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A STUDY OF TEMPERATURE VARIATIONS OF SOME REACTION ENTHALPIES SUITABLE AS CALIBRATION STANDARDS IN DTA

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ABSTRACT

The variation of the enthalpies of transition (ΔH_{tr}) for Na_2SO_4, K_2SO_4, $BaCO_3$ and $SrCO_3$ and of the enthalpy of decomposition of Mn_2O_3 to Mn_3O_4 with temperature have been studied using tabulated data[3] and the techniques of DTA, TG and DTG.

The decomposition enthalpies of Mn_2O_3 are estimated for two temperature ranges of reaction with the aid of kinetic conversion factors determined empirically from both TG curves and DTA peak areas. A quantitative evaluation of ΔH_{tr} for $BaCO_3$ made by two methods suggests a difference of ca. 10% between the exothermal and endothermal peak areas.

INTRODUCTION

In determining unknown reaction enthalpies (ΔH) by the technique of quantitative DTA[1] these enthalpies are generally correlated to the areas of the DTA peaks. The temperature dependence of the peak areas requires calibrating of the DTA cells used.

The compounds employed as calibration standards are frequently those undergoing a reversible transition ($L(s) \rightleftarrows H(s)$) or decomposition ($A(s) \rightleftarrows B(s) + C(g)$). These reactions usually occur over a range of temperature. Since the enthalpies of formation for the products and the reactants in general vary differently with temperature the calibration values of ΔH obtained from the DTA peaks may be considerably at variance with the reversible ΔH values at the equilibrium temperature of transition (T_{tr}) or those of decomposition at constant temperature and pressure.

Barshad[2] proposed that an empirical value may be assigned to the enthalpies of decomposition reactions such that the reaction enthalpy at this temperature equals that determined from DTA.

The aim of the present study is to estimate in general the magnitude of these enthalpy variations using the recently tabulated ΔH data[3] and attempt to determine the enthalpies of some reactions using the DTA- or combined TG–DTG–DTA-technique. The reactions studied are the transitions of Na_2SO_4, K_2SO_4, $BaCO_3$ and $SrCO_3$ and the decomposition reaction of Mn_2O_3 to Mn_3O_4.

THEORETICAL CONSIDERATIONS

The enthalpy change for a reaction occurring over a temperature range at constant pressure may be written in an integral form as

$$\Delta H = \int_{T_1}^{T_2} [\Delta H_p(T) - \Delta H_r(T)] \left(\frac{\partial\alpha(T)}{\partial T}\right) \mathrm{d}T \tag{1}$$

where T_1 = temperature of the observable onset of reaction; T_2 = temperature of the completion of reaction; $\Delta H_p(T)$,$\Delta H_r(T)$ = enthalpies of formation of the products and the reactants, resp., as functions of temperature; $\alpha(T)$ = kinetic conversion factor (varying between 0 and 1) for the reaction as a function of temperature.

To evaluate this integral exactly the enthalpies may for instance be expressed analytically and $\alpha(T)$ obtained from the reaction mechanism if this is known. For practical purposes, the integral may, without substantial loss of accuracy, be replaced by the summation over a number of temperature intervals so that

$$\Delta H = \sum_{i=1}^{n} [\Delta H_p(\overline{T}_i) - \Delta H_r(\overline{T}_i)] \cdot \underbrace{[\alpha(T_i + \Delta T) - \alpha(T_i)]}_{\alpha(\overline{T}_i)} \tag{2}$$

