

## **CRTA FOR THE THERMOANALYTICAL SCREENING OF VOLATILE COMPOUNDS**

### **1. Calibration of standard Q-derivatograph sample holders vs. vapor partial pressures during quasi-isobaric quasi-isothermal heating**

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### **Abstract**

Quasi-equilibrium thermogravimetry (variant of CRTA) is utilized as a thermoanalytical screening method for volatile compounds, standard Q-derivatograph sample holders (plate-like holder, open crucible, crucible with lid, and conical holder) were calibrated against the partial pressures of metal  $\beta$ -diketonate vapor (in sublimation and evaporation processes) in the range 0.0006–0.11 atm. The mathematical relationship between the vapor partial pressure, the holder construction, the vapor molecular mass, and the mutual diffusion coefficient of the gas was derived and considered. It is possible to obtain a rough  $p$ - $T$  relationship for volatile compounds by using stabilized temperatures of sublimation (evaporation) processes in four pressure-calibrated sample holders.

**Keywords:** coordination compounds, CRTA, quasi-equilibrium, TG, thermodynamics, volatility

### **Introduction**

The primary information of the thermal properties of volatile coordination compounds is important for the serial synthesis of new compounds, e.g. during the synthesis of  $\beta$ -diketonates with variously substituted ligands. This information can include the data on the melting temperature, the temperature interval of vapor formation (sublimation or evaporation), the initial temperature of pyrolysis, and the kinetic parameters of all processes.

The method of quasi-equilibrium thermogravimetry can be used to obtain approximate data on the  $p$ - $T$  relationship. Quasi-equilibrium thermogravimetry is a variant of CRTA (controlled rate thermal analysis) [1, 2]. The heating of the sample is carried out so as to maintain a small constant rate of mass loss (any in

the interval 0.1–6.0 mg min<sup>-1</sup>). Such a regime narrows the temperature interval of thermolysis, and the process becomes quasi-isothermal. There are special sample holders which hinder the escape of the evolved gas to different extents; these are responsible for the self-generated atmosphere of this gas above the sample.

It is found that the partial pressure of the evolved gas under such quasi-isothermal conditions is stabilized and maintained constant up to the end of the process; this pressure depends on the holder construction (plate-like, open crucible, crucible with lid, conical, labyrinth, etc.). The process of gas evaluation proceeds quasi-isobarically.

Such a quasi-isobaric and quasi-isothermal regime for the reactions with fast establishment of equilibrium results in a quasi-equilibrium: the stabilized temperatures of the processes closely match the equilibrium temperatures (at corresponding pressures of the gas-reaction product) [1, 2].

For the thermal dissociation reaction  $\text{CaCO}_3 = \text{CaO} + \text{CO}_2$ , the corresponding partial pressures of  $\text{CO}_2$  are 0.01 atm (plate-like holder), 0.05 atm (open crucible), 0.2 atm (crucible with lid), 0.8 atm (conical holder), and 1.0 atm (labyrinth holder). This stabilization of the temperature is very high (2–5 K for 20–70% conversion).

In principle, if thermoanalytical data are available on stabilized temperatures in a set of sample holders, it is possible to obtain the  $p$ – $T$  relationship (although not very accurately).

However, during a study of some volatile silicon-organic compounds and  $\beta$ -diketonates, we discovered that the quasi-equilibrium vapor partial pressures of such large and heavy molecules are noticeably below the known pressures for  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .

We have derived a mathematical relationship between the vapor partial pressure, the holder construction, and the physicochemical properties of the vapor and the gaseous medium (air, for example) [3]:

$$p_o = p(1 - e^{-aq})$$

where

$$a = \frac{LRT10^{-6} \text{ min}}{MDSp60 \text{ mg}}$$

with  $p_o$  vapor partial pressure (atm);

$p$  gas pressure of medium (atm);

$q$  constant rate of mass loss (mg min<sup>-1</sup>);

$R$  gas constant;

$T$  temperature (K);

$D$  coefficient of mutual diffusion (cm<sup>3</sup> s<sup>-1</sup>);

$M$  molecular mass of evolved gas (g);

$S$  and  $L$ -section and length of the conventional channel (in the model holder) for gas evolution (cm) [3].

