Concentration of CO_2 over Melting Ice Oscillates

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We report that the concentration of CO_2 over melting ice oscillates as long as water and ice coexist. A phenomenological model involving melting of CO_2 containing ice leading to its release, readsorption of the vapor on ice, and dissolution in water is proposed. Thermokinetics of these processes lead to nonlinearity of the dynamics. This phenomenon is also observed over impure ice contaminated with salts or in the presence of nitrogen or air. Oscillations have been observed in several other solute or ice-water systems.

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Nonlinearity in reaction kinetics can lead to the interesting phenomenon of chemical oscillations. While the most studied of this category of reactions is the Belousov-Zhabotinskii reaction [1,2], an increasingly large number of oscillatory phenomena have been identified in the recent past, especially in heterogeneous catalysis [3]. The most ubiquitous heterogeneous system on our planet is the ice-water system, on which there has been extensive research [4]. Our experiments consisted of the measurement of concentration of carbon dioxide (CO_2) as a function of time over melting ice using mass spectrometric techniques. They revealed the existence of oscillations in the concentration of CO_2 as long as water and ice coexist. This is in contrast to the general expectation that a constant vapor pressure exists when a gaseous species is present over the condensed phase of another. Apart from CO_2, several other molecules are also shown to exhibit oscillations over the ice-water system. Previous reports of CO_2 oscillations in the vapor phase have been in the context of oxidation of CO on solid catalytic surfaces of Pt group metals [3] and in plant photosynthesis, where rhythmic diurnal release of CO_2 has been observed [5].

In a typical experiment, 10 ml of water was taken in a glass bulb of one-liter capacity and the system was evacuated to 10^{-2} torr. Water was subjected to freeze-pump-thaw cycles, to remove dissolved gases, and was subsequently cooled slowly to prepare ice samples. The desired quantity of the molecule of choice was deposited on ice at 123 K, making sure that deposition occurred only on ice, leading to $\sim 10^5$ layers for 1.33×10^{-3} mol of CO_2. The bulb was left to warm up and the mass spectral intensities of specific ions (mass to charge ratio, m/z 18, 28, 32, 44 due to H_2O^+, N_2^+, O_2^+, and CO_2^+, respectively) were measured continuously with a quadrupole mass spectrometer. Temperature variation, if any, in the ice phase was below our detection limit (± 0.01 K). Sampling was done by a quartz capillary of 0.45 mm diameter, 1.5 m long, which could be exposed to atmosphere maintaining a vacuum of 1×10^{-7} mbar in the analyzer chamber. The amount of gas sampled was too small to affect the observed phenomenon.

In Fig. 1, we present the mass spectral data corresponding to 1.33×10^{-3} mol of deposited CO_2. The data show an expected pattern until 273 K, when ice starts melting. As a sufficient amount of ice melts to form water, the mass spectral intensity corresponding to the CO_2 concentration begins to oscillate about a relatively constant mean. Subsequently, when melting of ice is complete, the oscillations cease. After this, CO_2 intensity increases with temperature.

Oscillations are very sensitive to the amount of CO_2 deposited and are observed only in a specific range (for a fixed quantity of ice). The mass spectral intensity data in the oscillatory region for deposited CO_2 ranging from

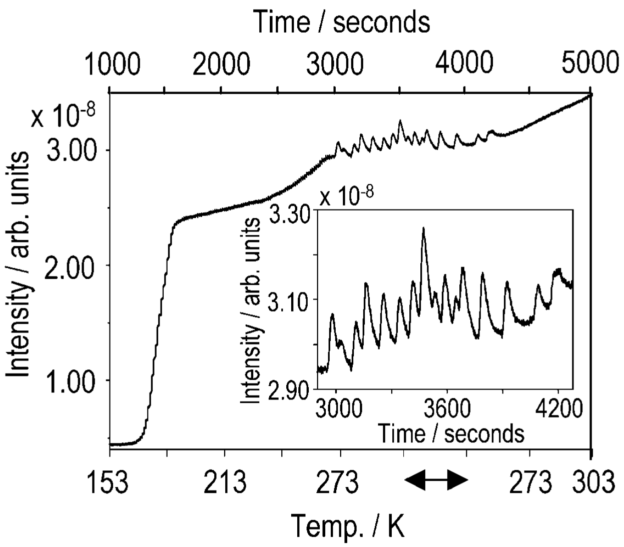

FIG. 1. Oscillations in mass spectral intensity of gas phase CO_2 (m/z 44) as a function of temperature/time. The bottom *x* axis is temperature, from 153 to 303 K; at 273 K bulk ice melts. The arrow shows the constant temperature region. The top *x* axis is the time, measured from the start of warm-up. The inset is an enlarged view of the oscillations.

