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Application of transpiration theory to TGA data: calcium carbonate and zinc chloride

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Abstract

Thermogravimetric analysis (TGA) data for vaporization of $CO_2(g)$ from $CaCO_3(s)$ and vaporization of $ZnCl_2(l)$ are analyzed using theory from the transpiration method. Transpiration theory uses coupled diffusive and hydrodynamic flow. Temperature dependence of the TGA data yields reliable values for $\Delta_{vap}H^{\circ}$. Analyses of the TGA data show that the viscosity coefficient has no significant effect. Fitting of experimental data at different flow rates of carrier gas yields the diffusion coefficient parameter and an experimental vaporization coefficient α_{vap}. The experimental vaporization coefficient has contributions from a true vaporization coefficient and from desaturation associated with the apparatus design.

Keywords: Calcium carbonate; TGA; Transpiration; Zinc chloride

1. Introduction

Data from a thermogravimetric analysis (TGA) experiment originate from the mass loss of a sample suspended from a vacuum balance during a programmed heating while a carrier gas is flowing around the sample. The heated sample undergoes a vaporization reaction producing gaseous species. Sample mass is lost by two mechanisms: (1) diffusion of gaseous species away from the sample, and (2) transport of gaseous species in the carrier gas. The pressures in the apparatus are

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near atmospheric pressure and are such that the transport of gaseous species under (2) is by gaseous viscous flow.

Coupled flow by viscous transport and diffusion occurs in multiple experiments. We have analyzed the coupled flow in the Ruff experiment [1] and in the transpiration experiment [2]. This analysis was extended to the TGA experiment [3]. Experimental data should be capable of being analyzed by the given equations [3].

The final equation of Ref. [3] which is applicable to the TGA experiment is Eq. (12a), i.e.

$$P(\text{calc}) = P_{2i}/\{1-\exp[-\dot{n}_1/A]\}\{1+[\dot{n}_1/CP_\text{F}^2]\}^{1/2} \tag{1}$$

where subscript 1 refers to the carrier gas and subscript 2 refers to the sample, $\dot{n}_1$ is the molar flow rate (or the volume flow rate, a simple proportionality relates these flow rates) of the carrier gas, P_F is the total pressure inside the furnace zone of the TGA apparatus, P_{2i} is the vapor pressure of the sample at the site of the sample. The usually calculated vapor pressure is indicated by $P(\text{calc})$

$$P(\text{calc}) = P_\text{F}[\dot{n}_2/(\dot{n}_1+\dot{n}_2)] \tag{2}$$

Thus, $P(\text{calc})$ is calculated assuming Dalton's law regarding the ratio of the vapor pressure of the sample to the total pressure in the apparatus, and this is a first order calculation of the vapor pressure. It is possible to easily calculate $P(\text{calc})$ from laboratory measurements of the molar flow rate of carrier gas and the molar flow rate of sample. The values of the other terms are

$$A = \pi r^2 D'/RTl \tag{3}$$

$$C = \pi r^4/16RTl\eta \tag{4}$$

where r and l are the radius and length of the furnace tube from the sample to the end of the furnace, R is the universal gas constant, T is absolute temperature, D' is the product of the gaseous interdiffusion coefficient D_{12} and the total pressure, and η is the gaseous viscosity. Equations for D_{12} and η are given by the kinetic theory of gases; see Ref. [4]. As noted in Eq. (3), A depends upon the gaseous interdiffusion coefficient which is dependent on both the carrier gas and the sample gas. The gaseous viscosity η in Eq. (4) should be that for the carrier gas because C depends on the flow of the nearly pure carrier gas because the vapor pressure of the sample is small.

The importance of the C parameter of Eq. (4) will now be discussed. Experimental data for the gaseous viscosity of several gases are given by Hirschfelder et al. [4]. Nitrogen is frequently used in experiments, and it was used in experiments reported in this paper. For an apparatus similar to the DuPont TGA, the radius of the furnace tube is 10 mm with an actual half-length of 5.5 cm (the constant temperature zone is certainly shorter, estimated to be about 3.0 cm). For nitrogen at 1000 K, η is $4.011 \times 10^{-4}\,\text{kg m}^{-1}\,\text{s}^{-1}$. The calculated C value is 2.689×10^7 $\text{cm}^3\,\text{s}^{-1}\,\text{atm}^{-2}$. With a C value this large, with P_F being 1 atm, and with $\dot{n}_1$ being less than $10\,\text{cm}^3\,\text{s}^{-1}$, the following term becomes

