complete metastable phase equilibrium (in the aqueous solution) between the carbonate and carbon components; and the third stage is characterized by the attainment of complete thermodynamic equilibrium in the aqueous solution–gas subsystem. This provisionally assumed qualitative scheme can be further refined on the basis of experimental data on the kinetics of decarboxylation reactions [11] and systematic geological observations [5, 12–14, and others].

The aforementioned three stages is the ultimate idealization of the process. In nature, these processes are concurrent but proceed with different rates. The saturation of the aqueous solution with carbon acids can be attained only if the formation rate of these acids at a carbon–water interface is greater than the rate of decar-

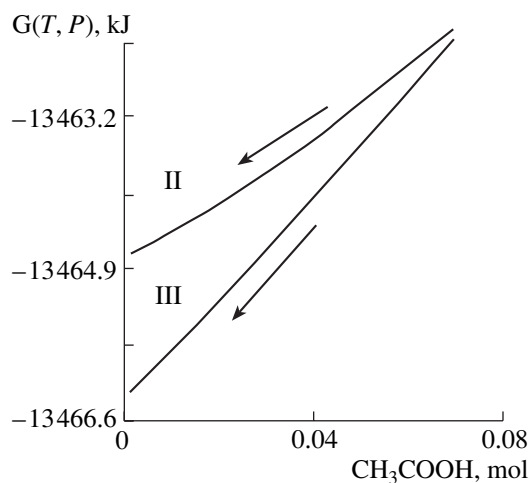


Fig. 2. Variations in the $G(T, P)$ as a function of the CH_3COOH concentration in 1 kg of aqueous solution ($T = 95^\circ\text{C}$, $P = 1$ bar) during stages II and III of the carbon interaction with water.

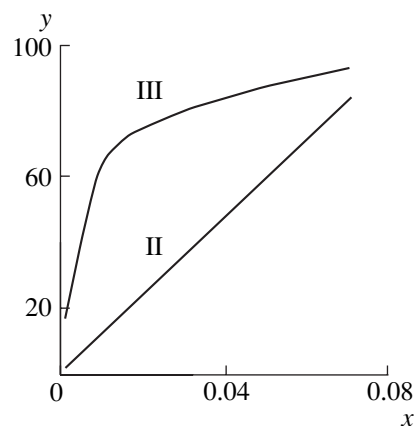


Fig. 3. Abscissa—number of acetic acid (CH_3COOH) moles left after the reaction, ordinate—percentage (wt %) of the sum of carbonate + carbon components for stages II and III of the interaction.

boxylation with the release of carbonate components, CH_4^0 , H_2^0 , and CO^0 to the aqueous phase and $\text{CH}_{4(\text{g})}$, $\text{CO}_{2(\text{g})}$, $\text{CO}_{(\text{g})}$, and $\text{H}_{2(\text{g})}$ to the gas phase. As soon as the carbon–water contact interaction ceases to exist, the aqueous solution irreversibly tends to approach a state of complete thermodynamic equilibrium. The proportions of the carbon and carbonate + (CH_4^0 , H_2^0 , and CO^0) dependent components thereby continuously change toward an increase in the amount of the latter. The Gibbs free energy (the isobaric–isothermal potential) of the aqueous solution–gas phase subsystem should thereby decrease, and it reaches its minimum at a complete thermodynamic equilibrium. The degree of metastability controls the proportions of carbon and carbonate components.

The character of the change of the Gibbs free energy for the C–Cl–Na–O–H–e system during stages II and III is shown in Fig. 2 as depending on the metastable concentration of CH_3COOH , which is specified by the imposing of additional constraints onto the molar concentration of acetic acid. Note that stage III in Fig. 2 corresponds to the metastable equilibrium in the aqueous solution–gas subsystem. Complete thermodynamic equilibrium in the aqueous solution–gas subsystem can be reached when the limitations imposed onto the concentration of acetic acid are eliminated. The proportions of the concentration of CH_3COOH that was not decomposed and the percentage of carbon components (their weight percent of the sum of carbonate and carbon components in the C–Cl–Na–O–H–e system with a fixed chemical composition vector for independent components) are shown in Fig. 3 for stages II and III.

This concept is consistent with the high concentration of carbon acids not only in waters at boundaries of hydrocarbon accumulations but also (and this is partic-

ularly important) in regionally spread formation waters of sedimentary rocks that contain organic matter. The example of the Western Siberian Artesian Basin is addressed to in [14] to demonstrate the regional character of the occurrence of carbon acids in the formation waters of this basin and a correlation of their presence with the concentration of OM in the rocks. The half-life time of CH_3COOH at 50°C is approximately 66 years [11], and, thus, the metastable existence of intermediate carbon-bearing compounds is one of the crucial factors that controls physicochemical processes in natural waters. The time spans needed for the irreversible decomposition of these metastable complexes are sufficient for these complexes to notably affect physicochemical interactions in systems aqueous solution–gas–minerals–carbon by participating in the processes of dissolution, transfer, and precipitation of major (Al, Si, Ca, and Fe) and other elements in the zones of weathering, supergenesis, and catagenesis.

This publications touches upon only two issues in the broad spectrum of problems pertaining to the physicochemical mechanisms of interactions in the carbon–water–gas system. These two problems are related to the constructive development of the HDOM concept. First, we determined the general trend in the distribution of carbon-bearing compounds with various oxidation states between phases. Second, we proposed a qualitative three-stage scheme for the evolution of the system carbon–aqueous solution–gas, from its original disequibrated state to a complete thermodynamic equilibrium. Under metastable equilibrium, the aqueous solution contains relatively high concentrations of carbon acids with carbon having oxidation states of 2 and ≥ -4 .

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