2.66×10^{-4} to 2.13×10^{-3} mol are shown in Fig. 2. Although the overall behavior of the spectra remains the same, the oscillations become insignificant outside the range of 5.32×10^{-4} to 1.33×10^{-3} mol for CO_2.

A phenomenological model is proposed to account for the experimental results. This is adapted from a generic model introduced by Sal'nikov for thermokinetic oscillations [2,6]. Our model is based on the following assumed mechanism:

$$M \xrightarrow{k_0} V \qquad \text{(i)}$$

$$V \xrightarrow{k_1(T)} V_{\text{ad}} + \Delta H_1 \qquad \text{(ii)}$$

$$V \xrightarrow{k_2(T)} V_{\text{diss}} + \Delta H_2 \qquad \text{(iii).}$$

Reaction (i) describes the melting of CO_2 containing ice (M) and consequent release of CO_2 vapor (V) into the gas phase. The vapor thus formed can readsorb on the ice [reaction (ii)], forming V_{ad}, and can dissolve in the water formed, giving rise to V_{diss} [reaction (iii)]. Both reactions (ii) and (iii) are taken to be exothermic [7,8] and hence are considered to have temperature dependent rate constants $k_1(T)$ and $k_2(T)$, respectively.

Adoption of the above thermokinetic model is motivated by the observations, viz., (a) oscillations occur only during the melting of ice and (b) it is seen only for those molecules which have significant solubility and associated enthalpy changes.

The model has been constructed with the following assumptions:

(a) The endothermic melting of ice is isothermal and hence decoupled from other thermokinetic events. Thus, we have $M(t) = M_0 e^{-k_0 t}$, where k_0 is the rate constant of melting and M_0 is the initial concentration of M.

(b) The temperature dependent rate constants take the Arrhenius form: $k_i(T) = A_i e^{-(E_i/RT)}$ for $i = 1, 2$. E_1 and E_2 are the activation energies of adsorption and dissolution processes, respectively.

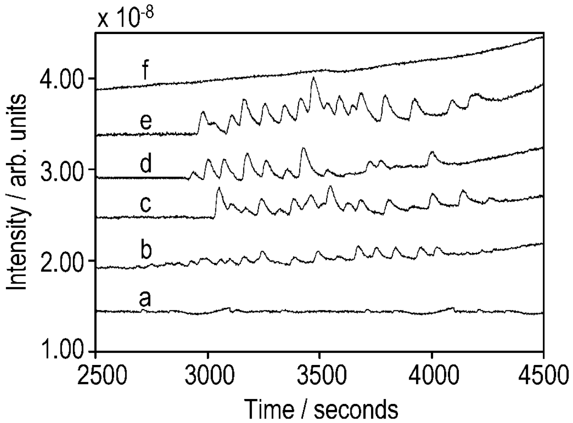

FIG. 2. Mass spectral intensity of varying quantities of CO_2 deposited over 10 g of ice. a, b, c, d, e, and f correspond to 2.66×10^{-4}, 5.32×10^{-4}, 7.98×10^{-4}, 1.06×10^{-3}, 1.33×10^{-3}, and 2.13×10^{-3} mol of CO_2, respectively.