$$\{1+[\dot{n}_1/CP_\text{F}^2]\} = 1 \tag{5}$$

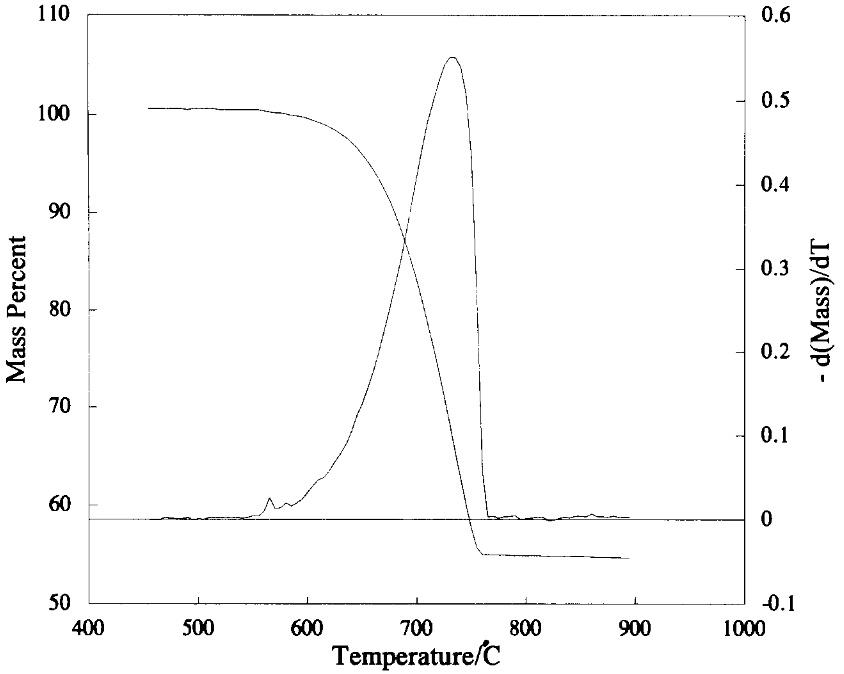

Fig. 1. Typical experimental TGA data showing mass of the sample and $-\mathrm{d}m/\mathrm{d}t$ vs. temperature of the sample. Data were acquired while the temperature of the sample was increased at a constant rate $\mathrm{d}T/\mathrm{d}t$. The data are from run 42 with $CaCO_3$.

Thus, the gaseous viscosity does not make a significant contribution to the results, and Eq. (1) can be rewritten as

$$P(\mathrm{calc}) = P_{2i}/\{1 - \exp[-\dot{n}_1/A]\} \tag{6}$$

For vaporization reactions, the vapor pressure of the sample in the apparatus, P_{2i}, depends upon the temperature of the sample as given by van't Hoff equation and upon the vaporization coefficient α_{vap} of the condensed phase. The introduction of vaporization coefficients and their relationship to equilibrium vapor pressures have been discussed by Paule and Margrave [5]. The van't Hoff equation gives the equilibrium vapor pressure P_{eq}

$$P_{\mathrm{eq}} = \exp[-\Delta_{\mathrm{vap}}H^{\ominus}/RT]\exp[\Delta_{\mathrm{vap}}S^{\ominus}/R] \tag{7}$$

The vaporization coefficient represents the fraction of the equilibrium vapor pressure which is the actual pressure in the apparatus

$$P_{2i} = P_{\mathrm{eq}}\alpha_{\mathrm{vap}} \tag{8}$$

A small vaporization coefficient may result from an inhibited vaporization caused by structural aspects of the crystal and vapor species or may be caused by undersaturation of the space around the sample. Replacing P_{2i} in Eq. (6) with Eqs. (7) and (8) gives

$$P(\text{calc}) = \alpha_{\text{vap}} \exp[-\Delta_{\text{vap}}H^{\ominus}/RT] \exp[\Delta_{\text{vap}}S^{\ominus}/R]/\{1 - \exp[-\dot{n}_1/A]\} \tag{9}$$

Equation (9) shows the dependence of P(calc) on the substance being studied, α_{vap}, $\Delta_{\text{vap}}H^{\ominus}$, $\Delta_{\text{vap}}S^{\ominus}$, on the flow rate of carrier gas $\dot{n}_1$, on the total pressure in the apparatus P_{F}, and on the A parameter.

