

ISOTHERMAL HEAT FLOW CALORIMETER

T.K.Wright* and C.W.Butterworth*

Reaction Calorimeters are used to simulate experimentally the behaviour of large scale (semi) batch chemical processes. The measured heat flow profile is used to size forced cooling systems, to determine safe reactant addition times and to detect induction periods and other accumulations of reactants and intermediates which could lead to runaway hazards.

A simple calorimeter has been developed based on the compensation heating principle and the principles of design are discussed. The merits and limitations of this type of calorimeter are compared with those of the commercially available but expensive variable heat flow calorimeters. Examples of the use of the calorimeter are given. Isothermal calorimetry complements adiabatic calorimetry and the use of both is required to define the normal process, the effect of maloperations and runaway consequences.

KEYWORDS: Reaction Calorimeter, Heatflow, Kinetics.

INTRODUCTION

For the assessment of chemical reaction hazards in plant operation three types of calorimetry are used.

Scanning calorimetry is useful as a screening test. It can give a preliminary indication of the size of the normal process exotherm (if reactants can coexist at ambient) and indicate the existence of potential decompositions. It does not offer a direct simulation of the normal semi batch process used in chemical manufacture, its maloperation, and runaway reaction therein.

Experimental simulation of reactor runaway and the production of quantitative power output and kinetic data for stability and venting calculations is best achieved by adiabatic calorimetry.

In this technique steps are taken to minimise heat losses from the reactants to both the container and the environment and thereby simulate the conditions prevailing in large scale chemical plant with loss of cooling or inadequate cooling.

*Imperial Chemical Industries PLC (Organics Division)
Hexagon House, Blackley, Manchester.

power will normally be ca 25 watts but this will be divided into a starting electrical power of 20 watts for exotherms with 5 watts for endothermic processes. With this arrangement the peak measurable power will lie in the range 100-200 watts/lit comfortably above normal process power dissipation by jacket cooling (Table 1). The attractiveness of the display is enhanced by ensuring that materials are added in a uniform way. For the scale of operation used and with the objective of direct simulation of process addition times the peristaltic pumps must be capable of delivering uniformly materials of a frequently aggressive nature at rates as low as 5 ml/hr.

Since the calorimeter is located in an oven a decision has to be made on the sensible heat input with the feed reactant. For ambient feed the feed tube will be jacketted with a coolant.

Desirably the weight of material added should be logged during the course of the experiment to assist in subsequent interpretation of power output changes. Electrical (compensation) power is supplied to the calorimeter via a Nichrome heater (ca 25 ohms) in a thin glass sleeve, using for safety reasons a controlled 50 volt supply.

Most conveniently digital computer techniques are used to run the calorimeter. The calorimeter temperature is measured by a thermocouple, converted to a digital value and the deviation from set point via a suitable control algorithm is used to generate a binary signal in the range 0-255 to operate a solid state relay. The SSR supplies alternating current to the calorimeter heater and the proportion of the AC cycles allowed to pass is governed by the driver value. Nichrome wire has a sufficiently low temperature coefficient for a linear relationship to be obtained between SSR driver value, cycles passed and power supplied.

The SSR driver value is calibrated using an electronic wattmeter, is displayed during the course of the experiment and is logged. SSR driver value sets a limit on resolution at $25/256 = 0.1$ watt.

Control strategy demands a fast response if rapid chemical changes are to be followed and temperature to remain constant. The algorithm must be appropriately tuned. Primary screen display Fig.2 is not attractive but the data can later be processed/smoothed off line to eliminate short term control spikes.

