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RATE OF SOLVENT LOSS FROM SPHERICAL DROPLETS OF SOLUTIONS ILLUSTRATED WITH AQUEOUS MANGANESE(II) NITRATE

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ABSTRACT

The simple first order rate law applicable to the dehydration of aqueous solutions under conditions of constant surface area is modified to allow for the simultaneous change in surface area accompanying such a reaction. A spherical droplet is used as a model. Isothermal weight loss experiments were performed using aqueous solutions of mangane(II) nitrate to show the applicability of such a hybrid rate law.

INTRODUCTION

Previous work has shown that the rate of water evaporation from aqueous solutions of manganese(II) nitrate having a constant exposed surface area is proportional to the amount of water remaining, *i.e.*, follows the first order rate law[1]. If α is defined as the fraction reacted, then the rate law is expressed as

$$\frac{d\alpha}{dt} = k(1-\alpha) \tag{1}$$

or

$$kt = -\ln(1-\alpha) \tag{2}$$

This is reasonable for the surface controlled rate since the number of water molecules at the surface available for evaporation would be proportional to their relative population, and for the diffusional controlled rate, the rate is also first order. Such a rate law should hold for aqueous solutions in general, until the loss of water results in a marked change of structure, mechanism, or geometry such as would accompany the formation of a solid phase.

For manganese(II) nitrate solutions this was found to be near the composition $Mn(NO_3)\cdot 2H_2O$ at which point the material appears to set to a very hygroscopic glass-like material[1,2].

Implicit in the simple first order rate equation is the assumption of a constant area of the reacting surface. This is true in evaporation from most vessels which are open at one end and have essentially constant cross sectional area. This area is simply reflected in the value of the observed rate constant. However, when the evaporation of water from aqueous solutions of manganese(II) nitrate solution within the pores of or adhering to an inert substance was investigated it was found that geometrical considerations became important[3].

It is the purpose of this brief paper to consider the inter-relation of surface area with the first order rate equation. For simplicity and experimental convenience a spherical droplet will be assumed. If the first law is expressed so as not to include the reaction area (surface area in this case) in the rate constant, then it is

$$\frac{d\alpha}{dt} = k_1 S(1-\alpha) \tag{3}$$

In this work α will be determined from weight loss measurements and so α is expressed as

$$\alpha = \frac{w_0 - w}{w_0 - w_\infty} \tag{4}$$

and

$$w = w_0 - (w_0 - w_\infty)\alpha \tag{5}$$

Assuming a spherical shape and a density that is directly proportional to the concentration, then the volume, V, may be written as the sample weight over the density

$$V = \frac{4\pi}{3} r^3 = \frac{w_0 - (w_0 - w_\infty)\alpha}{d_0 + k_2\alpha} \tag{6}$$

where d_0 is the initial density of the solution at the appropriate reaction temperature and k_2 is the constant expressing the dependence of density upon concentration. Rearranging gives

$$r^2 = \left[\frac{3}{4\pi}\left(\frac{w_0 - (w_0 - w_\infty)\alpha}{d_0 + k_2\alpha}\right)\right]^{2/3} \tag{7}$$

which can be substituted for r^2 in the formula for the surface area of a sphere (S) to give

$$S = 4\pi\left[\frac{3}{4\pi}\left(\frac{w_0 - (w_0 - w_\infty)\alpha}{d_0 + k_2\alpha}\right)\right]^{2/3} \tag{8}$$

Substitution of this expression for S back into the first order rate law (Eqn. 3) yields

$$\frac{d\alpha}{dt} = k_1'(1-\alpha)\left(\frac{w_0 - (w_0 - w_\infty)\alpha}{d_0 + k_2\alpha}\right)^{2/3} \tag{9}$$

where k_1' is the new rate constant $\sqrt[3]{36\pi}\, k_1$.

This has the disadvantage that k_1' has the dimensions of $\sec^{-1}\text{cm}^{-2}$ and is dependent upon sample size. The units can be changed to the desired sec^{-1} and the sample size dependence removed by rearranging to

$$\frac{d\alpha}{(1-\alpha)\left(\frac{1-(1-k_3)\alpha}{1+k_4\alpha}\right)^{2/3}} = k''dt \tag{10}$$

where $k_3 = w_\infty/w_0$ and $k_4 = k_2/d_0$. The normalized observed rate constant is now k''_1 which equals $(36\pi w_0^2/d_0^2)^{1/3}\, k_1$ and has the desired dimensions. Since k_3, k_4, w_0, and d_0 are all determined prior to the numerical analysis there are no added degrees of freedom to the fit of the data.