A parameter which we have computed (the calculation will be discussed later) from experimental data is

$$\alpha = P(\text{calc})/P_{\text{eq}} \tag{10}$$

An equation for α is given by Eqs. (7) and (9)

$$\alpha = \alpha_{\text{vap}}/\{1 + \exp(-\dot{n}_1/A)\} \tag{11}$$

which shows the fraction of the equilibrium vapor pressure which is present in the sample chamber region.

In the TGA experiment, the sample temperature is ramped (the usual case is for a constant $\mathrm{d}T/\mathrm{d}t$ ramp, where t is time). The mass of the sample versus sample temperature and the derivative of the above data are plotted. The typical experimental curve is shown in Fig. 1. Note that the derivative of the data, $-\mathrm{d}m/\mathrm{d}t$, increases as the sample temperature increases because of the temperature dependence of the vapor pressure which is shown by the van't Hoff equation (Eq. (7)). Note that there is a peak in the derivative curve (at higher temperature the mass loss is zero or small) indicating that the sample has been exhausted or that mass loss by a particular vaporization reaction has ended.

Wahlbeck [3] pointed out that for an experiment with constant flow rate of carrier gas (constant $\dot{n}_1$), plots of $\ln P$(calc), or $\ln(-\mathrm{d}m/\mathrm{d}t)$ versus $1/T$ will yield slopes which are $\Delta_{\text{vap}}H^{\ominus}/R$ based on Eq. (9). In order to calculate P(calc) from $-\mathrm{d}m/\mathrm{d}t$ data

$$\dot{n}_2 = -(1/M)\, \mathrm{d}m/\mathrm{d}t \tag{12}$$

where M is the molar mass of the vapor species.

A series of experiments may be performed with different carrier gas flow rates and different initial sample masses.

Values of α have been calculated from the peak in the derivative data of Fig. 1 by using an iterative calculation or a successive approximation calculation. The mass of the original sample, the carrier gas flow rate, and the heating rate are entered. The iterative calculations are begun at a low temperature, the temperature of the sample is increased in the calculations, the mass loss rate of the sample is calculated, and the remaining mass of the sample is calculated. When the calculations indicate that the sample is exhausted, the temperature should correspond with the peak in the derivative data of Fig. 1. If the calculated peak temperature is lower than the actual peak temperature, the value of α is decreased until the calculated and observed peak temperatures agree.

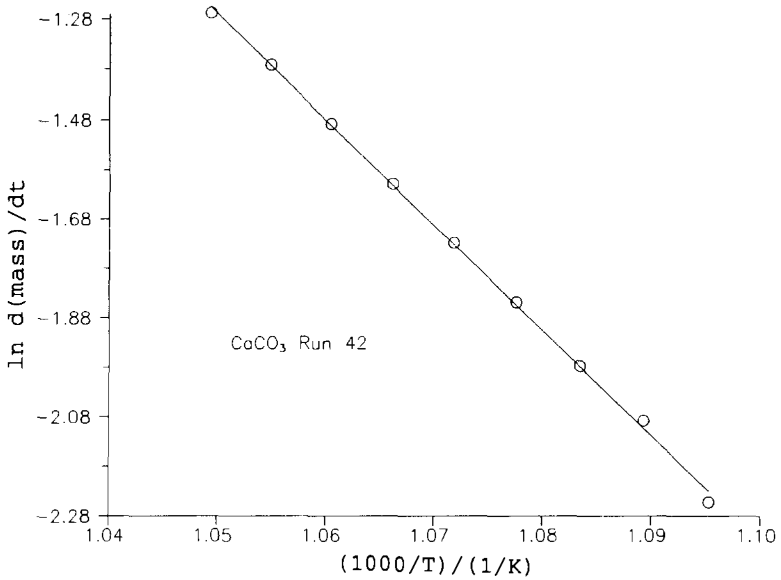

Fig. 2. $CaCO_3$ data for ln(−dm/dt) vs. $1/T$. The slope of the straight line is $\Delta_{\mathrm{vap}}H^{\ominus}/R$. Data are from run 42; heating rate was 15 deg min^{-1}.