Power loss to the cooling system should remain constant during any simulation. Power loss is given by eqn 1. Heat transfer area A is controlled by using a bottom cooling jacket the area of which is smaller than the wetted area of the initial agitated calorimeter charge. This ensures that A does not change during semi batch operation. The service side temperature T_s must be accurately controlled. For a cooling area of ca 80 cm² and an electrical compensation power dissipation of 20 watts the value of $T_p - T_s$ will be about 10K - equivalent to an OHTC of 250 w/m²/K. Since power is directly proportional to $T_p - T_s$ a variation of ± 0.1 K in bath temperature will produce a power swing of $\pm 1 \times 20/15 = \pm 0.13$ watt and this also sets a limit on accuracy. Substantially larger values of $T_p - T_s$ can lead to crystallisation problems with some industrial processes and are not recommended.

The calculated overall heat transfer coefficient with this arrangement at ca. 250 w/m²/K is comparable to the values obtained with industrial reactors despite the low conductivity of glass.

OHTC receives contributions from service side film resistance, glass resistance and process side film resistance. Service side film resistance is controlled by ensuring a good and stable velocity of coolant from the constant temperature cooling baths which are available commercially.

The major problem with this simpler design of calorimeter lies in the effect of process side heat transfer changes. Process side heat transfer is controlled only in so far as agitation speed is controlled at ca 500 rpm. Film transfer resistance is not controlled and problems arise if the batch thickens or otherwise has a substantial change in process side film coefficient. A change in OHTC is perceived as a change in compensation power between start and end of simulation base lines. Fig.3

In our experience of process simulation by isothermal calorimetry, about 10% of processes suffer a heat transfer change of sufficient magnitude to present interpretation problems. The problem is particularly acute for protracted low power output processes. In such cases the process can be diluted, the time scale reduced to increase power output and reduce interpretation errors or adiabatic calorimetry can be used.

A system designed to overcome the problem of changing OHTC - a truly constant heat flux calorimeter has been described by Igarishi & Katayama (9) based on a diathermic envelope used in DTA systems. The system operates by maintaining a constant heat flux across a secondary barrier outside the reactor but adjacent to it. Constant heat flux is ensured by using a cooling bath and external heater combination with a differential temperature controller which keeps ΔT constant across the secondary barrier. As heat transfer across the reactor wall falls due to OHTC change the mean temperature between the faces of the outer barrier falls but not the temperature difference and this reinstates the heat flow through the reactor jacket to the constant value. The system has not been investigated.

Gas Measurement

The calorimeter aims to measure both heat and gas flow. Gas evolution is measured using a U tube containing oil. Gas delivered into one side of the U-tube displaces the oil and when 100 ml have been displaced a valve is opened for 2 seconds to allow the gas to escape. The event is logged and gas evolution is eventually displayed as a series of 100ml steps which for the larger volumes that will be of concern for scrubber sizing is an acceptable output.

DATA PROCESSING

(a) Power output/Heat of reaction/Changes in OHTC/gas rates

Power, weight and gas evolved data logged on disk are processed off line at the end of the simulation using a microcomputer. The electrical (compensation) power data are recalled from disk to calculate the average value of start power over the 10 minutes prior to the start of reaction.

For the chemical reaction period the average electrical power PE is calculated at intervals of 1/140 of the total run time. A value of the average electrical power is also calculated when the reaction is complete and the baseline re-established. The values of PE and time are stored in an array in the micro.

To calculate the chemical power PC from the measured electrical power PE it is necessary to construct a power baseline between the start and end of the process and to calculate from that base line a value of the chemical zero power PB associated with each value PE. Chemical power PC is given by

$$PC = PB - PE \dots \dots \dots (3)$$

Options for the baseline as shown in Fig.3 are:-

1. Start to end of work-off
2. Start to end of addition to meet final power extrapolated back
3. Start extrapolated forward
4. Final power extrapolated back
5. Start to end proportionally rated to heat evolved

and all are made available within the software.

The choice of baseline depends on the cause of the OHTC change and the availability of start/final power values but 5 will be the most generally used option the assumption being made that concentration of the material causing the baseline change is directly related to the heat evolved. The program assumes baseline 1 in an initial calculation of PC. Area integration of the plot of PC v time is then carried out to determine an initial heat of reaction.

