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Note

A CURVE FIT MODEL FOR OBTAINING KINETIC DATA FROM NONISOTHERMAL TG

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A large number of kinetic expressions have been employed in treating nonisothermal kinetic data [1—6]. However, it has been shown that correlation coefficients are not a reliable way to distinguish a particular mechanism from others [6]. Recently, we have shown that for the decomposition of $(NH_4)_2CO_3$ and NH_4HCO_3 several different assumed reaction orders did not give very different results when used with the Coats and Redfern equation [7]. As a continuation of our application of kinetic models, we have used a semilogarithmic curve fit (SLCF) model to relate α and T, where α is the

$$\alpha = a\, e^{b/T} \tag{1}$$

fraction of reaction completed, T is temperature (K), and a and b are empirical constants. This model takes no regard of order and is not based on a derivation which assumes a particular mechanism. It is, however, most directly comparable to a zero order treatment. The model has been applied to the decomposition of $(NH_4)_2CO_3$ and NH_4HCO_3 and this report presents the results of that work.

EXPERIMENTAL

Reagent grade ammonium carbonate and ammonium bicarbonate were used without further treatment. Thermogravimetric analyses were carried out using a Perkin-Elmer thermogravimetric system Model TGS-2. Procedures employed have been previously described [8]. Curve fitting was carried out using a Texas Instrument TI-59 programmable calculator, and a linear regression analysis was used to compute the equation parameters. The data for α and T were fit to the equation

$$\alpha = a\, e^{b/T} \tag{1}$$

and, for comparison, to the Coats and Redfern equation [9]

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = \ln\left[\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)\right] - \frac{E}{RT} \tag{2}$$

where α is the fraction reacted, β is the heating rate, T is temperature (K), A is the frequency factor, n is the reaction order, E is the activation energy, and R is the molar gas constant.

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RESULTS AND DISCUSSION

The usual relationship for $d\alpha/dT$ is given as [9]

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{-E/RT}(1-\alpha)^n \tag{3}$$

where A is the frequency factor, β is the heating rate, and the other symbols have their usual meaning. If A is expressed in min^{-1} and β is in deg min^{-1}, then each side of eqn. (3) has the units of deg^{-1}. One approximate solution of eqn. (3) results in the Coats and Redfern equation.

Fitting the equation

$$\alpha = a\, e^{b/T}$$

to the kinetic data is, of course equivalent to

$$\ln \alpha = \ln a + \frac{b}{T}$$

where b will be a negative quantity related to E/R.

Differentiation of eqn. (1) with respect to T gives

$$\frac{d\alpha}{dT} = -\frac{ab}{T^2} e^{b/T} \tag{4}$$

The negative sign will be removed in practice owing to the fact that b is negative. Dimensionally, $d\alpha/dT$ has the units of deg^{-1}. Now a is a unitless constant although its value does depend on the units used to express the other quantities. In order for the equation to have the correct units in the exponential, b must have units of deg. But since the constant b also contains the activation energy, it must, therefore, be related to E/R (its units must be kJ $mole^{-1}$/kJ $mole^{-1}$ deg^{-1}). Thus, both sides of eqn. (4) reduce to deg^{-1} as does the "correct" eqn. (3).

The frequency factor, A, is obtained from this SLCF model by equating A/β to $-ab/T^2$, where a and b are determined from the regression analysis. The value used for T in this case is the temperature at which $\alpha = 0.5$. These temperatures are 373 K and 410 K for $(NH_4)_2CO_3$ and NH_4HCO_3, respectively. Thus, the kinetic parameters A and E can be estimated from a form of the differential equation [eqn. (3)] without going through an approximate integrated form. Thus the SLCF model should provide results that approximate those from the Coats and Redfern equation.

Because there is total mass loss, the decomposition of ammonium carbonate and ammonium bicarbonate serves as a convenient model for testing kinetic expressions for nonisothermal studies [7]. These reactions were studied in the range $0.04 \leqslant \alpha \leqslant 0.80$ using the SLCF model described here and the Coats and Redfern equation. For comparison, zero and first order equations were used here, although it has been shown that the first order provides the best fit in these reactions [7]. Tables 1 and 2 show the results of a comparison of the SLCF model and those obtained from the Coats and Redfern equation.