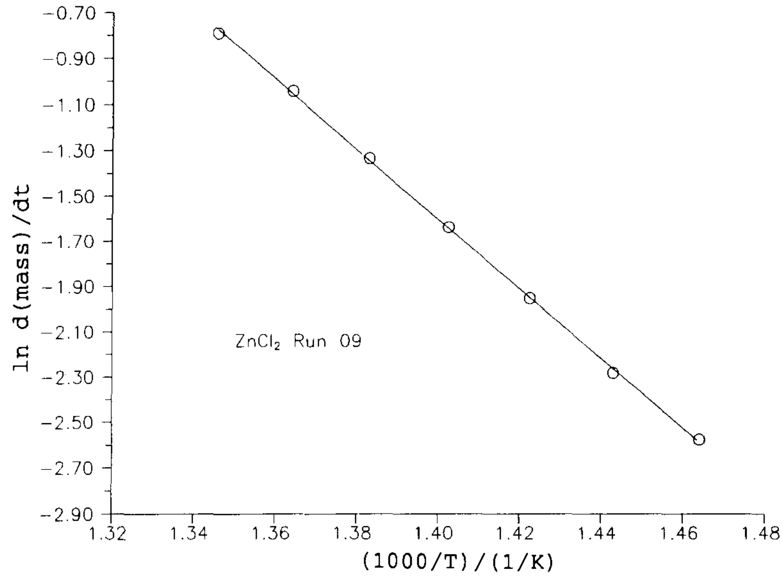

Fig. 3. $ZnCl_3$ data for ln(−dm/dt) vs. $1/T$. The slope of the straight line is $\Delta_{\mathrm{vap}}H^{\ominus}/R$. Data are from run 9; heating rate was 10 deg min^{-1}.

The parameter α is related by Eq. (11) to α_{vap}, $\dot{n}_1$, and A. A direct comparison between experimental α with a given $\dot{n}_1$ as determined by the successive approximation calculation to Eq. (11) will yield values of α_{vap} and A.

Table 1
Experimental data for $CaCO_3$

Expt.	Mass/mg	Flow rate/ (cm^3 s^{-1})	Peak temp./°C	$\Delta_{vap}H^{\ominus}$/ (kJ mol^{-1}) [a]	α [b]
Heating rate = 10 K min^{-1}					
1	1.315	1.7268	693.27	181.779	0.0122
2	3.175	0.5600	713.70	176.428	0.0563
3	2.226	0.7539	719.71	173.043	0.0254
7	1.465	1.2248	692.07	177.722	0.0197
8	4.122	1.2135	730.50	178.635	0.0226
9	5.446	0.1580	759.37	169.776	0.121
13	4.821	0.1893	737.74	176.953	0.144
14	3.247	1.5229	718.51	175.973	0.0187
15	3.132	3.5652	711.30	175.976	0.00912
16	3.650	0.1238	719.71	173.921	0.254
17	4.045	1.7014	701.68	177.623	0.0315
18	1.164	1.7314	692.07	176.526	0.0111
19	5.352	0.0367	738.94	178.117	0.811
Heating rate = 15 K min^{-1}					
28	3.065	4.1728	741.03	171.226	0.00569
29	3.423	2.9629	726.88	172.856	0.0126
30	1.709	2.5316	733.75	181.499	0.00628
31	6.037	3.2134	744.73	186.784	0.0136
32	2.260	3.3467	731.51	176.132	0.00657
33	8.089	2.4331	745.93	173.209	0.0236
34	9.216	2.1259	750.98	174.229	0.0275
35	3.217	4.9505	728.99	185.244	0.00677
36	4.813	3.8109	728.29	176.947	0.0132
37	4.501	1.8142	731.15	173.621	0.0242
38	3.375	3.1813	722.23	176.772	0.0127
39	7.467	8.0000	729.85	173.851	0.00951
40	5.158	1.6268	743.87	166.556	0.0235
41	5.337	1.1989	729.62	177.442	0.0456
42	4.382	0.2189	732.17	176.191	0.191
43	5.558	0.1169	746.14	174.296	0.331
44	4.548	0.6098	723.03	178.551	0.0877
Heating rate = 5 K min^{-1}					
50	3.114	0.2928	674.20	182.437	0.138
51	4.431	2.3063	684.82	177.767	0.0194
52	2.063	1.3196	660.30	172.985	0.0294
53	2.607	0.3247	676.22	183.949	0.0995
56	3.303	0.8427	697.35	175.676	0.0286
57	1.634	0.5994	657.21	177.143	0.0199
Heating rate = 2 K min^{-1}					
71	3.147	0.1461	656.68	174.347	0.181
72	9.381	1.3369	656.40	174.537	0.0588
73	2.409	2.0048	649.06	175.318	0.0121
76	3.175	2.5189	642.77	176.511	0.0154
78	3.546	1.8619	628.68	175.727	0.0346