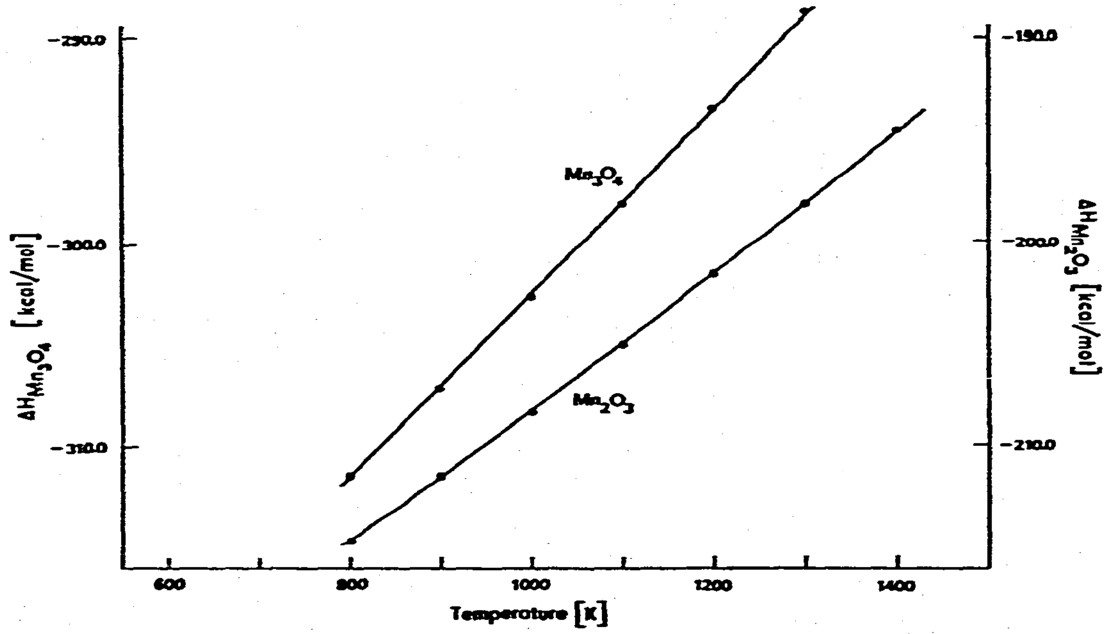


Fig. 1. The enthalpies of formation of Mn_2O_3 and Mn_3O_4 as functions of temperature.

where T_1 and T_n are identical to T_1 and T_2 in eqn. (1), respectively and $\bar{T}_i$ is a mean value of two adjacent temperatures.

Over a limited temperature range, the enthalpies may often be given in the form $\Delta H(T) = aT + b$, where a and b are constants or, determined directly from a plot such as shown in Fig. 1 for the system Mn_2O_3–Mn_3O_4.

For the transition reactions only the DTA curve is usually available. When the DTA peak can be correlated to the reaction kinetics the $\alpha(\bar{T}_i)$ factors may be estimated approximately using the frequently employed relation[1] between the heat released during a reaction and the corresponding area of the DTA peak. One obtains then

$$\alpha(\bar{T}_i) = \frac{\int_{T_i}^{T_{i+1}} T_d(T)\mathrm{d}T}{\int_{T_1}^{T_n} T_d(T)\mathrm{d}T} \tag{3}$$

where T_d = differential temperature as a function of temperature.

A certain error is introduced by the fact that the DTA peak is used simultaneously to determine the $\alpha(\bar{T}_i)$ factors and to evaluating the variation of the total enthalpy change with temperature. This error may be minimized considerably when the DTA peak is subdivided into a sufficient number of temperature intervals (about 10 in practice).

The decomposition reactions can be followed by the combined DTA–TG–DTG measurements. This offers advantages over the transition reactions in that

the $\alpha(\bar{T}_i)$ factors may be determined unequivocally from the TG curve,

the amount of the compound which gives rise to the observable heat effect during the reaction can be found (in the case of low enthalpy values) and

comparison of the form and maxima of the DTG and DTA peaks may reveal whether or not the DTA curve is representative of the kinetics of the reaction studied.

EXPERIMENTAL

A microthermobalance (Mettler)[4] was employed and DTA or TG–DTG–DTA curves were recorded simultaneously as a function of time and temperature. In studying the decomposition of Mn_2O_3 to Mn_3O_4 the samples were heated continuously over the temperature range of the reaction as indicated in Fig. 2. Sample weights were ca. 300 mg and crucibles of S-platinum and sintered alumina were employed. The transition reactions were investigated using both small and larger samples 30–60 and 400–600 mg, respectively. The runs were made in S-platinum crucibles and both the exothermal and endothermal transitions were recorded.

