APPLICATIONS OF REACTION CALORIMETRY IN CHEMICAL ENGINEERING

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Abstract

Reaction calorimetry strongly penetrated process development laboratories in the fine chemicals industry. Applications of calorimetry to different fields of process optimization, chemical reactions and physical unit operations were developed. Applications were first developed in the field of process safety. The thermal data of reaction obtained in the calorimeters allow us to check if a reaction will be controllable at full scale under normal operating conditions and in case of equipment failure. Further, the accurate temperature control and heat flow measurement opened the door to more engineering related data, in the fields of phase equilibria like vapour liquid, solubilities, crystallization and also in the mixing techniques. Some examples of developments in these different fields will be reviewed.

Keywords: heat transfer, mass transfer, phase equilibria, process safety, reaction calorimetry

Introduction

Scale up is often perceived as a difficult engineering problem, expecially in the fine chemicals industry where chemists with a broader chemical than engineering knowledge are in charge of this task. Reaction Calorimetry is a powerful tool to guide in solving different problems in the field of scale up.

A preliminary condition to solve these problems is that the principle of similarity is applicable, i.e. a reaction calorimeter must be able to simulate accurately the plant scale processes as well as simultaneously measuring the heat effects that are occurring. Reaction calorimeters that fulfill these conditions are commercially available. These instruments use a reactor sufficiently large in scale to contain an agitator, feed lines, a condenser, sensors, etc. Most of the common operations of the industrial production of fine chemicals can be performed in such an instrument exactly as done at the plant scale. Therefore, these reaction calorimeters can directly monitor the course of nearly all process steps – the ones accompanied by thermal effects – revealing and quantifying the phenomena necessary to understand them.

The aim of this paper is to present a short review of calorimetric methods which can be used to solve engineering problems. A first review was given by Regenass [1] in 1978. In the mean time, numerous users of reaction calorimeters developed new and original methods for the determination of engineering data. These are classified in three groups: reaction kinetics and related data, heat transfer and thermal data, and finally mass transfer data.

Reaction kinetics and related data

Heat release rate of a reaction

The knowledge of the maximum heat release rate of a reaction is essential to ensure the thermal control of a reaction. Often reaction conditions must be adapted to the cooling capacity of the industrial equipment. The later can be estimated from the overall heat exchange coefficient (U) which can also be measured in the reaction calorimeter (see below). The measured heat release rate can be compared to the cooling capacity of the industrial reactor, thus it is one of the essential parameters required for a safety assessment.

Reaction calorimeters deliver a signal which is proportional to the heat release rate of a reaction. Some calorimeters are based on the principle of heat flux calorimetry, i.e. the heat flux is measured by the temperature difference between the reaction mass and the jacket whose temperature is controlled. In this case the measure is a function of the overall heat transfer coefficient. Therefore the calorimeter is calibrated by Joule effect using an electrical heater. This calibration must be repeated during the experiment in order to take into account the variations of the physical properties of the reaction mass especially the viscosity [2]. Other calorimeters use the principle of heat balance, where the heat release rate is measured using a heat balance in the jacket. The measurement is independent of the overall heat transfer coefficient but the flow rate in the jacket must be controlled and the reactor temperature can usually not be maintained as constant as in heat flux calorimeters.

$$q_{ex} = UA(T - T_c) \qquad (1)$$

In semi-batch reaction, the heat exchange area may vary during the operation leading to a variation of the cooling capacity. Further, the cooling effect of the feed (q_{dos}) must also be taken into account in scale up as shown in Fig. 1.

Macro kinetics

Knowledge of the reaction kinetics is an essential step in the design of a reactor. It allows one to calculate the production capacity (in discontinuous operation, the reaction time) and to improve the selectivity of reactions.

