5. Reaction Calorimetry

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5.1. Introduction

Basic thermodynamic and kinetic data of chemical reactions, and some physicochemical properties of reaction mixtures, can be determined experimentally using so called bench scale reaction calorimeters. These have typical reaction volumes from 10 to 100 ml up to several litres. They usually consist of a stirred reaction vessel and offer the possibility of carrying out chemical reactions in batch, semi-batch or –usually with modifications of the device-, in the continuous mode. A condenser can be added to study the reaction under reflux and special reactors are available in order to carry out reactions under high pressure. Areas of application of reaction calorimetry include:

-   determination of calorimetric data for reactor and process design (e.g., overall heat release or supply during physical changes or chemical reactions, heat transfer coefficients, specific heat capacity, adiabatic temperature rise, reactant accumulation.)
-   study of the kinetic behaviour of chemical reactions and or of physical changes.
-   on-line monitoring of heat release rate and other analytical parameters for subsequent process development for batch-, semi-batch and continuous reactions. (E.g., study of the influence of mixing, errors in the charges or recipe, feed rate errors, improper feed sequences and the effect of impurities, temperature or concentration of reactants).
-   development and optimisation of chemical processes with the objective, for instance, of an increase of yield, selectivity or profitability.

5.2. Fundamentals

The basis of reaction calorimetry is to perform a heat balance on the reaction vessel. The heat rate (power) released by, or supplied to, the chemical reactions, or physical changes, can be determined as a difference between terms for the heat production, heat accumulation and heat exchanged with the surroundings in a macroscopic heat balance [Hemminger te al. (1984), Barton et al. (1997), Mathot (1994), Moritz (1995)].

5.3 Isothermal, isoperibolic and adiabatic modes.

Reaction calorimeters can operate in modes so that they closely approximate to isothermal, isoperibolic or adiabatic systems. Usually, the more sophisticated devices can be used in all of these modes. The most simple devices usually operate isoperibolically.

Isothermal calorimeters need an active temperature control system: this can be achieved e.g. by using a reactor with a jacket and changing the temperature of the jacket fluid. Another method, called "power compensation" consists on keeping the jacket fluid isothermally some 10 to 20°C below the temperature of the reactor. The power supplied to an electrical heating element (preferably with a large surface area) submerged within the reactor is then continuously manipulated so as to maintain the reactor at the desired temperature. As an exothermic reaction develops the power supplied by the heater is backed off by an amount exactly equal to the power generated by the reaction or physical change under study.

In the **isoperibolic** mode the surroundings of the reaction mass (usually a jacket) are maintained at a constant temperature. Exothermic or endothermic changes will produce a temperature increase or decrease in the reactor. If the heat exchange between the reactor and the jacket is very fast then the temperature gradient between them will not exceed a few degrees Celsius.

For the more sophisticated devices, a **quasi-adiabatic** mode is achieved by actively adjusting the temperature of the reactor jacket such that heat losses are small. During an exothermic change, the temperature of the reactor and the jacket will both rise with little heat exchange between the two of them and in such a manner that heat exchange with the surroundings stays essentially constant.

Detailed information can be found in survey articles that present different designs of calorimeters and their applications to the investigation of chemical reactions [Nilsson et al. (1983), Lathi et al. (1995), Grønlund et al. (1991)].

5.3.1. Heat balance equations

According to the previous definitions, even a simple reaction flask in an oil bath with a stirrer and a thermometer could be a reaction calorimeter. This would be true if the user is able to perform a heat balance and calculate or measure the resulting power (energy

per unit time) being released from (or supplied to) the chemical reactions or physical changes in the mixture being studied.

5.3.2. Devices using a jacketed vessel and control of the jacket temperature

Mainly two types of calorimetry calculations can be described.

      a) Heat balance calorimetry

The first approach is very similar to what happens in an industrial reactor: the control of the reactor temperature is achieved by changing the inlet temperature of the circulating fluid in the jacket. For example, if an exothermic change occurs in the reactor then the temperature will initially start to rise. This is detected and then a temperature control loop is used to manipulate the temperature of the fluid entering the reactor jacket such that (essentially) isothermal conditions are restored in the reactor as quickly as possible. If the reactor is operated in this essentially isothermally manner and if the mass flow, specific heat capacity, inlet and outlet temperatures of the jacket fluid are known, then the heat release rate due to chemical reactions, or physical changes, in the reactor can be calculated as follows:

$$\dot{q}_r = m_c \cdot c_{pc} \cdot (Tc_{out} - Tc_{in}) + \dot{q}_{loss} \qquad \text{[Eq. 5.1]}$$

where:
$\dot{q}_r$: heat release rate
m_c: mass flow of the jacket fluid
c_{pc}: specific heat capacity of the jacket fluid
Tc_{in}: inlet temperature of the jacket fluid
Tc_{out}: outlet temperature of the jacket fluid
$\dot{q}_{loss}$: heat losses