The other characteristic parameters of the runs were as follows: sensitivity of the measurements: DTA, 50 μV; TG, 5×10^{-2} mg; DTG, 10 mg min^{-1}; Pt–Rh

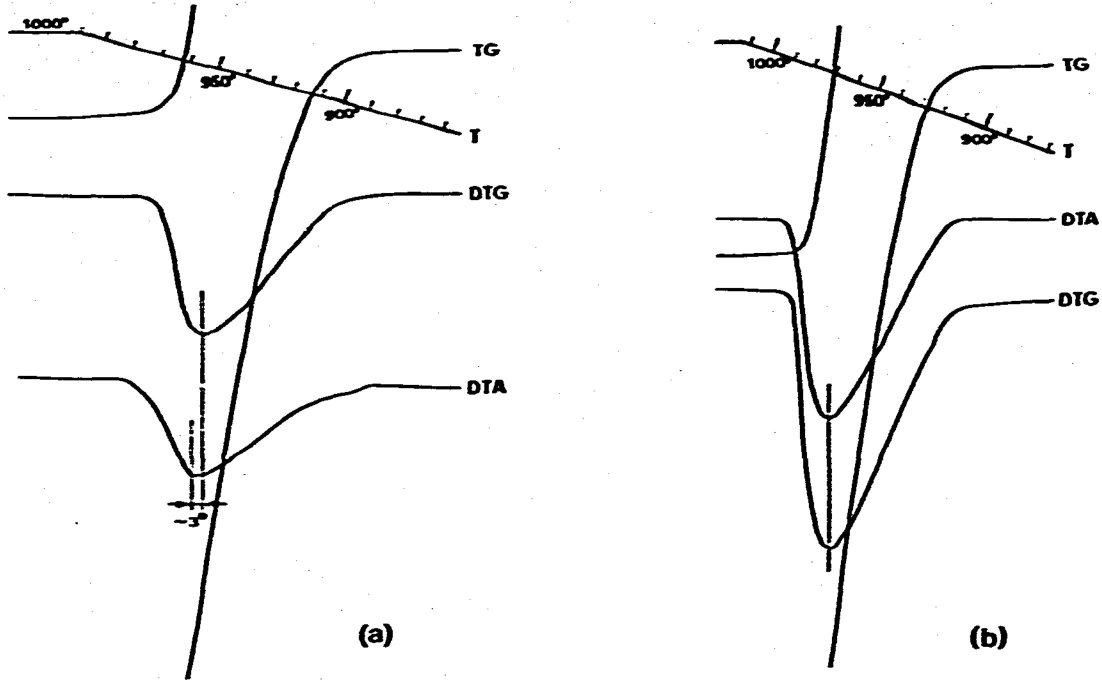


Fig. 2. The thermograms obtained for the reaction of Mn_2O_3 to Mn_3O_4 in air in (a) sintered alumina, (b) S-platinum crucibles.