Since the heat release rate of a reaction is directly proportional to the reaction rate, kinetic information is contained in the heat release rate curve [3].

$$q_{rx} = rV(-\Delta H_R)$$

and for n^{th} order kinetics:

$$r = k_\infty \exp(-E/RT)C_{A0}^n(1 - X)^n \qquad (2)$$

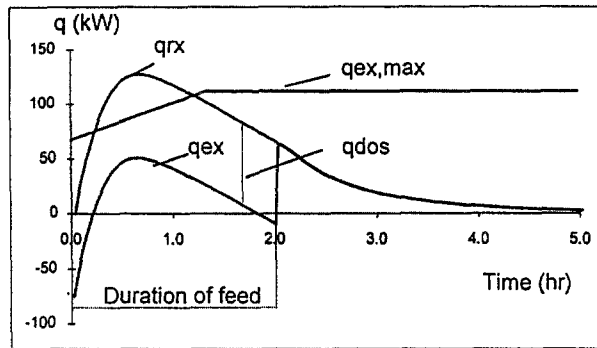The conversion can be calculated from the thermal signal by:

Fig. 1 Thermoanalytical curves showing the cooling effect of the feed

$$X_{Therm} = \frac{\int_0^t q(t)\,dt}{\int_0^\infty q(t)\,dt} \qquad (3)$$

This conversion can then be used for the calculation of the rate constant.

By using calorimetry to measure kinetic data, the proportionality between chemical and thermal conversion is assumed. Since calorimetry always delivers a signal which may be the sum of different thermal effects (among them also physical effects), the correspondence between chemical and thermal conversion must be verified by chemical analysis, for example. During the measurement of kinetic data, isothermal conditions are preferred to avoid the influence of the exponential term of the Arrhenius law. Further physical effects must be avoided. Usually this type of measurement is performed by adding small portions of one of the reactants and evaluating the resulting depletion of the heat release rate curve.

Heat transfer and thermal data

Reaction enthalpy

The enthalpy of reaction is not by itself relevant to engineering considerations, but is a basic physical chemical characteristic of a reaction. However, in combination with the concentration, it allows one to estimate the thermal effect of similar reactions or, for a given reaction, it allows one to calculate the overall heat output for different concentrations. The integration of the heat flux curve yields the energy of a reaction from which the reaction enthalpy can be computed. During the measurement of the reaction enthalpy, perturbations by physical effects like crystallization, melting, dissolution or evaporation etc. must be avoided.
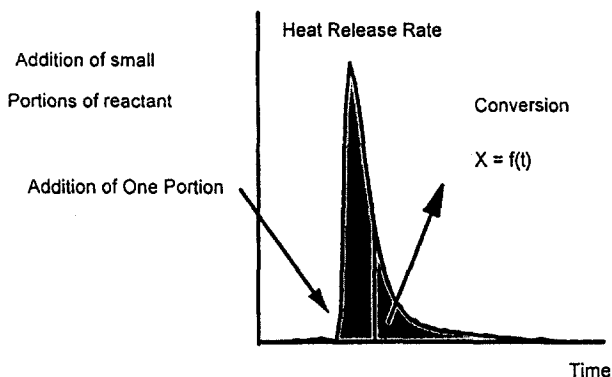
Fig. 2 Determination of kinetic data by calorimetry

Heat capacity

The heat capacity is necessary for the calculation of the amount of energy required to heat or to cool a reaction mass. Further, the heat capacity appears in several heat transfer correlations, as for example in the Prandtl number.

If the contents of a heat flux calorimeter are heated at a constant rate, at the beginning of the heating process the temperature of the jacket is instantaneously increased by a step. The height of this step contains the information for the computation of the heat capacity of the reactor contents [4]. Obviously, the signal must be corrected by the heat capacity of the reactor and its inserts.

The calibration consisting in the determination of the heat capacity of the reactor and its contents must be carefully performed. During the measurement itself, the temperature control parameters must be accurately adjusted.

Heat transfer coefficient

The overall heat transfer coefficient of a reactor is essential to determine whether the thermal control of a reaction will be possible or not.