Unfortunately the left hand portion of Eqn. 10 cannot be readily integrated analytically. Numerical integration is performed by a computer and the applicability of the equation is demonstrated with kinetic studies on the dehydration of manganese-(II) nitrate solutions.

EXPERIMENTAL PROCEDURES AND RESULTS

Materials

Aqueous manganese(II) nitrate manufactured by the Lehigh Valley Chemical Company (capacitor grade, density 1.65) was used. Results of emission spectrographic analysis of the oxide resulting from heating a portion of this solution to 250°C overnight indicated magnesium was present at the tenth of a weight percent level and calcium, copper, and iron were present in 10–100 p.p.m. amounts. Three different concentrations of this solution were employed in the study. Dilutions were made with triply distilled water. Densities of these solutions were 1.645, 1.528, 1.449 g/cm^3 at 25°C. The density of $Mn(NO_3)_2 \cdot 2H_2O$ was estimated by extrapolating a smooth curve through these three densities and that of 1.82 for $Mn(NO_3)_2 \cdot 4H_2O$ (Ref. 4). Crude estimates of the densities at the reaction temperature were obtained assuming the same temperature dependence as pure water. Fortunately the calculations are relatively insensitive to small changes in density, *e.g.*, the calculation of rate constants based on room temperature densities gave only 1–3% difference compared to these values determined with the corrected densities.

Isothermal weight change

A Perkin–Elmer thermobalance was modified to give weight and temperature as a function of time[5]. For these isothermal studies, only the weight portion was operated. The weight was averaged over predetermined constant intervals of time and automatically punched on paper tape. Time intervals ranged from 3–30 sec depending upon the rate of weight loss. The control temperature of each experiment was determined by measuring the voltage of the Perkin–Elmer UU-1 controller and comparing it with the calibration equation. This equation was based upon the use of magnetic standards as previously described[5]. The heating rate for the calibration experiment was 1.25°C/min. This temperature is only an approximation of the actual sample temperature because of the significant but undetermined self cooling effect of the endothermic vaporization.

A 0.05-mm platinum wire was bent to support a droplet of solution about 2 mm in diameter. The empty harness was carefully tared. A small droplet was delivered from a microburette and surface tension served to hold the droplet on the support wire. Dry oxygen flowed through the sample compartment at about 20 cm^3/min. An initial sample weight was obtained as quickly as possible and then the control temperature was raised at a rate of approximately 320°C/min to a temperature in the range of 110–155°C. The data acquisition unit was started as soon as the UU-1 controller reached the control point. Data was collected at this temperature until essentially constant weight was reached at which time data taking was stopped and the sample cooled to room temperature.

Computer analysis

The weight data on the tape was transferred to cards using a GE-635 computer. These data cards served as the input for three stages of computer processing. The first stage was to obtain a graphical output of the weight as a function time. Fig. 1 is an example of such an output for a sample run at 140°C.