Table 1 continued

Expt.	Mass/mg	Flow rate/ ($cm^3\ s^{-1}$)	Peak temp./°C	$\Delta_{vap}H^{\ominus}$/ ($kJ\ mol^{-1}$) [a]	α [b]
79	3.685	2.6548	619.66	174.076	0.0328
80	4.532	0.1638	670.98	181.606	0.161

[a] The values of $\Delta_{vap}H^{\ominus}$ in this column were calculated using the temperature dependence of $-dm/dt$.
[b] The values of α were calculated using the average $\Delta_{vap}H^{\ominus}$ from the experiments, $\Delta_{vap}S^{\ominus}$ from the literature, the initial sample mass, the carrier gas flow rate, and the peak temperature from the rate of mass loss. An iterative procedure described in this paper was used.

The purpose of the research reported in this paper is to test through experimental measurements the equations which have been developed. The chemical substances studied in this paper are $CaCO_3$ and $ZnCl_2$. The vaporization reactions for these substances are

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g) \tag{13}$$

$$ZnCl_2(l) \rightarrow ZnCl_2(g) \tag{14}$$

These chemical systems have provided some interesting insights into the TGA experiment.

2. Experimental part

2.1. Chemicals

Experiments were performed with the following chemicals obtained from the indicated sources: $CaCO_3$, Johnson-Matthey, analyzed sample better than 99.99% pure; $ZnCl_2$, Fisher, certified ACS reagent grade. Both chemicals were dried by initially heating to 100°C. The carrier gas for the TGA experiments was standard grade nitrogen obtained from Brown Welding Supply, Wichita, KS.

2.2. Apparatus

The TGA apparatus was manufactured by DuPont (now TA Instruments, Inc.) as model 951. The computerized data acquisition program was DuPont TA-2000 with the DuPont interface.

2.3. Procedure

The procedure for the experiments was as follows. The sample was placed on a platinum sample pan directly attached to the vacuum electrobalance. The initial mass of the sample (usually a few milligrams) was determined by the computerized data acquisition program. The heating ramp data dT/dt was constant during an experiment and was selected by the experimenter. The flow rate of the carrier gas

Table 2
Experimental data for $ZnCl_2$

Expt.	Mass/mg	Flow rate/ $(cm^3\ s^{-1})$	Peak temp./°C	$\Delta_{vap}H^{\ominus}$/ $(kJ\ mol^{-1})$ [a]	α [b]
Heating rate = 10 K min^{-1}					
1	24.10	4.807	538.46	120.539	0.0635
2	7.939	3.406	508.17	128.541	0.0654
3	9.837	0.270	512.50	128.521	0.918
4	8.235	1.224	499.52	124.694	0.999
5	5.132	0.494	520.29	127.069	0.211
6	3.102	1.786	518.86	125.300	0.0371
7	7.760	1.344	541.34	128.269	0.0677
8	6.646	0.266	524.16	120.480	0.456
9	5.917	0.988	523.25	127.411	0.112
10	7.975	0.681	529.99	126.666	0.187
11	3.311	0.481	505.61	128.113	0.211
12	3.553	4.513	521.69	127.629	0.0155
13	5.540	1.309	510.91	128.933	0.112
14	4.201	1.057	515.39	129.159	0.0921
15	10.52	0.867	542.80	130.518	0.138
16	4.196	2.323	526.43	130.093	0.0312
17	5.537	1.283	513.09	130.121	0.105
18	3.665	0.711	484.98	127.991	0.286
19	7.498	1.540	530.71	134.740	0.0758
20	3.071	2.290	498.24	126.401	0.0497
21	4.817	1.700	509.29	129.284	0.0774
Heating rate = 5 K min^{-1}					
30	2.658	0.833	457.48	123.081	0.201
31	8.542	1.540	489.79	129.837	0.133
32	4.400	0.583	529.20	122.391	0.0603
33	2.683	2.530	478.17	122.223	0.0351
34	1.843	0.377	456.35	128.149	0.317
36	7.704	0.283	480.25	128.042	0.851
37	3.881	0.989	471.41	127.472	0.161
38	5.647	1.224	475.65	129.381	0.167
39	2.684	0.564	440.34	131.316	0.517
40	5.203	0.946	462.74	131.621	0.405
44	4.773	1.353	461.87	127.007	0.195
45	17.45	0.952	493.39	122.023	0.392
46	2.550	2.256	455.86	126.077	0.199
49	4.816	0.977	461.51	121.642	0.273
Heating rate = 15 K min^{-1}					
61	6.301	1.770	517.69	122.390	0.117
63	5.506	0.687	477.86	128.741	0.821
66	5.261	1.143	577.90	124.326	0.0336
67	8.081	0.794	560.57	131.082	0.0878
68	5.439	1.295	568.06	128.741	0.0379
69	5.601	0.513	574.20	133.400	0.0856
70	8.928	1.482	579.76	122.697	0.0421
71	3.148	2.146	674.65	131.262	0.00137
72	5.472	0.236	563.31	131.723	0.236