In a reactor working under normal operating conditions, meaning the heat exchange system is working as designed, the mechanism of heat transfer is forced convection. The reaction mixture is agitated or flows through a tube and the coolant also flows through the coil or the jacket. The overall resistance to heat transfer consists of three resistances in series.

$$\frac{1}{U} = \frac{1}{h_R} + \frac{d}{\lambda} + \frac{1}{h_c} = \frac{1}{h_R} + \frac{1}{\varphi} \qquad (4)$$

$$\underset{\substack{\text{depends on} \\ \text{reaction mass}}}{} \qquad \underset{\substack{\text{depends} \\ \text{on reactor}}}{}$$

The first term only depends on the reactor contents and on the rate of agitation. The remaining two terms depend on the reactor itself and on the heat exchange system. Applying Nusselt's correlation to the internal film:

$$Nu = C^{te}Re^{2/3}Pr^{1/3}\left(\frac{\eta}{\eta_w}\right)^{0.14} \tag{5}$$

with: Cte depending on the type of stirrer

$$\text{Nusselt number} \quad Nu = \frac{h_R d_R}{\lambda}$$

$$\text{Reynolds number} \quad Re = \frac{Nd_s^2\rho}{\eta}$$

$$\text{Prandtl number} \quad Pr = \frac{\eta C_p}{\lambda}$$

The last term i.e. the ratio of the viscosity of the reaction mass to its viscosity at the temperature of the wall, can generally be neglected. By grouping the terms, the heat transfer coefficient of the reaction mass can be written as a function of the geometry and operating conditions of the reactor and of the physical chemical data of the reaction mass:

$$h_R = C^{te}\frac{N^{2/3}d_s^{4/3}}{d_R g^{1/3}}\sqrt[3]{\frac{\rho^2\lambda^2 C_p g}{\eta}} = z\gamma \tag{6}$$

$$\underbrace{\hspace{3cm}}_{\substack{\text{engineering data} \\ \text{of the reactor}}} \quad \underbrace{\hspace{3cm}}_{\substack{\text{physical-chemical data} \\ \text{of the reaction mass}}}$$

Thus for a given reaction mass, the heat transfer coefficient of the internal film can be influenced by the stirrer speed and its diameter. The value of z can be calculated using the geometric characteristics of the reactor. The value of γ can either be calculated from the physical chemical constants (if they are known) or measured by the method of the Wilson plot in a reaction calorimeter [5].
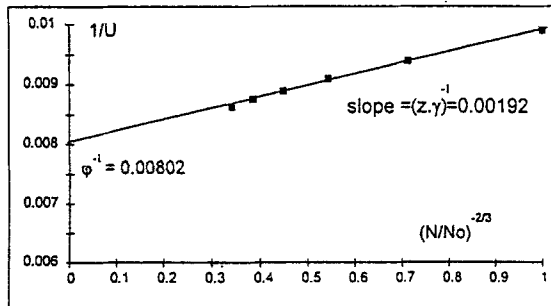

Fig. 3 Wilson plot

As a first step, the calorimeter is calibrated for this measurement using a substance with known physical properties and with a viscosity as close as possible to the viscosity of the reaction mass. This calibration allows one to determine the values z and φ of the calorimeter configuration. In a second step, the actual measurement is performed.

According to Eq. (4), once the heat transfer coefficient of the internal films is known, the heat transfer coefficient of the wall and external film – i.e. the reaction vessel – is also required. The resistance of the reactor wall (d/λ) and external film (h_C) can be determined in a cooling experiment done directly with the production reactor filled with a known amount of a substance with known physical chemical properties. Then the overall heat transfer coefficient for a reactor containing the reaction mass is obtained from:

$$\frac{1}{U} = \frac{1}{h_R} + \frac{1}{\varphi}$$

(7)

For this measurement, the stirrer geometry used in the calorimeter should be similar to the industrial equipment and the position of the inserts and of the agitator must not be changed between the calibration of the calorimeter and the actual measurement. Additionally, to avoid the effect of the heat exchange area, the reactor should be filled to a level above the jacket.