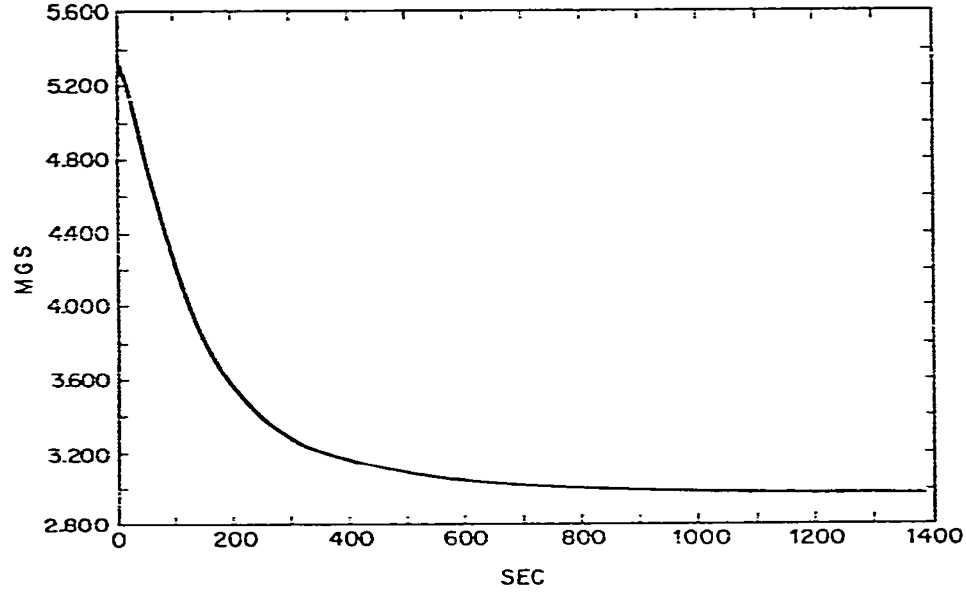

Fig. 1. Weight loss *vs.* time for aqeuous manganese(II) nitrate solution ($d^{25°} = 1.645$ g/cm^3) in oxygen at 140°C.

Plots of this type gave an overall view or check on the experiments and served also as the basis for the determination of the initial and final weights for each step.

The second stage of data handling consisted of utilizing the initial and final weights for each step to determine values of α. The computer having calculated the values of α for each point then plotted these to conform to the simple first order equation, the contracting spherical volume equation, and the hybrid equation. To use the hybrid equation, the numerical integration of Eqn. 10 was performed using Simpson's Rule and breaking the integral from 0 to α into 100 parts. This was shown to provide a value for the function correct to at least five places.

As examples, the family of lines resulting from the hybrid equation ($\alpha = 0.1$–0.9) using the solution of density 1.645 g/cm^3 is shown in Fig. 2.

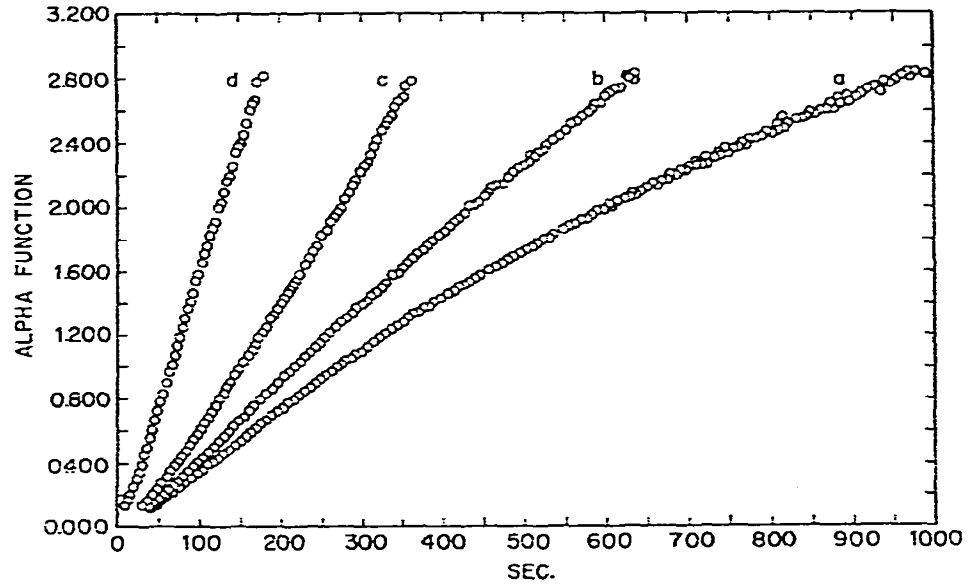

Fig. 2. $F(\alpha)$ vs. time using the hybrid equation for the thermal dehydration of aqueous manganese-(II) nitrate solution ($d^{25°} = 1.645$ g/cm^3) in oxygen at; (a) 111°C, (b) 125°C, (c) 140°C, and (d) 154°C.

The best equation was determined by the standard deviation in α arising from the computer fit of the data to a least squares straight line with the calculation of k from the slope in the third stage of processing. The calculation of the standard deviation in α was done by finding for each time point the α-value which corresponded to the ideal straight line value of the α-function and computing the standard deviation between these α-points and the experimental α-points. In the case of the hybrid equation it was necessary to determine these ideal α-values numerically using a Newton–Raphson iteration technique. After each iteration, the hybrid α-function corresponding to the new α-value was calculated using the numerical integration described above and this value of the function compared with the ideal value. The iteration was continued until this difference was less than 10^{-6}. This generally occurred in about 5 iterations and gave a standard deviation in α correct in at least 4 decimal places. The average standard deviation in α for the nine experiments were for the hybrid equation 0.022, the simple first order equation 0.028, and the contracting spherical volume equation 0.045.