It is clear that the vapor partial pressure in different sample holders depends both on the vapor molecular mass and on the coefficients of mutual diffusion (vapor – gas of the medium); therefore, this quasi-equilibrium vapor partial pressure will vary from one compound to another. The values (0.01–1.0 atm) indicated in the literature related only to substances with small molecular masses in the vapor state ( $\text{CO}_2$  and  $\text{H}_2\text{O}$ ).

We are considered the tabulated data on the molecular masses and coefficients of mutual diffusion [4]. With increasing molecular mass of the vapor ( $M$ ), the coefficient of mutual diffusion ( $D$ ) for the system vapor – air will decrease; the value of  $M \cdot D$  increases rapidly at average values of  $M$  and becomes practically constant at large values of  $M$  (Table 1). Therefore, at  $M > 200$  the quasi-equilibrium partial pressure of the evolved vapor ( $p_0$ ) will not depend on the nature of the compound. The measurement and calculation of parameters  $L$  and  $S$  for standard sample holders presents difficulties, the values of the coefficients of mutual diffusion of gases for the systems air –  $\beta$ -diketonates (or helium –  $\beta$ -diketonates) are unknown.

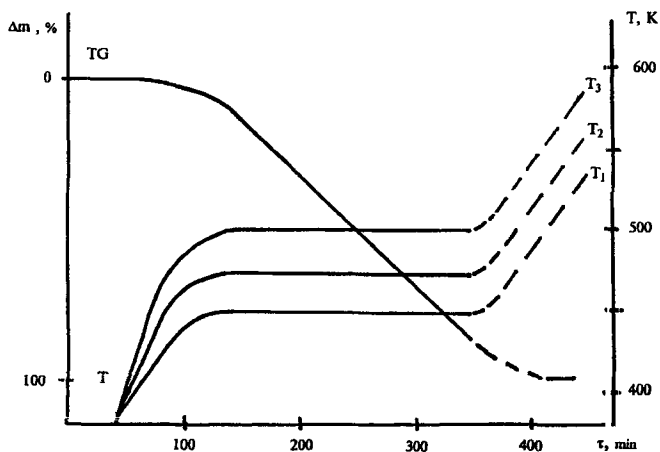
**Table 1** Molecular masses of gases and coefficients of the mutual diffusion in the system "air-gas" (room temperature) [4]

Gas	$M/g$	$D/\text{cm}^3 \text{ s}^{-1}$	$[M \cdot D]$
He	2	0.63	1.26
$\text{NH}_3$	17	0.227	3.86
$\text{H}_2\text{O}$	18	0.227	4.99
$\text{CO}_2$	44	0.16	7.04
$\text{C}_6\text{H}_6$	78	0.09	7.02
$\text{C}_7\text{H}_8$	92	0.08	7.36
$\text{C}_8\text{H}_{18}$	114	0.06	6.57
$\text{C}_{16}\text{H}_{34}$	226	0.04	8.86
$\text{C}_{17}\text{H}_{36}$	240	0.04	10.13
$\text{C}_{18}\text{H}_{38}$	254	0.04	10.16
$\text{C}_{22}\text{H}_{44}\text{O}_2$	340	0.03	10.20

Therefore, for evaluation of the volatility of such compounds it may be possible to calibrate the sample holders on  $\beta$ -diketonates (with large enough molecular masses) with known thermodynamic relations  $\ln p = B - A/T$ .

## Experimental and discussion

The sublimation and evaporation of two acetylacetonates,  $\text{Al}(\text{AA})_3$  and  $\text{Cr}(\text{AA})_3$ , were studied by means of a Q-1500-D derivatograph (MOM, Hungary). Four types of sample holders were used: plate-like, a standard open crucible, a crucible with a lid, and a conical holder. The  $\beta$ -diketonates were synthesized by known methods and purified by sublimation in vacuum.