New base line values PB are then calculated with the baseline change allocated according to heat evolved. Recalculation of PC and area integration yields a new heat of reaction. 2/3 such iterations are sufficient to produce convergence.

Both heat evolved during reactant addition and heat evolved during work off are calculated and give a quantitative indication of the size of reactant accumulations. Power, weight added and gas evolution data are finally plotted on a Hewlett Packard 7470 A plotter.

Display of accumulation is shown in Fig.4 for the addition of acetic anhydride (1.5 mol) to methanol (3.0mol) at 60°C. In this example 66% of the acetic anhydride has accumulated at the end of addition.

An example of an accumulation leading to runaway is shown in Fig.5 for the nickel catalysed reduction of a nitro compound by hydrazine at 77°C. In the process as operated all the nitro compound and nickel were present prior to the start of hydrazine addition and under these conditions the nitro compound oxidises the nickel catalyst to an inactive form and allows the hydrazine to accumulate. Eventually there is sufficient hydrazine present to reduce the catalyst back to its active form, but the accumulation then works off leading to runaway and calorimeter saturation at 24 watts. Addition of the catalyst after the start of hydrazine addition improves the power profile Fig.6, but it is still not satisfactory for large scale plant operation.

The change in calorimeter baseline caused by OHTC change can be used to give an indication of the likely change in process OHTC - an important factor both in power dissipation/safety and in process cycle time/productivity.

Electrical power being dissipated by the cooling system is defined by equation 1. Other losses.gains (C) are assumed constant so that the total electrical compensation baseline power is given by:

$$PB = (OHTC \times SA \times \Delta T) + C \dots \dots \dots (4)$$

The calorimeter can be calibrated with water as process fluid to yield a relationship between electrical power and ΔT . Provided the same coolant is retained the relationship can be used to calculate the power dissipation expected for water at the value of ΔT being used in the process simulation experiment. Actual start and final baseline power dissipations in the simulation can then be referred to the water value to give the % heat transfer rate relative to water before and after reaction.

Gas evolution rate is calculated from the volume logged by the gas burette event counter and the time elapsed between counts and is divided by the weight present.

(b) Kinetics

The calorimeter can also be used to generate isothermal kinetic data. For power decay curves, power output P can be converted into chemical reaction rate using

$$P \text{ watts/lit} = \frac{dc}{dt} \text{ mol/lit/sec} \times \Delta H \text{ joules/mol} \dots \dots \dots (5)$$

Concentrations can be inferred (with some assumptions) from the heat remaining to be evolved. For the reaction $A + B \rightarrow$ using the rate expression

$$-\frac{dA}{dt} = k [A]^n [B]^m \dots \dots \dots (6)$$

a plot of rate against $[A]^n [B]^m$ should yield a straight line through the origin of slope k.

Power v time data from the acetic anhydride/methanol reaction Fig.4 during work-off have been processed by the technique. At the degree of conversion examined a good fit is obtained for first order behaviour in acetic anhydride Fig.7 with a rate constant of $3.6 \times 10^{-4} \text{ sec}^{-1}$ at 60°C.

CONCLUSION

Isothermal calorimeters equipped to measure heat and gas flows are powerful tools for the quantitative simulation on the laboratory scale of large scale (semi)batch process operations. The simulations

- (a) Highlight problems with heat and gas flows likely to lead to hazard in large scale manufacture and provide a ready means of exploring the effects of process changes.

- (b) Improve process understanding.
- (c) Provide quantitative thermodynamic, stoichiometric and kinetic data for process design.