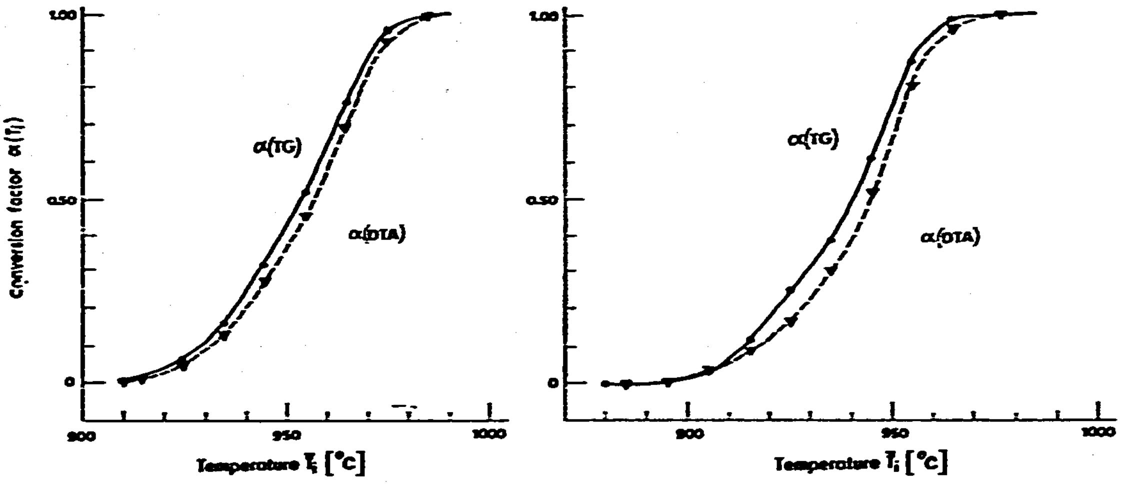
thermocouples; temperature control: ±1.5°C; heating (cooling) rate: 10°C min^{-1}; gas atmospheres employed: air, air + 5 vol.% CO_2 in the case of carbonates; gas flow: ca. 6 l h^{-1}. For the reaction of Mn_2O_3 to Mn_3O_4 the $\alpha(\bar{T}_i)$ factors were determined using the DTA peaks as well as the TG curves corresponding to the temperature range of the DTA peaks.

RESULTS AND DISCUSSION

The thermograms obtained for the decomposition of Mn_2O_3 to Mn_3O_4 are shown in Fig. 2 for the samples run in platinum and alumina crucibles. It may be noted that generally the departure from the DTA baseline is not observable until ca. 1–2% of Mn_2O_3 has reacted. Similarly, this baseline has been approached when about 98–99% of Mn_2O_3 has been converted into Mn_3O_4. The DTA peak area seems thus to be relatable to only 96–98% of this reaction at the DTA sensitivity selected.

As indicated in Fig. 2 the maximum of the DTA peak is shifted towards higher temperature by about 3°C from the maximum of the DTG peak in the case of alumina crucibles. Since the hot junction of the thermoelement touches the surface of the crucible, this shift is probably mainly due to a temperature gradient (∇T) through the crucible wall.

In order to determine the ΔH values for the reaction $3Mn_2O_3 \rightleftarrows 2Mn_3O_4 + \frac{1}{2}O_2$ the $\alpha(\bar{T}_i)$ factors were evaluated using both the TG curves and the DTA peaks



(a) (b)

Fig. 3. The kinetic conversion factors ($\alpha(T_i)$) as functions of temperature ($\bar{T}_i$) obtained from TG and DTA curves for the reaction of Mn_2O_3 to Mn_3O_4 using (a) S-platinum and (b) sintered alumina crucibles.

in the manner previously mentioned. Figure 3 shows these factors obtained for Pt and Al_2O_3 crucibles as a function of temperature. It is seen that the factors obtained from DTA peaks are shifted relative to those from the TG curves towards lower values over almost the whole temperature range. The shift is as expected larger for the Al_2O_3 than for the Pt crucibles. The occurrence of the shift for the Pt crucibles seems to reveal the presence of a certain ∇T through the sample even when the maxima of the DTA and DTG curves appear to coincide.

The ΔH values calculated (eqn 2) for this reaction when observed in the range 890–985°C are, in the case of Al_2O_3 crucibles, equal to 17.69 kcal and 17.63 kcal per 3 mole Mn_2O_3 when using the $\alpha(\bar{T}_i)$ factors from TG and DTA curves, respectively. For Pt crucibles (910–990°C) these values are 17.40 kcal and 17.35 kcal per 3 mole Mn_2O_3.

The enthalpies evaluated from the DTA peaks appear to be only slightly lower compared to those obtained using the TG curves even in the case of Al_2O_3 crucibles. This suggests that DTA peak areas may be used as well to obtain these reaction enthalpies with satisfactory accuracy. The differences between the ΔH values for the above different temperature ranges illustrate the marked dependence of these enthalpies on temperature.