**Fig. 1** Thermoanalytical curves for  $\text{Cr}(\text{AA})_3$  under quasi-equilibrium conditions in different sample holders ( $m=100$  mg,  $q=0.3$  mg  $\text{min}^{-1}$ ):  $T_1$ =plate-like holder;  $T_2$ =open standard crucible;  $T_3$ =standard crucible with lid

Conditions: sample mass 100 mg, TG sensitivity 50 mg, designated decomposition rate  $q=0.16$  mg  $\text{min}^{-1}$  (real experimental sublimation rate 0.3 mg  $\text{min}^{-1}$ ), initial voltage 50 V, and chart velocity 0.1 cm  $\text{min}^{-1}$ ) (Fig. 1). The recording was performed in coordinates ( $\Delta m, T$ ) – time; this allows the constancy of the decomposition rate  $q$  to be followed. The thermal equilibrium (and the corresponding

**Table 2** Partial pressures of  $\text{Al}(\text{AA})_3$ -vapor in different sample holders calculated on quasi-equilibrium temperatures of sublimation and evaporation

Sample holder	Quasi-equilibrium temperature/K	Partial pressures of $\text{Al}(\text{AA})_3$ -vapor/atm
Open standard crucible	$457 \pm 4^*$	$0.009 \pm 0.001^*$ sublimation
Standard crucible with lid	$475 \pm 3^*$	$0.023 \pm 0.002^*$ evaporation
Conical crucible	$516 \pm 4^*$	$0.11 \pm 0.02^*$ evaporation

\* standard deviation

Literature data [5, 7], used for the calculation of  $p_0$ :

$\ln p = 23.71 - 13027/T$  (sublimation);

$\ln p = 15.82 - 9326/T$  (evaporation);  $T_{\text{melt}} = 468$  K

**Table 3** Partial pressures of  $\text{Cr}(\text{AA})_3$ -vapor in different sample holders calculated on quasi-equilibrium temperatures of sublimation and evaporation

Sample holder	Quasi-equilibrium temperature/K	Partial pressures of $\text{Cr}(\text{AA})_3$ -vapor/atm
Plate-like holder	$446 \pm 1^*$	$0.0006 \pm 0.0002^*$ sublimation
Open standard crucible	$483 \pm 8^*$	$0.009 \pm 0.002^*$ evaporation
Standard crucible with lid	$503 \pm 3^*$	$0.022 \pm 0.002^*$ evaporation

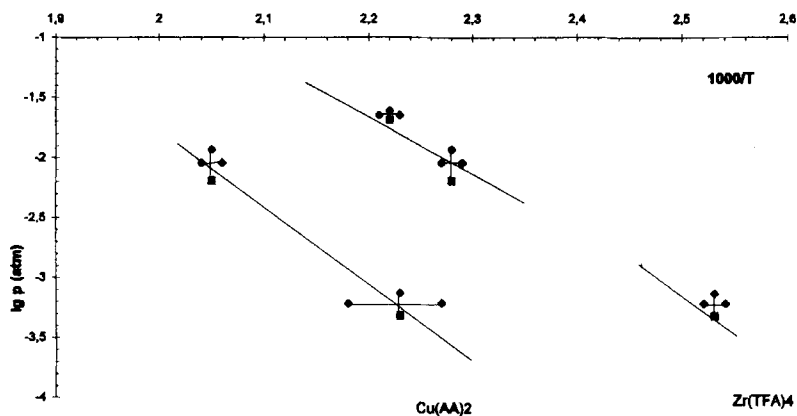
\* standard deviation

Literature data [5, 7], used for the calculation of  $p_0$ :

$\ln p = 26.82 - 15298/T$  (sublimation);

$\ln p = 16.14 - 10028/T$  (evaporation);  $T_{\text{melt}} = 489 \text{ K}$

constancy of the decomposition rate  $q$  and temperature  $T$  are fixed only after 2–3 h of heating. Further, the stabilized temperature did not change during 2 h, and this value of temperature was used for the calculation of the quasi-equilibrium partial pressure of the vapor in the sample holder. Tables 2 and 3 list the calculated quasi-equilibrium vapor partial pressures for different sample holders.



**Fig. 2**  $p$ - $T$  relationship for  $\text{Cu}(\text{AA})_2$  and  $\text{Zr}(\text{AA})_4$ : — literature data; + experimental data

We checked this method by studying the sublimation and evaporation processes of the acetylacetonate of copper and the trifluoroacetyl-acetone of zirconium (Fig. 2). The qualitative agreement between the literature data [6–7] and our experimental findings is rather good. Therefore, quasi-equilibrium thermogravimetry appears to be an effective method for study of the volatility of compounds. This rather rough  $p$ - $T$  relationship is much better (from a physical-chemical point of view) than the traditional set of thermal curves obtained with a single standard crucible (at an indeterminate vapor pressure) under linear heating.

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