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THERMAL AND DYNAMIC ANALYSIS OF THE REACTIONS BETWEEN FORMIC ACID AND TRIETHYLAMINE

N. Balbi, J. H. Balbi, L. Elegant** and Y. Girault*

* UNIVERSITE DE CORSE, CMCS, QURTIER GROSETTI BP52-20250 CORTE
**UNIVERSITE DE NICE, LABORATOIRE DE THERMODYNAMIQUE EXPERIMENTALE,
PARC VALROSE 06034 NICE, CEDEX, FRANCE

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It is possible to study the problems of thermal regulation and energy storage by utilizing chemical reactions. For this purpose, a method of dynamic and global modelling is used to determine the enthalpy of reaction of formic acid and triethylamine.

Introduction

The study and analysis of the Vignola solar power-station has shown that the 'storage' subsystem is a delicate point. In the operation of many thermal systems, the heat-bearing fluid must maintain a constant output temperature, whatever variations the system undergoes, which poses numerous problems.

For this purpose, a method of modelling has been developed laboratory and tested on thermal systems [1].

In this approach, a first study was carried out by the team of Elegant [2–4] on the system acetic acid-triethylamine, which offers many advantages, including cheap products and liquid-phase operation (no heat transfer problems). The process of dynamic modelling [5] has provided results identical to those obtained with conventional calorimetry. The study is being continued on reactions of the same type, with the aim of finding acid-base couples with high reactional enthalpy.

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Reactions between formic acid and triethylamine

In their works on the interactions between carboxylic acids and amines, F. Kohler and his collaborators pointed out a number of addition compounds. Among these, we have noted two possible compounds between formic acid and triethylamine:

– one compound with three moles of formic acid for one mole of triethylamine,

– one compound with two moles of formic acid for one mole of triethylamine:

$$3\,\mathrm{HCOOH} + \mathrm{Et_3N} \overset{\Delta H_{A,B}}{\rightleftarrows} (\mathrm{HCOOH})_3 - (\mathrm{Et_3N})$$

$$2\,\mathrm{HCOOH} + \mathrm{Et_3N} \overset{\Delta H_{A,B}}{\rightleftarrows} (\mathrm{HCOOH})_2 - (\mathrm{Et_3N})$$

In the following part of this work, *A* stands for formic acid and *B* for triethylamine.

Experimental procedure

A 50 cc glass reactor is placed above a magnetic agitator and contains one of the reagents (the amine). It is fitted with a thermocouple connected to a measurement apparatus. A dropping funnel allows introduction of the second reagent (the acid) by means of a drip flow.

The temperatures of the reaction and ambient media are measured via thermocouples connected to a system acquiring and recording data, the rate being one acquisition every 8 seconds.

The mass of the reactor is determined before and after addition of the reagent, and at the end of each experiment. The heat given off by the reactor causes the temperature of the medium to rise. At the end of the reaction, it decreases regularly (relaxation of the system).

Dynamic modelling nevertheless requires the knowledge of certain water-equivalent masses in the system and of the calorific capacity of the constituents.

Dynamic calorimetry

The proposed approach may the summarized as follows: modelling – identification – determination of the thermodynamic magnitude (complexation enthalpy).

Experimental recording and model construction

Phase 1 is the chemical reaction phase with heat emission for duration τ. Phase 2 is the relaxation phase.

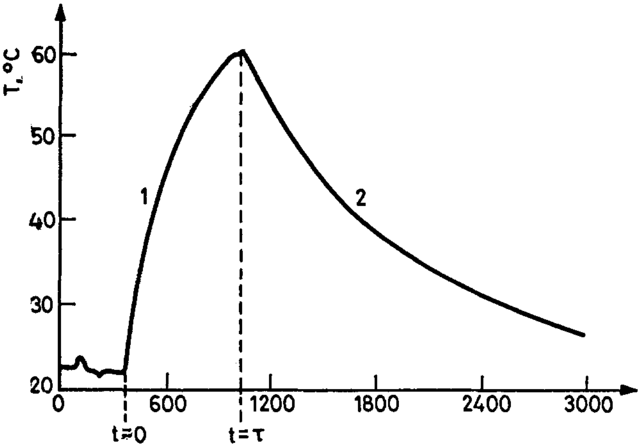

Fig. 1 Experimental recording

At time $t = 0$, the system containing triethylamine has a water-equivalent mass of M_0.

At any time t, during phase 1, the water-equivalent mass of system M is variable.

At time $t = \tau$, the complex is formed: the water-equivalent mass of the global system M_f.

Let h be the amount of heat generated by the reaction per time unit and q the mass flow of reagent A.

The model is built up from the energetic balances in phases 1 and 2.