If the reaction calorimeter is not operated isothermally, a heat accumulation term must be added to the balance (Eq. 5.2):

$$\dot{q}_r = m_c \cdot c_{pc} \cdot (Tc_{out} - Tc_{in}) + m_r \cdot c_{pr} \cdot \frac{dT_r}{dt} + \dot{q}_{loss} \qquad \text{[Eq. 5.2]}$$

where:
$\dot{q}_r$: heat release rate
m_c: mass flow of the jacket fluid
c_{pc}: specific heat capacity of the jacket fluid
Tc_{in}: inlet temperature of the jacket fluid
T_r: temperature of the reaction mass
Tc_{out}: outlet temperature of the jacket fluid
$\dot{q}_{loss}$: heat losses
m_r: reaction mass

c_{pr}: specific heat capacity of the reaction mass

$\dfrac{dT_r}{dt}$: rate of temperature change

$\dot{q}_{loss}$: heat losses

Note that mr, the reaction mass, will also have to account for the reactor parts submerged in the reactants, e.g. baffles, probes, calibration heater, stirring system, etc.

In order to perform the balance, the rate of change of the temperature should be determined continuously and the heat capacity of the reaction mass must be known, or be determined by calibration. For example, electrical power can be added to the reactor in the absence of other thermal effects due to reactions or physical changes. Eq. 5.2 is then modified to the form in Eq. 5.3,

$$\dot{q}_c = m_c \cdot c_{pc} \cdot (Tc_{out} - Tc_{in}) + m_r \cdot c_{pr} \cdot \frac{dT_r}{dt} \qquad \text{[Eq. 5.3]}$$

where $\dot{q}_c$ is the calibration power. According to the previous assumptions, the only unknown term is the specific heat capacity of the reaction mass that can thus be determined. If all the values in the equations Eq 5.1, Eq. 5.2 and Eq. 5.3 are known or measured (e.g. online), even a large-scale industrial reactor can be considered as a reaction calorimeter. In fact, modern computer controlled reactors can use the on-line calculated heat release rate as a variable in a cascade or feed forward temperature control loop. On the lab scale, reaction calorimeters operating according to this principle are useful for studying reaction masses with poor film heat transfer rates that are subject to variation during reaction, such as for example polymerisations (reaction calorimeter RC1 modified by Moritz et al., isothermal heat balance reaction calorimeter (Zeton)) [(Mackenberg et al. (1998), Schulz (1996), Baranek et al. (1999), Pauer et al. (1999), Tschonkou (1996)]. Furthermore the overall heat transfer coefficient can be determined as a function of time and/or conversion: this gives important information for thermal reactor design and reactor safety. If the other parameters are known and the heat release rate *qr* can be measured according to Eq. 5.1, a determination of the term *UA* is possible during a reaction or physical change using Eq. 5.4.

b) Heat flow (or heat flux) calorimetry

In a second type of calorimetry calculation, the temperature of the jacket is kept essentially constant at any time by ensuring a high mass flow rate of the fluid in the jacket. According to Eq. 5.1 if the term mc·cpc increases significantly, the temperature difference between the inlet and outlet of the jacket fluid will decrease even for high heat release rates in the reactor. For example, with a calibration power input of 25 W in a 2-litre metal reactor of a well known bench scale reaction calorimeter, a typical temperature difference between the reactor and jacket might be T_r-T_j = 2,5 K, whereas the difference in temperature of the cooling fluid at jacket outlet and inlet would be ~0.025 K. As a direct consequence the heat flow rate signal is about 100-fold times that of the heat balance signal and is easier to measure accurately. The heat balance equation is now written:

$$\dot{q}_r = U \cdot A \cdot (T_r - T_j) + m_r \cdot c_{pr} \cdot \frac{dT_r}{dt} + \dot{q}_{loss} \qquad \text{[Eq. 5.4]}$$

where:
U: overall heat transfer coefficient
A: heat transfer area
T_r: temperature of the reaction mass
T_j: jacket temperature

In principle, implementation of this method requires the knowledge of the overall heat transfer coefficient and the heat transfer area throughout the whole course of the reaction. In practice, a constant value determined from one calibration, or a linearly interpolated relationship for the heat transfer coefficient determined from two calibrations before and after the reaction, is used.