With these assumptions, the reaction scheme (i)–(iii) leads to the following two variable dimensionless system of equations based on the law of mass action and heat balance [2]:

$$\frac{d\alpha}{d\tau} = \mu - \kappa_1 \alpha e^{\theta} - \kappa_2(\alpha_0 - \alpha)e^{k\theta}, \qquad (1)$$

$$\frac{d\theta}{d\tau} = \alpha e^{\theta} + q\alpha e^{k\theta} - \theta. \qquad (2)$$

Here α refers to the dimensionless concentration of CO_2 gas in the vapor phase and α_0 the saturation concentration of CO_2 in water at temperature T, beyond which no dissolution takes place. θ is the dimensionless temperature difference $(T - T_m)$ between T, the temperature of the ice melt at the surface where adsorption and dissolution take place, and T_m, the constant temperature of the solid ice at melting. τ is the scaled time, μ is the mass of ice containing CO_2, and μ_0 is its initial value. $k_1(T)$ and $k_2(T)$ are taken as $k_1(T_m)e^{\theta}$ and $k_2(T_m)e^{k\theta}$, respectively [2]. κ_1 and κ_2 are the dimensionless rate constants for reactions (ii) and (iii). k is the ratio of activation energies, E_1/E_2, and q is given by $\kappa_2 \Delta H_2 / \kappa_1 \Delta H_1$. The dimensionless form of k_0 is denoted as ε.

Microscopic mechanism of oscillations implied in Eqs. (1) and (2) is the following. Melting of CO_2 containing ice results in its release into the vapor phase, increasing its concentration. However, this increase leads to greater rates of depletion through readsorption on ice and dissolution of water. The nonlinear Arrhenius dependence of these rates on temperature autocatalyzes the depletion processes. The depletion rate eventually overtakes the rate of increase, leading to rapid reduction in the vapor concentration. As dissolution and adsorption rates increase, the temperature of the surface melt increases, again nonlinearly. But this increase in θ is countered by Newtonian cooling of the melt by the surrounding ice. The concurrent occurrence of these processes gives rise to oscillations in α and θ that continue until all ice melts.

The dimensionless set of equations [(1) and (2)] was solved using MATLAB V.5.3. Most of the experimental quantities such as activation energies, heats of reaction, and rate constants required to estimate *a priori* the parameters appearing in Eqs. (1) and (2) are unavailable at present. Hence, we have used the following optimal set of parameters: $\kappa_1 = 0.101$, $\kappa_2 = 0.14$, $\alpha_0 = 0.009$, $k = 0.1$, and $q = 0.01$. Damped oscillatory solutions exist for the following ranges of parameters: viz. $0.06 \leq \mu \leq 0.28$, $0.04 \leq \kappa_1 \leq 0.16$, $0.05 \leq \kappa_2 \leq 0.4$, and $0.001 \leq \alpha_0 \leq 0.5$. α_0, the saturation concentration of the solute in water, is found to be the most sensitive parameter affecting the amplitude of oscillations in α and θ.

The simulated time series is compared with the experiment in Fig. 3. The simulation reproduces the following key features of the experimental observations:

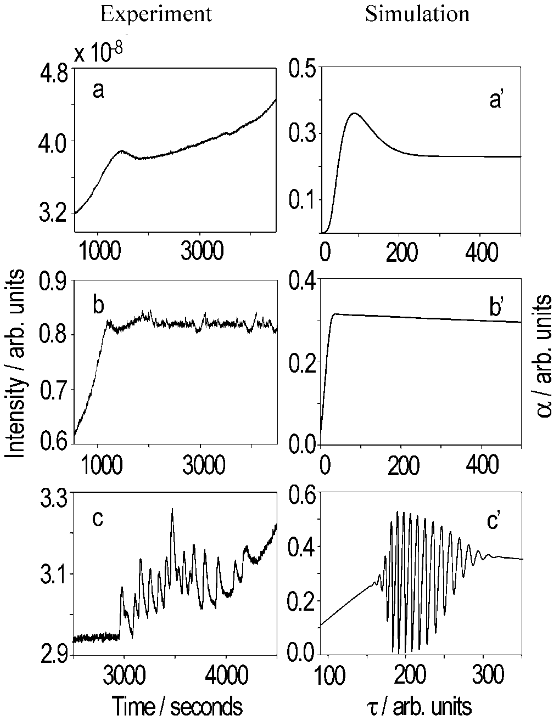

FIG. 3. Experimental time series of CO_2 for (a) 2.13×10^{-3} mol (no oscillations), (b) 2.66×10^{-4} mol (no oscillations), and (c) 1.33×10^{-3} mol. Simulated oscillations for (a′) $\mu_0 = 1.6$, $\varepsilon = 0.04$, (b′) $\mu_0 = 0.01$, $\varepsilon = 0.001$, and (c′) $\mu_0 = 0.8$, $\varepsilon = 0.01$.