Phase 1: during time dt:

$$Mc\mathrm{d}T = k(T - T_a)\,\mathrm{d}t - \mathrm{d}m_A c_A\,(T - T_a) + h\mathrm{d}t$$

$$\theta = T - T_a \qquad\qquad q = \frac{\mathrm{d}m_A}{\mathrm{d}t}$$

For convenience, the notations $\dot{T} = \frac{\mathrm{d}T}{\mathrm{d}T}$ and $\theta = \frac{\mathrm{d}\theta}{\mathrm{d}t}$ are used below.

Mc varies in time and we get a model with variable coefficients, i.e. a non-invariant model:

$$\dot{\theta} = -\frac{k + qc_A}{Mc}\theta + \frac{h}{Mc}$$

If $T(0) = T_a$ at time $t = 0$, which requires a few operating precautions, we can write

$$t = 0, \qquad \theta = 0 \qquad \text{and} \qquad \dot{\theta}(0) = \frac{h}{M_0c}$$

$\theta(0)$ is the slope at the origin, the measurement of which allows access to h, provided that M_0c is determined.

Phase 2: This is a matter of simple relaxation. Phase 2 begins at time $t = \tau$:

$$M_fc\dot{T} = -k\,(T - T_a)$$

Let us state that $\alpha = \frac{k}{M_fc}$

$$\dot{\theta} = -\alpha\,\theta$$

$$\theta = \theta\,(\tau)\exp\left[-\alpha\,(t-\tau)\right]$$

Determination of equivalent masses M_f and M_0

This determination is carried out by a standard logarithmic linearization of the experimental curve in phase 2; the determination of α allows the calculation of M_fc. Recording the relaxations with variable masses of the system is sufficient.

In the relaxation phase, the temprature is in the form

$$\frac{\theta}{\theta(\tau)} = \exp\left[-\alpha\,(t-\tau)\right]$$

We draw the curve $\ln\left(\frac{\theta}{\theta(\tau)}\right) = f(t) = -\alpha\,(t-\tau)$, whose slope allows the determination of α, but also the checking of the validity of the hypotheses we have formulated.

The only problem is to gain access to the value of M_fc, which is solved by recording experiments of relaxation in which the mass of the complex is made to vary during careful maintenance of the same operating conditions.

In the general case:

$$\alpha = \frac{k}{M_{f}c}$$

$$\alpha_{i} = \frac{k}{M_{f}c - \Delta m_{i(AB)}c_{AB}}$$

where Δm_i is the variation in mass of the complex.

After the determination of M_f, it remains, after measurement of the slope at the origin $\theta(0)$, to determine M_0.

Let us call M_s the water-equivalent massof the system containing no reagent, which is determined by reference manipulations in which the reactor contains variable quantities of water.

Under these conditions, we can write

$M_0c = M_sc + m_Bc_B$

$M_fc = M_sc + m_{AB}c_{AB}$

$M_fc = M_0c - m_Bc_B + m_{AB}c_{AB}$

Masses m_B and m_{AB} are determined by weighing.

Experimental results

Determination of the calorific capacities of compounds A_3B and A_2B

Successive relaxations of the system are conducted, in which the mass of the compound is variable. At each manipulation, the value of α is determined; the water-equivalent mass of the total system is written as follows:

$$M_fc = M_sc + m_{A3B}\,c_{A3B} \qquad \alpha_{A3B} = \frac{k_{A3B}}{M_sc + c_{A3B}\,m_{A3B}}$$

$$c_{A.B} = 0.48\,\mathrm{cal\,g^{-1}\,K^{-1}} \qquad c_{A.B} = 0.46\,\mathrm{cal\,g^{-1}\,K^{-1}}$$

Reactional enthalpies

Measurement of the slope at the origin $\theta(0)$, and determination of M_o allow access to the reactional power and the reactional enthalpy:

$$h = \dot{\theta}(0)M_0c \qquad \Delta H = -\frac{h\,\tau}{n}$$

a) Reaction $3\,A + B \rightleftarrows A_3B$:

$$\Delta H = -67.92\,\text{kJ mol}^{-1}$$

b) Reaction $2\,A + B \rightleftarrows A_2B$:

$$\Delta H = -50.37\,\text{kJ mol}^{-1}$$

Conclusion

Dynamic modelling proves to be an efficient and powerful tool, making it possible to work in an open system with the help of an unsophisticated experimental apparatus.

In this work, it has been possible to determine the calorific capacities and reaction enthalpies of the two reactions considered. The addition of one of the reagents drop by drop allows control of the reaction time (which is very short if one resorts to instant addition), and thereby increase of the measuring accuracy.

This variable-coefficient model is an efficient one and it is now desirable to seek other chemical reactions of interest as regards their storage capacity and likely to be used in thermal regulation, taking into account that the model can also be adapted to slow reactions.

References

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Zusammenfassung — Probleme der thermischen Stabilisierung und der Energiespeicherung können mit Hilfe von chemischen Reaktionen untersucht werden. Zu diesem Zwecke wurde ein dynamisches und globales Modell benutzt, um die Enthalpie der Reaktion von Ameisensäure mit Triethylamin zu bestimmen.