Most calibration devices in reaction calorimeters are simply an electrical resistance heater submerged in the reaction mixture. It can be used to determine unknown variables, usually in the absence of chemical reactions or physical changes. If the reactor temperature remains constant then the overall heat transfer coefficient multiplied by the heat transfer area (factor $U \cdot A$) can be determined according to Eq. 5.5. This can be applied to both the steady state before calibration and the steady state during calibration. By subtracting these 2 equations there is no need to determine the heat loss term (which is assumed to remain constant.)

$$\dot{q}_c = U \cdot A \cdot (T_r - T_j) + \dot{q}_{loss} \qquad \text{[Eq. 5.5]}$$

where:
$\dot{q}_c$: heat power introduced by the electrical heater

Significant changes in overall heat transfer coefficient as well as a change in effective heat exchange area during batch and semi-batch reactions can be due to changing viscosity or density, reactor wall fouling or increasing reactor fill level (and consequently changing stirring vortex.) These changes are often strongly non-linear with either reaction time or reactant conversion. It is not easy to correct for these effects using either stirrer torque measurements or geometrical filling height calculations. Such corrections are normally sufficient for thermal measurements related to safety studies of chemical processes. However, these types of calorimeter are not optimally suited to perform precise measurements if big changes in the overall heat transfer coefficient (due e.g., to changes in the viscosity) are observed during the reaction.

c) Temperature oscillation calorimetry

The principle of Temperature Oscillation Calorimetry was developed in the Technical University of Berlin by the group of Prof. Reichert. It allows the on-line evaluation of the change in the heat transfer coefficient and the study of mixing in high viscosity systems. The principle of temperature oscillation calorimetry is based on an oscillatory response that is evaluated during a reaction or physical change in the calorimeter [Carloff et al. (1994), Tietze et al. (1995)]. A sinusoidal variation of small amplitude (1-2°C) is imposed on the reactor set point temperature. The oscillation is transferred to the

reactor and jacket temperature in a way that depends on the heat transfer rate. The phase shift between the temperature variations of the jacket and the reactor makes it possible to infer the value of the heat transfer coefficient during the reaction. The frequency response analysis involved requires linearisation of the reaction kinetics at the mean value of the temperature range used. This new method allows quasi-isothermal heat flow calorimetric studies under conditions of continuously variable heat transfer coefficient and requires only the use of a mathematical procedure for evaluation of the measured data and a slightly modified process operation (TOC calorimeter Bocal [Ferrara et al. (1998)], modified reaction calorimeter RC1).

d) Adiabatic calorimetry

Some commercially available devices can also operate in a pseudo adiabatic mode. In this case the jacket temperature is set at any time close to the value of the reactor temperature. The applications of adiabatic calorimetry for investigation of chemical reactions and the definition of the chemical and safety data like the adiabatic temperature rise and the value for the "Time to maximum rate" (TMR) are described in the literature [Singh (1992), Townsend (1980), Steinbach (1998), Mosebach et al. (1997)]. Extreme caution is advised when carrying out pseudo adiabatic experiments on the scale of one or two litres. Violent runaway reactions can, and have, occurred. The possibility of these being induced must first be eliminated using the thermal screening techniques described in chapter 3 of HarsBook, or the small scale adiabatic techniques described in Chapter 6.

5.3.3. Devices using a constant surrounding temperature (e.g. a jacketed vessel with a constant jacket temperature)

a) Isoperibolic calorimetry

The **isoperibolic** operation mode requires a constant surrounding temperature (e.g., a jacketed vessel with constant jacket temperature) (e.g., reaction calorimeter RC1, CAL*WIN*, SETARAM DRC) [Grønlund (1990), Küssner (1987), Stockhausen et al. (1992), Stockhausen (1996)]. Ideally, the calorimeter should be designed in such a way that the maximum temperature difference between the reactor and the surroundings is limited to few Kelvin. The advantages of this quasi-isothermal mode of operation can then be used: mass and heat balances can be simplified and solved as independent equations. For this type of calorimeter the heat balance equation Eq. 5.4 applies.

With some calorimeters both heat flow and heat balance calorimetry is possible, for example by adding an additional vessel (filled with water or oil) between the reactor and the jacket. By a combination of the heat flow from the reactor to this additional vessel (the thermal ballast) and the heat flow from this vessel to the jacket, which is held isothermal during the reaction, it is possible to determine the chemical heat flow independently from the heat transfer value and also the change of the heat transfer value during the reaction. (CAL*WIN* by Moritz et al). Other isoperibolic calorimeters use a second reference vessel in order to compensate for fluctuations in the temperature of the heat exchange medium.