Thermal conductivity

The thermal conductivity appears in different correlations for the estimation of heat transfer of industrial equipment. It appears explicitly in the Nusselt and Prandtl numbers.

The thermal conductivity can be measured by two methods:

– If the dynamic viscosity and the heat capacity are known, Eq. (6) can be used to compute the thermal conductivity:

$$\lambda = \sqrt{\frac{\eta \gamma^3}{\rho^2 C_p g}}$$

(8)

– For solids or viscous liquids, a method based on Fourier's law can be used [6]. The calorimeter is filled with the substance. Without stirring, the jacket is heated to the desired temperature and the system is thermally equilibrated. Then the temperature of the jacket is changed by steps and the response of the content's temperature is monitored. Following the theory of thermal conduction, the thermal diffusivity (a) can be calculated and in turn the thermal conductivity can be determined:

$$a = \frac{\lambda}{\rho C_p}$$

(9)

The first method is useful for liquids with low viscosity ($\eta < 1$ mPa s): the measurements have an accuracy of 15%. With high viscosity, the error may reach 50%. The second method assumes that the heat transfer occurs exclusively by conduction. Therefore, natural convection must be avoided: this gives the limit of the method for high viscosity. For these non classical measurements, external perturbations must strictly by avoided.

Mass transfer

Dynamic viscosity

The stirrer speed is controlled by a PID-Controller. The integral part of the controller (called Rint in the Mettler RC1) is proportional to the torque of the stirrer. Since the torque itself is proportional to the dynamic viscosity, Rint can be used to measure the viscosity of a reaction mixture. Once the system is calibrated with liquids of known viscosity, it can be used for measurements [7].
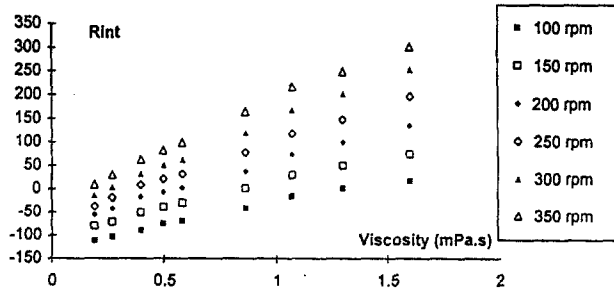
Fig. 4 Calibration of the calorimeter for viscosity measurement

The viscosity is required for a large number of scale up problems ranging from heat transport to fluid dynamics. Often an order of magnitude of the viscosity, but measured under conditions close to the application, is sufficient.

For an accurate measurement of the torque, disturbing friction of the shaft can be avoided if a metal cover, with low friction fittings, is used. It is also good engineering practice to measure the viscosity as a function of temperature and to correlate the data with a model.

Stirrer Power

The speed of mixing influences the rate and the selectivity of fast and of heterogeneous reactions. For high viscosities, the power dissipation by the stirrer also becomes an economical factor which must be optimized. Therefore the scale up of such reactors is often a difficult engineering problem. For mass transfer controlled reactions, the specific stirrer power (kW m^{-3}) is mostly used as a scale up criterium. This requires the determination of the power number.

In turbulent flow, the power dissipation by the stirrer is described by the following equation:

$$P = N_\text{p}\rho N^3 d_\text{s}^5 \tag{10}$$

At constant temperature and without reaction, the heat balance is reduced to the heat losses, which are constant and the energy dissipation of the stirrer. Therefore the latter can be measured as a function of the stirrer speed and represented in a graph which aids the determination of the power number [8].