Table 2 continued

Expt.	Mass/mg	Flow rate/ ($cm^3\ s^{-1}$)	Peak temp./°C	$\Delta_{vap}H^{\ominus}$/ ($kJ\ mol^{-1}$) [a]	α [b]
73	10.50	0.264	589.57	125.207	0.221
75	4.620	1.453	572.53	131.274	0.0261
76	8.823	0.658	580.68	130.032	0.0914
77	4.607	0.336	567.65	128.338	0.127

[a, b] See footnotes to Table 1.

was manually adjusted; the flow rate was measured by using a bubble buret at the conclusion of the experiment. The computer data acquisition program was run.

The data from the computerized data acquisition were mass, time, and temperature. The calculation of the rate of sample mass loss $-dm/dt$ was performed by the TA-2000 computer program; these data permitted the calculation of $\dot{n}_2$, dn_2/dt by Eq. (12). The computer output data from the experiments could be plotted or printed.

3. Results

Data for $CaCO_3$ and $ZnCl_2$ are given in Tables 1 and 2, respectively. These data are for experimental runs performed in which meaningful results were obtained. The chemical reactions being studied are given by Eqs. (13) and (14).

3.1. Temperature dependence

The temperature dependence of P(calc) is given by Eq. (9). This equation may be directly used in a single TGA experiment in which the flow rate of the carrier gas $\dot{n}_1$, the heat ramp rate, and the furnace pressure P_F, are constants. Thus, Eq. (9) for this case could be written as

$$P(\text{calc}) = \exp[-\Delta_{vap}H^{\ominus}/RT]\kappa \qquad (15)$$

where κ is a constant. As indicated following Eq. (9), if Eq. (15) is valid, a plot of $\ln(-dm/dt)$ versus $1/T$ should give a straight line with a slope of $\Delta_{vap}H^{\ominus}/R$. Such straight line plots are shown for $CaCO_3$ as Fig. 2 and for $ZnCl_2$ as Fig. 3. The $\Delta_{vap}H^{\ominus}$ values for each run are reported in Tables 1 and 2. The averaged $\Delta_{vap}H^{\ominus}$ values are $176.51 \pm 3.86\ kJ\ mol^{-1}$ at an average peak temperature of 707°C (980 K) for $CaCO_3$ and $127.36 \pm 3.81\ kJ\ mol^{-1}$ at an average peak temperature of 519°C (792 K) for $ZnCl_2$.

3.2. α Calculations

Values for α were computed using the iterative method. The iterative method of calculation described earlier in this part was used for those calculations. Input data