The plots of the enthalpies of formation[3] ($\Delta H(T)$) against temperature for the salts studied have been extrapolated in the range of ca. ± 100 K beyond the equilibrium temperatures of transition and expressed in terms of relation $\Delta H(T) = aT + b$. Table 1 shows the values of the constants a and b obtained for this temperature range. In Table 2 the observed temperatures of departure from the DTA baseline (T_1) and the observed maximal temperatures of approach to the DTA baseline (T_2) are

TABLE 1

THE VALUES OF CONSTANTS a AND b OF THE RELATION $\Delta H(T) = aT + b$ FOR THE ENTHALPIES OF FORMATION AT TEMPERATURES $T_{tr} \pm 100$ K FOR THE VARIOUS SALTS USED

L = low temperature form, H = high temperature form.

	Na_2SO_4		K_2SO_4		$BaCO_3$		$SrCO_3$	
	L	*H*	*L*	*H*	*L*	*H*	*L*	*H*
$a \times 10^2$ (kcal deg^{-1})	3.72	4.39	4.69	4.59	3.15	3.71	3.01	3.40
$-b$ (kcal)	343.17	344.20	360.07	357.07	302.92	304.42	306.17	306.10

TABLE 2

THE TEMPERATURES OF OBSERVABLE DEPARTURE (T_1) FROM AND OF APPROACH (T_2) TO THE DTA BASELINE FOR THE VARIOUS SALTS USED

Salt	*Endo*		*Exo*	
	T_1 (°C)	T_2 (°C)	T_1 (°C)	T_2 (°C)
Na_2SO_4	235	315	230	190
K_2SO_4	580	645	580	530
$BaCO_3$	810	885	790	720
$SrCO_3$	930	995	930	880

TABLE 3

THE VALUES OF MOLAR TRANSITION ENTHALPIES (kcal mol^{-1}) FROM THE LITERATURE[3] AT T_{tr} AND THOSE CALCULATED USING THE CONSTANTS IN TABLE 1 FOR THE TEMPERATURE VALUES T_2 IN TABLE 2

Salt	Na_2SO_4	K_2SO_4	$BaCO_3$	$SrCO_3$
$\Delta\bar{H}(T_{tr})$	2.58	2.14	4.5(0)	4.7(0)
$\Delta\bar{H}(T_{2,endo})$	2.91	2.09	4.78	5.01
$\Delta\bar{H}(T_{2,exo})$	2.08	2.20	4.06	4.56

given approximately for the larger samples. The maximal temperatures are chosen to illustrate the magnitude of temperature range obtainable for these transitions.

A comparison of the DTA peaks for the smaller and larger samples shows a shift to higher temperatures by 2–5°C of the peak maxima for the larger ones. This indicates the presence of a certain ∇T within the larger samples. In the above decomposition reaction a shift of this magnitude is generated when using Al_2O_3 crucibles. It is shown that this introduces only a minor error in evaluating the reaction enthalpy.

The literature values[3] of molar transition enthalpies ($\Delta\bar{H}_{tr}$) at T_{tr} and those calculated at temperatures T_2 in Table 2 are shown in Table 3 for the respective salts. They give a measure of the type and extent of the variation of these enthalpies with temperature. The effect of temperature seems to be strong particularly for $\Delta H_{tr}(BaCO_3)$ since the H-form of $BaCO_3$ is subject to a considerable "supercooling".

The quantitative evaluation of $\Delta \bar{H}_{tr}$ for $BaCO_3$ has been made (eqns 2 and 3) assuming that the obtained DTA peaks may be taken as approximately representative of the conversion kinetics of this transition. For the endothermal and exothermal transitions of the larger samples (Table 2) the values calculated are 4.75 and 4.25 kcal mol^{-1}, respectively. Provided that the reference value[3] is correct numerically the exothermal peak area then ought to be about 90% of the endothermal one. This compares reasonably well with the value of 92% determined for the DTA peaks obtained experimentally. The error in the area determination has been about 3%.

Considering the transition enthalpies in Table 3, it may be anticipated that simply taking the arithmetrical mean of the appropriate values ought also to provide quite satisfactory values of $\Delta \bar{H}(T_{tr})$ or the exothermal and endothermal transition enthalpies for calibration.

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