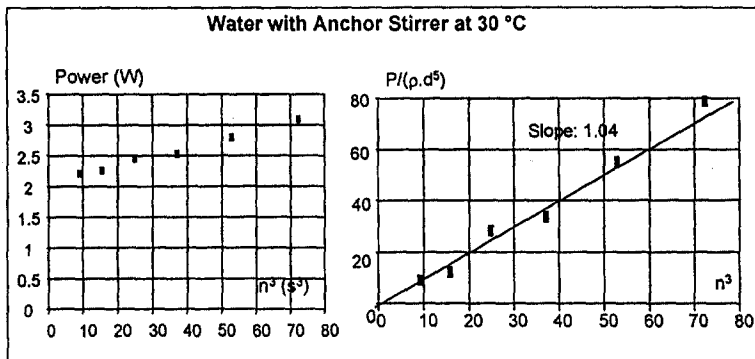$$\frac{P}{\rho d_\text{s}^5} = f(N^3) \tag{11}$$

Fig. 5 Determination of the power number

This measurement requires the maximum sensitivity of the calorimeter. Thus thermal effects, like variation of the room temperature etc., which could disturb the measurement, must be avoided.

Another method combining the determinations of the viscosity and the power number was presented by Kost and Berger [9].

$$Ne = \frac{P}{\rho d_\text{s}^5 N^3} = \frac{2\pi R int}{\rho k d_\text{s}^5 N^2} \tag{12}$$

The calibration constant k must be determined either by a calibration with a torque device or by the method presented above for the determination of the dynamic viscosity.

Gas–liquid equilibrium

The gas–liquid mass transfer coefficient can be determined during an absorption experiment in the reaction calorimeter. The reactor must be degassed before the experiment, then the gas is admitted with the required pressure in the head space of the reactor which is not stirred. After equilibration of temperature and pressure, the stirrer is started. The pressure depletion in the reactor is measured with a fast pressure transducer, and can be evaluated using following equation [10]:

$$\ln \left[\frac{P_m - P_f}{P - P_f} \right] = kla \left[\frac{P_m - P_e}{P_f - P_e} \right] t \tag{13}$$

The kla is an essential property for the design of gas liquid reactors.

This experiment can be repeated at different temperatures. For each temperature a straight line is obtained: the slope is the corresponding kla.

Phase equilibrium

Latent heat of vaporization

The calorimeter must be equipped with a condenser with heat balance. By a simple distillation with mass balance, the latent heat of vaporization can be determined.

The latent heat of vaporization is required for the design of distillation equipment or of reflux operation.

Heat losses between the reactor and the condenser must absolutely be avoided. Hence it is recommended to work with a thermostatic cover.

Vapour–liquid equilibrium

The vapour–liquid equilibrium data are required for the design of separation processes by distillation.

Two methods are possible: the isobaric which requires the measurement of the boiling point at a constant pressure or the isothermal where the pressure is varied at a constant temperature until the boiling point is reached. The air contained in the system must be withdrawn before the experiment. The temperature probe must be located at the interface between the liquid and vapour phases. Further it is essential to avoid heat losses between the reactor and the distillation system. This can be achieved by using thermostated cover and vapour tube.

The calorimeter must be equipped with the distillation unit. The pressure is regulated to the desired value and the actual boiling point is measured. The composition of the liquid phase can be changed by the addition of a known amount of one of the components. For each composition the boiling point is measured: this allows one to build the $T=f(P,X)$ diagram [11]. The data can be correlated by the Wilson or the Uniquac model.

Solid–liquid equilibrium (solubility)

Solubility data are important for the design of reactors as well as for crystallization processes.