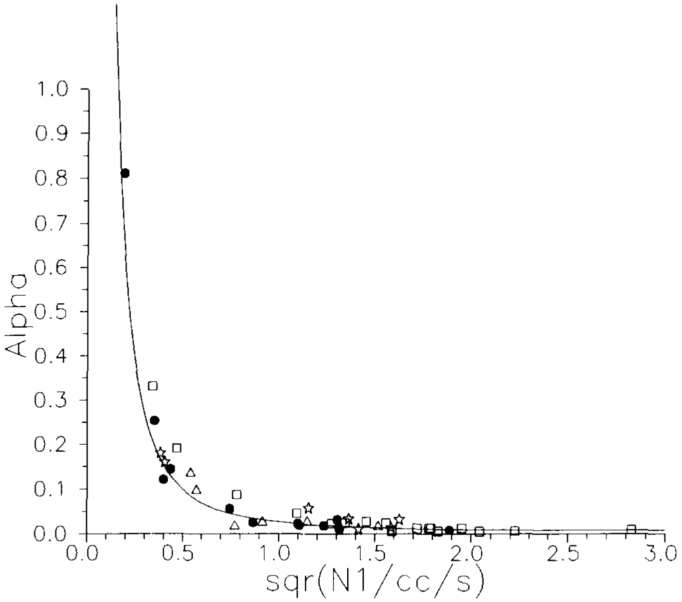

Fig. 4. Plot of α vs. the square root of the flow rate of carrier gas (nitrogen) for experiments where the sample was $CaCO_3(s)$ evaporating according to Eq. (13). The line is the line fitted to the experimental data (heating rate: ☆, 2°C min^{-1}; △, 5°C min^{-1}; ●, 10°C min^{-1}; □, 15°C min^{-1}) ($A = 3.8652$; $\alpha_{vap} = 0.00616$).

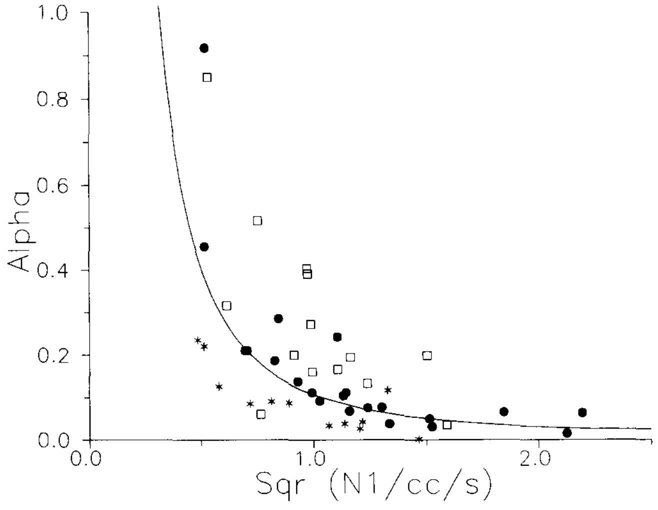

Fig. 5. Plot of α vs. the square root of the flow rate of carrier gas (nitrogen) for experiments where the sample was $ZnCl_2(l)$ evaporating according to Eq. (14). Heating rate: □, 5°C min^{-1}; ●, 10°C min^{-1}; ☆, 15°C min^{-1}. The dashed line is the line fitted to the experimental data with a heating rate of 10 deg min^{-1} ($A = 7.556$; $\alpha_{vap} = 0.00951$).

Table 3
Fitted values for A and α_{vap}

Substance	A (fitted)/ $(cm^3\ s^{-1})$ [a]	α_{vap} [a]
$CaCO_3$	3.865	0.00616
$ZnCl_2$	7.556	0.00951

[a] A non-linear least squares program was used for the fitting of the experimental data for α using Eq. (11). All $CaCO_3$ data and $ZnCl_2$ data for a heating rate of 10 deg min^{-1} were fitted.

were the peak temperature in the plot of the derivative $-dm/dt$ versus T, the average $\Delta_{vap}H^{\ominus}$ given in the preceding paragraph, $\Delta_{vap}S^{\ominus}$, initial sample mass, the heating ramp rate dT/dt, and P_{atm}. The value of $\Delta_{vap}S^{\ominus}$ was 153.95 J K^{-1} mol^{-1} for reaction (13) with $CaCO_3$; this value was based on thermochemical data from NBS [6] and from Kelley [7] with the provision that $\Delta_{vap}G^{\ominus}$ values agree. The value of $\Delta_{vap}S^{\ominus}$ was 127.85 J K^{-1} mol^{-1} for reaction (14) using $ZnCl_2$; this value was based on vapor pressure data from Stull [8]. The values of α for each TGA experiment are reported in Tables 1 and 2 and are plotted in Figs. 4 and 5. The abscissa on Figs. 4 and 5 is the square-root of the flow rate of carrier gas. Without the C term in Eq. (11), there is no theoretical reason for this choice. However, use of the square-root of the carrier gas flow rate does spread the low flow rate data so that the dependence of α on carrier gas flow rate may be more easily inspected.

In the case of experiments with $ZnCl_2$, a yellowish white residue remained. The mass of the residue was subtracted from the starting mass of the sample. An X-ray diffraction examination of the residue showed that ZnO was present. Because $ZnCl_2$ is very hygroscopic, a hydrolysis reaction can occur. As a consequence, the α values for $ZnCl_2$ show more scatter than the $CaCO_3$ data.