The reaction flask in an oil bath could be regarded as an isoperibolic calorimeter. The main problem is that the value of *UA* in Eq. 5.4 is unknown. This problem is solved in commercial calorimeters by calibration for the UA value using e.g., an electrical resistance heater.

b) Power compensation calorimetry

In Power Compensation calorimetry the reactor is maintained at constant temperature. The cooling jacket is also held isothermally some 10 to 20 $^{\circ}$C below the temperature of the reactor. The power supplied to an electrical heating element (preferably with a large surface area) submerged within the reactor is then continuously manipulated so as to maintain the reactor at the desired temperature. As an exothermic reaction develops the power supplied by the heater is backed off by an amount exactly equal to the power generated by the reaction under study. Electrical systems have much faster response times than circulating oil loops so power compensation can give excellent temperature control, particularly for reactions with fast kinetics. On the other hand the method may not be suitable for use with high viscosity systems or those where fouling of the electrical heater occurs.

5.4. Assessment of different types of reaction calorimeters

The advantages and disadvantages of the different calorimeter types and operation modes are shown in the following table:

Calorimeter type and operation mode	Advantages	Disadvantages
Heat balance calorimeter **Isothermal** T_R = const. T_J = f(t)	Useful if the overall heat transfer coefficient and/or the exchange area change strongly and non- linearly during the time of reaction or physical change	▪ Temperature difference in the jacket must be measured with high resolution ▪ A feedback temperature control system for the reactor must be implemented in the device ▪ If controlled temperature changes are to be allowed (e.g., a linear temperature ramp), the specific heat capacity of the reaction mixture and reactor internals must be known
Heat flow (or heat flux) calorimeter **Isothermal** T_R = const. T_J = f(t)	Useful if the overall heat transfer coefficient and/or the exchange area doesn't change strongly during the time of reaction or physical change	▪ The overall heat transfer coefficient must be determined (maybe at several times) by calibration ▪ A feedback temperature control system for the reactor must be implemented in the device ▪ If controlled temperature changes are are to be allowed (e.g., a linear temperature ramp), the specific heat capacity of the reaction mixture and reactor internals must be known

Power compensation **Isothermal** T_R = const. T_J = const.	• The response time of an electrical heating circuit is generally much faster than that of a circulating oil loop. Reactions with fast kinetics can therefore often be studied with better temperature control. • Calibration steps for UA are not required at the start and end of every reaction stage. For this reason experiments are generally much quicker than the equivalent heat flow experiment. • Reaction power outputs up to 100 Watts per liter can be handled.	• A large surface area heater should be used to minimize the surface temperature of the heating element. • Fouling on the surface of the heater may occur in very viscous systems or with heat sensitive materials. The use of power compensation calorimetry in these circumstances is not advised. • UA can vary during the course of an experiment so interpolation between the baseline power at the start and end of the reaction is still required. (This disadvantage applies equally to heat flow calorimetry.)
Isoperibolic T_R = f(t) T_J = const.	• Low cost equipment • Similar to an isothermal calorimeter if the heat transfer coefficient is high enough (i.e. the reactor temperature is only a few degrees above the jacket temperature).	• The temperature in the reactor depends on the heat release rate • No emergency cooling in the case of a "runaway" in the lab
Adiabatic T_R = T_J Heat losses are very small	• temperature is proportional to conversion (for a single reaction) • relatively small apparatus • fast reactions can be studied	• reactions and reaction rate depend on temperature • Separation of temperature and concentration effects is only possible by modelling • Can be hazardous for exothermic reactions. Careful hazard identification and risk assessment required before experiments are started

5.5. Conclusions

Reaction calorimeters allow the user to perform chemical reactions and induce physical changes (e.g., distillation, crystallisation) under desired conditions in the laboratory. Usually they offer the possibility of monitoring "on line" the heat exchanged by these processes. This is very useful as a basis for scale-up to the pilot or industrial scale. The thermal risks associated with the process can be easily assessed. Other analytical devices (e.g., on-line FTIR or Raman-spectroscopy, particle sizing probes, turbidity probes, pH or other ion selective probes, etc) can be used in association with a calorimeter to obtain data for modelling and process optimisation studies. It is thus strongly recommended that reaction calorimetry measurements should be performed throughout the different stages of the life of a chemical process (specially before the pilot production or if significant changes are to be introduced.)

5.6. References

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