Since the first derivative of the SLCF model is equivalent to using the differential form of a "correct" relationship as shown in eqn. (3) when n =

TABLE 1

Comparison of decomposition parameters for decomposition of $(NH_4)_2CO_3$

Sample	Coats and Redfern equation						SLCF model				
	E (kJ mole^{-1})		$\ln(A/\beta)$		Corr. coeff.		$-$ Slope (b)	$\ln a$	E (kJ mole^{-1})	$-ab/T^2$	Corr. coeff.
	$n=1$	$n=0$	$n=1$	$n=0$	$n=1$	$n=0$					
1	77.94	66.81	22.165	18.245	0.9999	0.9973	8749.24	22.677	72.74	4.35×10^9	0.9979
2	80.50	72.36	22.701	19.822	0.9983	0.9937	9418.39	24.269	78.30	2.35×10^9	0.9948
3	89.42	76.76	25.918	21.513	0.9999	0.9923	9947.64	25.959	82.70	1.34×10^{10}	0.9935
4	89.03	79.63	25.575	22.260	0.9924	0.9844	9326.17	24.579	77.53	3.17×10^9	0.9887
5	91.50	71.60	27.147	20.133	0.9995	0.9865	10 293.65	26.708	85.58	2.94×10^{10}	0.9866
$\bar{X}$	85.68	73.43	24.701	20.395	0.9980	0.9908	9547.02	24.838	79.37	1.05×10^{10}	0.9923
σ	6.04	4.94	2.160	1.560	0.0032	0.0053	595.76	1.566	4.95		0.0046

TABLE 2

Comparison of decomposition parameters for decomposition of NH_4HCO_3

Sample	Coats and Redfern equation						SLCF model				
	E (kJ mole^{-1})		$\ln(A/\beta)$		Corr. coeff.		$-$ Slope (b)	$\ln a$	E (kJ mole^{-1})	$-ab/T^2$	Corr. coeff.
	$n=1$	$n=0$	$n=1$	$n=0$	$n=1$	$n=0$					
1	95.78	80.03	24.899	19.919	0.9992	0.9939	10 403.70	24.534	86.49	2.80×10^9	0.9949
2	80.07	67.07	20.340	16.169	0.9972	0.9906	8846.05	20.787	73.54	5.60×10^7	0.9924
3	92.65	78.63	25.112	20.525	0.9997	0.9951	10 216.62	25.091	84.93	4.79×10^9	0.9959
4	76.70	65.82	19.189	15.692	0.9999	0.9960	8704.47	20.330	72.37	3.49×10^7	0.9968
5	81.33	71.25	20.474	17.250	0.9992	0.9924	9368.47	21.899	77.89	1.81×10^8	0.9939
6	90.59	69.99	23.970	17.738	0.9975	0.9887	8741.97	20.825	72.68	5.76×10^7	0.9876
$\bar{X}$	86.19	72.13	22.331	17.779	0.9988	0.9928	9380.21	22.244	77.98	1.32×10^9	0.9936
σ	7.80	5.92	2.619	4.216	0.0011	0.0028	761.12	2.064	6.32		0.0033

0, it would be expected to yield comparable results to those from other approximate treatments. It is interesting that for both $(NH_4)_2CO_3$ and NH_4HCO_3 the "activation energies" obtained from the SLCF model are only slightly different from those obtained from the "correct" Coats and Redfern equation, with the results being intermediate between the zero and first order results. The correlation coefficients are similar to those obtained using the Coats and Redfern equation and in most cases were above 0.99. Similarly, the "frequency factor" is within an order of magnitude of the "correct" one. It appears that the approximations in solving eqn. (3) do not result in a much better equation than the SLCF model which does not solve the equation at all. In fact, the results obtained from the SLCF model are comparable to those obtained from the Coats and Redfern equation when n has a value of about 1/2.

While there may be little theoretical justification for the approach taken here, there is also little theoretical justification for comparing several models based on entirely different mechanisms and assuming that the one giving the highest correlation coefficient is the correct one. Correlation coefficients have been shown not to be a sufficient criterion for distinguishing between such models [6]. The SLCF model gives sufficiently good agreement with the "correct" parameters that it is perhaps equally valid when the correct order is not known or there is no interest in determining which of several models provides a better correlation coefficient.

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