REFERENCES

1. Columbia Scientific Industries Corporation : Technical Information Bulletins 1-4.
2. Smith DW, Taylor, M.C., Young R and Stephens T. American Laboratory June 1980.
3. Hub, L. I.Chem.E.Symp Ser.No.68, 3K/1 1981
4. Wright, T.K. and Rogers, R.L. I.Chem.E.Symp.Ser.No.97, 121-132 (1986).
5. Anderson, H.M. J.Polymer Sci. Part A1 Vol.4 783-791 (1966).
6. Anderson, H.M. J.Polymer Sci. Part A1, Vol.7, 2889-2896, (1969).
7. Regenass, W. Am.Chem.Soc.Symp.Ser.No.65, 37-49 (1979).
8. Weir, E.D., Cravenstine G.W. and Hoppe, T.F. Plant/Operations Progress 5, No.3, 142-147, 1986.
9. Igarashi S, and Katayama, S. Eur.Polymer J. Vol.15 805-9 (1979).

TABLE 1

Jacket Heat Transfer Area and Power Dissipation for Specific Temperature Difference from Cooling Medium
For Overall Heat Transfer Coeff= 250 Watt/M²/K

Nominal Reactor Size	Jacket Area	Power Output in Watts/Lit for Temp Difference-K					
		20	40	60	80	100	
Gall	Lit	M ²					
5	23	.3	80.4	160.8	241.3	321.7	402.1
9	45	.7	82.2	164.4	246.6	328.8	411.1
19	90	.9	50.0	100.0	150.0	200.0	250.0
49	225	1.5	33.3	66.6	100.0	133.3	166.6
98	450	2.4	26.6	53.3	80.0	106.6	133.3
200	910	3.8	20.8	41.7	62.6	83.5	104.3
298	1360	5.7	20.9	41.9	62.8	83.8	104.7
498	2270	8.2	18.0	36.1	54.1	72.2	90.3
749	3410	10.4	15.2	30.4	45.7	60.9	76.2
998	4545	13.1	14.4	28.8	43.2	57.6	72.0
1498	6820	15.0	10.9	21.9	32.9	43.9	54.9
1997	9090	19.1	10.5	21.0	31.5	42.0	52.5
2997	13640	26.9	9.8	19.7	29.5	39.4	49.3
3996	18185	32.5	8.9	17.8	26.8	35.7	44.6
4995	22730	37.2	8.1	16.3	24.5	32.7	40.9
8791	40000	54.3	6.7	13.5	20.3	27.1	33.9