The solid–liquid equilibrium or solubility curve can be determined during a linear temperature ramp performed with a mixture. The crystallization and the dissolution are both accompanied by thermal effects which can easily be measured in the calorimeter. By increasing the temperature, the solubility curve is obtained, whereas by decreasing the temperature, the super solubility curve is obtained [12].
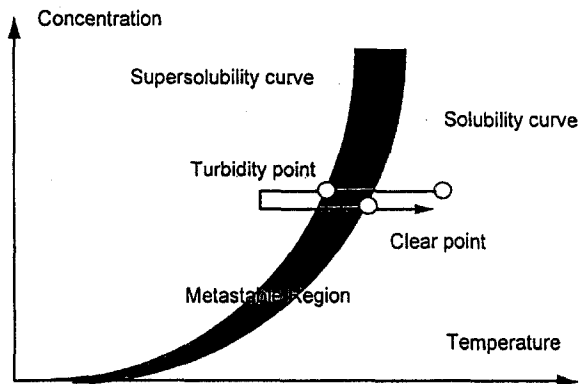
Fig. 6 Measurement of the solubility diagram

In addition to the thermal measurement, a turbidity probe which delivers an additional signal, can be used during the experiment. In order to ensure that equilibrium has been achieved during the measurement, it is recommended to scan through the dissolution and crystallization temperature range at different rates. This is essential in cases where the rate of dissolution or crystallization is slow.

Final remarks

During the five past years numerous different applications of reaction calorimetry, or more generally calorimetry, to the solution of chemical engineering problems have been published. The methods summarized in this paper represent a choice of the most representative problems. More information concerning the methods can be obtained in the original papers.

The reasons for the fast increase of calorimetric applications in the recent past are of different kinds. One fundamental reason is, that most of the operations used in chemical industry are accompanied by thermal effects. The second is of a more technical nature: it is related to the scale of the reaction calorimeters which accurately simulate process conditions and allow to apply the principle of similarity for scale-up.

Since most of the relevant unit operations for the fine chemical industry are accompanied by changes in the energy of the systems, calorimetric methods are fundamentally able to help in the determination of data or more directly in the design of the equipment. This opens the door to the development of more methods in the future.

Symbols and units:

a	thermal diffusivity	$m^2\ s^{-1}$
A	heat exchange area	m^2
h_C	heat transfer coefficient of cooling medium	$W\ (m^2\ K)^{-1}$
h_g	heat transfer coefficient of reactor medium	$W\ (m^2\ K)^{-1}$

C_{A0}	initial concentration of component A	mol m^{-3}
C_p	specific heat capacity	J (kg K)$^{-1}$
d	thickness of reactor wall	m
ΔH_R	molar heat of reaction	J mol^{-1}
d_R	diameter of reactor	m
d_S	diameter of stirrer	m
E	activation energy	J mol^{-1}
φ	heat transfer of the equipment	W (m^2 K)$^{-1}$
g	universal gravity constant	9.81 m s^{-2}
γ	physical constant for heat transfer	W (m^2 K)$^{-1}$
η	dynamic viscosity	Pa s
η_w	dynamic viscosity at wall temperature	Pa s
k_∞	frequency factor	unit depending on n
kla	gas–liquid mass transfer coefficient	s^{-1}
λ	thermal conductivity of reactor wall	W (m K)$^{-1}$
N	stirrer revolution speed	rps = s^{-1}
n	order of reaction	numeric value: 0, 1, 2...
N_p	stirrer power number	–
P	power	W
P	actual pressure	[barabs]
P_e	vapour pressure of the liquid	[barabs]
P_f	final pressure after saturation of the liquid phase	[barabs]
P_m	maximum pressure before stirring	[barabs]
q_{ex}	heat removal rate (power of the cooling system)	W
q_{rx}	heat release rate of a chemical reaction	W
R	universal gas constant	= 8.314 J (mol K)$^{-1}$
$Rint$	integral part of PID stirrer controller (Mettler RC1)	–
r	rate of reaction	mol m^{-3} s^{-1}
ρ	specific weight of reaction mass	kg m^{-3}
T	temperature of the reaction mixture	°C or K
t	time after start of the stirrer	[s]
T_c	temperature of the cooling system	°C or K
U	overall heat transfer coefficient	W (m^2 K)$^{-1}$
V	volume of reaction mixture	m^3
X	conversion	fraction: 0–1
z	equipment constant for heat transfer	–

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