The α values obtained from the experimental data were fitted to the reciprocal of Eq. (11) to obtain fitted values for A and α_{vap}. The fitted values are given in Table 3, and lines using these values are plotted on Figs. 4 and 5.

4. Discussion

4.1. Data for $\Delta_{vap}H^{\ominus}$

The average value found for reaction (13) for $\Delta_{vap}H^{\ominus}$ was 176.51 ± 3.86 kJ mol^{-1} at 980 K. This value agrees with the value of 176.98 kJ mol^{-1} at 980 K obtained by using $\Delta_fH^{\ominus}$ and $C_p^{\ominus}$ data at 298.15 K from the NBS tables [6]. The average value found for reaction (14) for $\Delta_{vap}H^{\ominus}$ was 127.36 ± 3.81 kJ mol^{-1} at 792 K. This value may be compared with the value of 127.92 ± 0.75 kJ mol^{-1} obtained by doing a second-law analysis on all the vapor pressure data from Stull [8], and it should be noted that the values agree within the uncertainties.

4.2. α Values

The α values for each experiment were calculated and are given in Tables 1 and 2 and are plotted in Figs. 4 and 5. These values were fitted to Eq. (11) to obtain fitted values for A and α_{vap}; these values are given in Table 3.

The fitted values of A may be compared with calculated values for A using the defining Eq. (3). The calculated values of A depend on D' which depends upon the molar mass and the molecular diameters σ of the gases being studied. In all current experiments, nitrogen was the carrier gas. When reaction (13) was studied, the gaseous species produced was CO_2. The molecular diameters for CO_2 and N_2 were given by Hirschfelder et al. [4]. Using a furnace tube radius of 10 mm and a furnace tube half length of 3.0 cm, one computes a value for A at 1000 K of 1.02 $cm^3\,s^{-1}$. Doubling this value, because diffusion can occur in both directions from the sample location (i.e. upstream and downstream in the flow of the carrier gas), the expected value of A at 1000 K would be 2.04 $cm^3\,s^{-1}$. The fitted value for A for reaction (13) was 3.865 $cm^3\,s^{-1}$ with a calculated value of 2.04; the agreement is modest. Molecular diameter data are not available for $ZnCl_2$ for studies of reaction (14). A molecular diameter was estimated using the molecular diameter for HgI_2 and ionic radii for Hg^{2+}, Zn^{2+}, Cl^- and I^-. The estimated value for σ was 4.34 Å. For $ZnCl_2$ diffusing into nitrogen, the value of A at 800 K was 0.5894 $cm^3\,s^{-1}$; doubling this value gave 1.18 $cm^3\,s^{-1}$. The fitted value for A for reaction (14) was 7.556 $cm^3\,s^{-1}$ which is quite different than the calculated value of 1.18 $cm^3\,s^{-1}$. Using the value of A of 9.748 $cm^3\,s^{-1}$, a value of 2.198 Å would be calculated for σ for $ZnCl_2$.

The values of α_{vap} for reactions (13) and (14) are 0.0062 and 0.0095, respectively. The observed α_{vap} values result from two effects: (1) a true limiting vaporization rate associated with the complex structural changes for the vaporization reaction, and (2) an undersaturation of the vapor in the furnace area of the experiment which is associated with the design of the equipment. The values of α were calculated by the temperature of the peak in the $-dm/dt$ data. At the time in the experiment in which the peak is observed, the vaporization reaction of the sample is nearly complete. In the case of reaction (13), CO_2 was diffusing through a crust of CaO. Inhibited vaporization of $CaCO_3$ has been studied by Searcy and co-workers [9]. In the case of reaction (14), $ZnCl_2$ was vaporizing from a residue consisting in part of ZnO. Inhibited vaporization is certainly part of the reason why α_{vap} was less than unity, but it may not be the only reason. Undersaturation due to apparatus design may also be significant.

Wahlbeck [3] indicated that it would be possible to calculate $\Delta_{vap}S^{\ominus}$ when data were collected at different flow rates. From Eq. (9), $\Delta_{vap}S^{\ominus}$ can only be determined in cases in which $\alpha_{vap} = 1$. Because the data in this study gave α_{vap} less than unity, $\Delta_{vap}S^{\ominus}$ could not be calculated reliably. The initial supposition regarding direct calculations of $\Delta_{vap}S^{\ominus}$ appears to have been too optimistic.

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