1. No oscillations are observed at high ($> 2.13 \times 10^{-3}$ mol) and low ($< 2.66 \times 10^{-4}$ mol) initial quantities of deposited CO_2. The model reproduces this behavior, when we take into account the increase of k_0 and M_0 with increasing quantities of deposited CO_2 [Figs. 3(a) and 3(a′) and 3(b) and 3(b′)].

2. Oscillations in vapor pressure commence sometime after melting begins and continue until melting is complete [Figs. 3(c) and 3(c′)]. In Fig. 3(c) the steady increase in the concentration of CO_2 after the oscillatory phase is due to the continuous heating of the system after complete melting, which is not taken into account for modeling, and, hence, the simulated time series reaches a steady state, as is seen in Fig. 3(c′).

3. The model predicts oscillations in θ concurrent with the oscillations in the concentration of CO_2. The temperature increases gradually until the melting starts, where it oscillates about a relatively constant mean, and after complete melting it further increases. This has been experimentally verified by temperature measurements.

4. The experimental system is always associated with some thermal noise. In order to take this into account, we added a suitable Gaussian noise component to θ. In Fig. 4 we show the power spectra of experimental mass spectral data [Fig. 4(a)], α before addition of noise component to θ [Fig. 4(b)], and α with the noise component [Fig.4(c)]. Improved agreement between the experiment and simulation as seen by the occurrence of additional frequencies after addition of the noise component [Fig. 4(c)] further supports the validity of the present thermokinetic model.

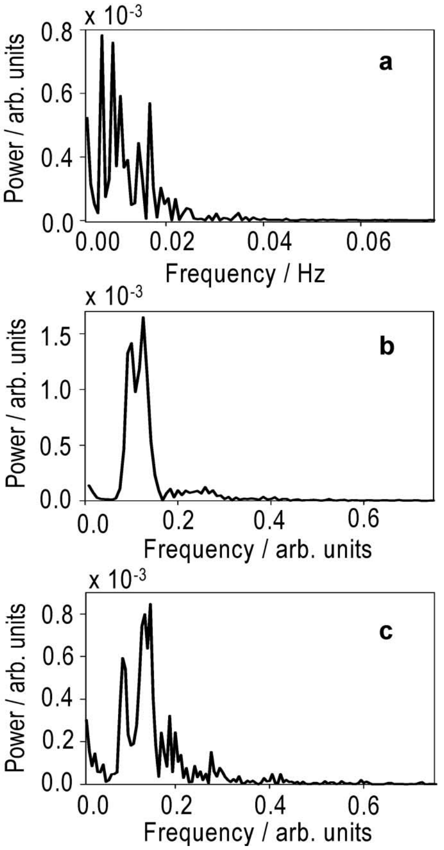

FIG. 4. Power spectra of (a) experimental data for 1.33×10^{-3} mol of deposited CO_2, (b) α without the noise component, and (c) α with addition of 0.5% Gaussian noise (with zero mean and unit variance) in each iterative solution step of θ, respectively.

We have carried out experiments with other solutes such as diethyl ether, acetone, carbon tetrachloride, and n-hexane. Oscillatory behavior similar to the CO_2 system is observed in all cases except in n-hexane, which is least soluble in water.

While oscillations are observed for several solute-ice systems, the implications may be more relevant for atmospheric gases such as CO_2. In this connection, it is interesting to note that oscillations in the atmospheric CO_2 concentration have been observed on geological time scales as well as annually [9]. However, our results may not be directly comparable to these phenomena in view of the different time scales, magnitude, and concentrations involved. Laboratory experiments show that such oscillations occur even for ice containing 3.5% NaCl, chosen to represent the concentration of seawater. It also occurs when nitrogen or air is present in the vapor phase.

Our findings are expected to be of general validity for the dynamics of the gas phase above a condensed system at the point of phase transition. It would be worthwhile to investigate this phenomenon in systems involving other gas phase species and condensed phases.

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