TABLE I

ARRHENIUS PARAMETERS FOR THE THERMAL DEHYDRATION. DEHYDRATION IN OXYGEN OF AQUEOUS MANGANESE(II) NITRATE ($d^{25°} = 1.645$ g/cm^3)

Rate law	*A* (*sec*$^{-1}$)	$\Delta H^{\ddagger}$ (*kcal/mole*)
$kt = -\ln(1-\alpha)$	2.70×10^4	13.7
$kt = 1-(1-\alpha)^{1/3}$	1.63×10^5	13.9
Hybrid[a]	1.83×10^5	13.8

[a] See text.

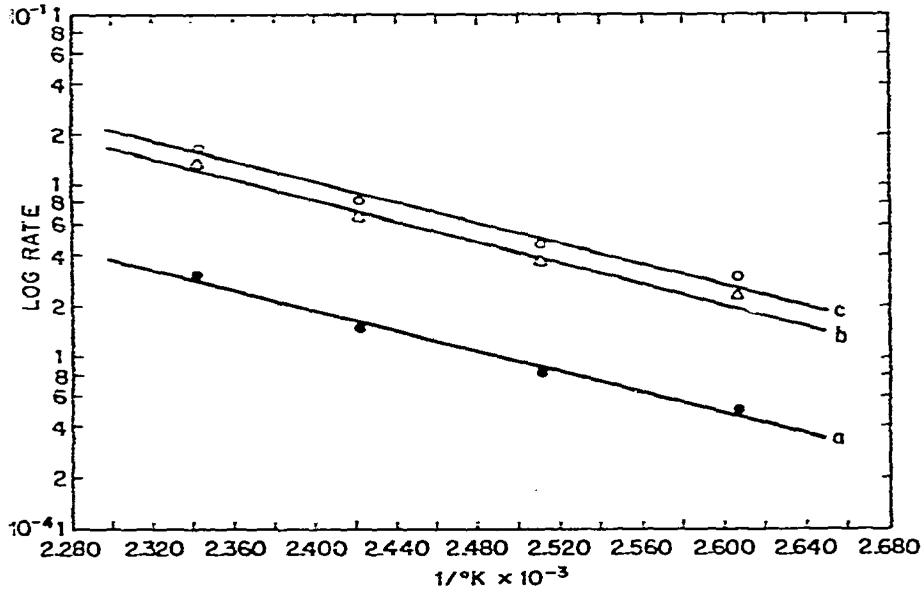

Fig. 3. Arrhenius plot for the thermal dehydration of aqueous manganese(II) nitrate solution ($d^{25°} = 1.645$ g/cm^3) in oxygen; (a) contracting volume equation, (b) simple first order equation, (c) hybrid equation.

A final program was devised to plot the values of log *k versus* the reciprocal of the absolute temperatures (Arrhenius plot) and a least squares fit was made to determine the best straight line. The resulting activation energies and pre-exponential terms were printed along with the plot. The values are listed in Table I for the solution having a density of 1.645. These values are only approximations due to the uncertain extent of the self cooling. Fig. 3 shows the family of Arrhenius plots for the decomposition series for this same solution using all three kinetic equations.

The data can frequently be fit moderately well by several equations. In all cases the apparent activation energies show very little variation with choice of rate equation. The differences are reflected in the pre-exponential term and the activation energy is virtually independent of the equation in accordance with the results of previous work[1,3].

DISCUSSION

The simple first order equation gives a decidedly better fit to the experimental data than does the contracting volume equation. This implies that the concentration dependence of the evaporation rate is greater than the geometrical dependence under this set of experimental conditions. The hybrid equation, however, represents a significant improvement over the uncorrected first order rate law.

The determination of an activation energy, is not particularly dependent upon a critical choice between various equations which nominally fit the data. The activation energy, 13.8 kcal/mole, determined from the spherical drop is not significantly different from that measured previously[1,3].

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