Reactor Data ex Sybron/Balfour

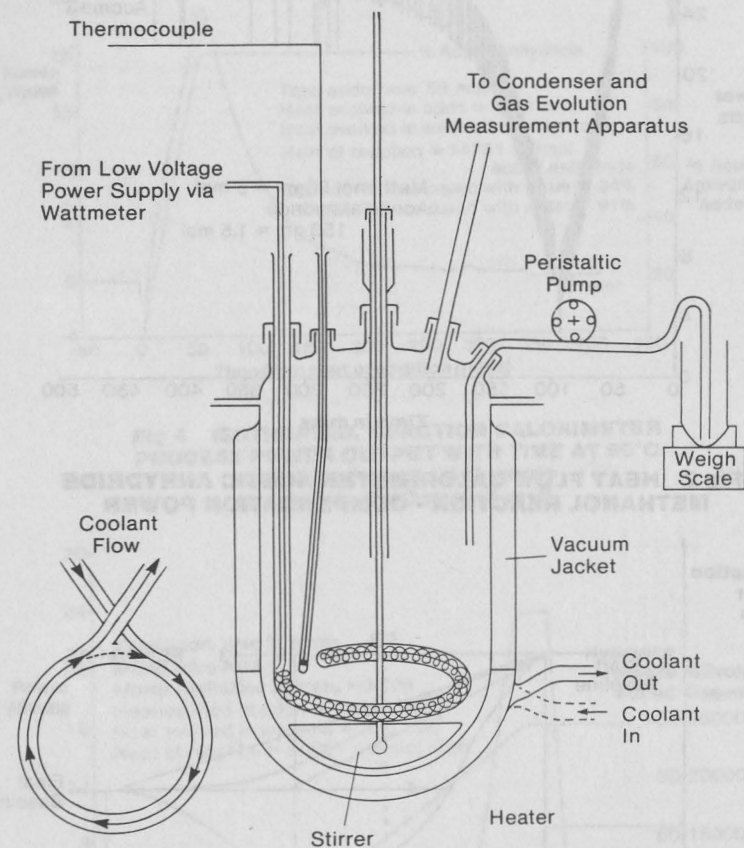


Fig 1 - ISOTHERMAL REACTION CALORIMETER (COMPENSATION HEATING)

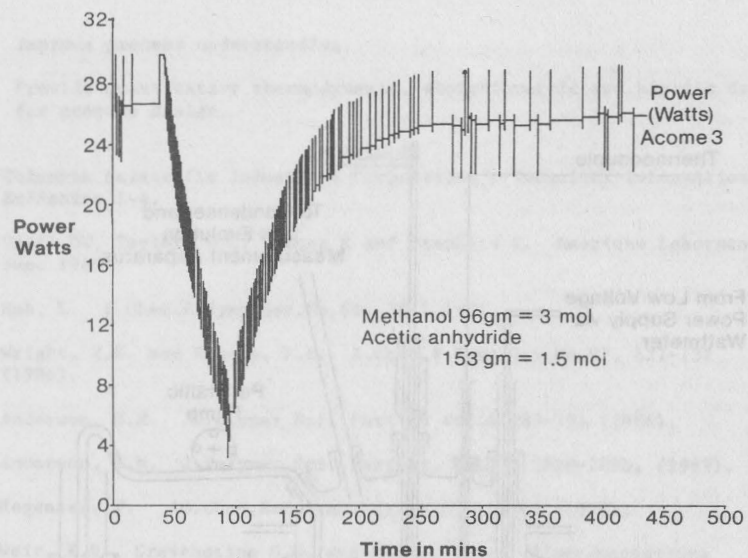


Fig 2 HEAT FLOW CALORIMETER ACETIC ANHYDRIDE METHANOL REACTION - COMPENSATION POWER

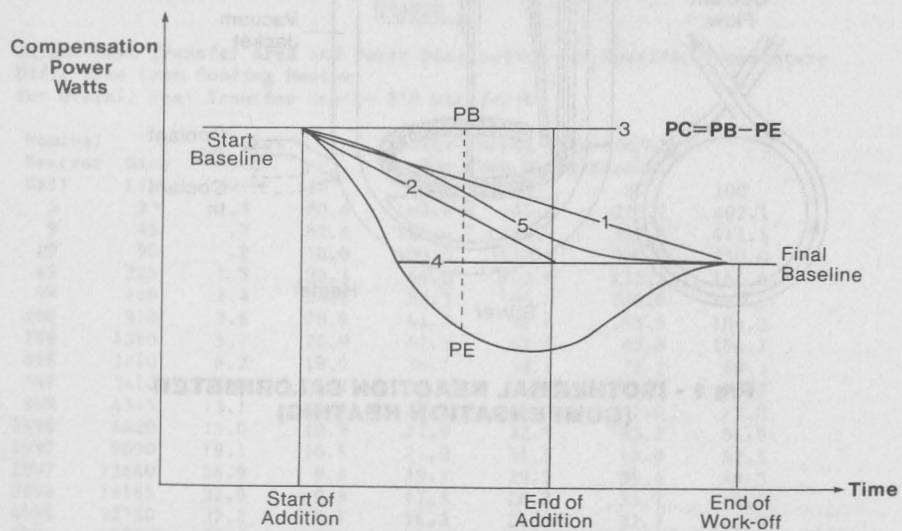


Fig 3 SMOOTHED PLOT OF COMPENSATING POWER AGAINST TIME-TO SHOW BASELINE TYPES AND CALCULATION OF CHEMICAL POWER

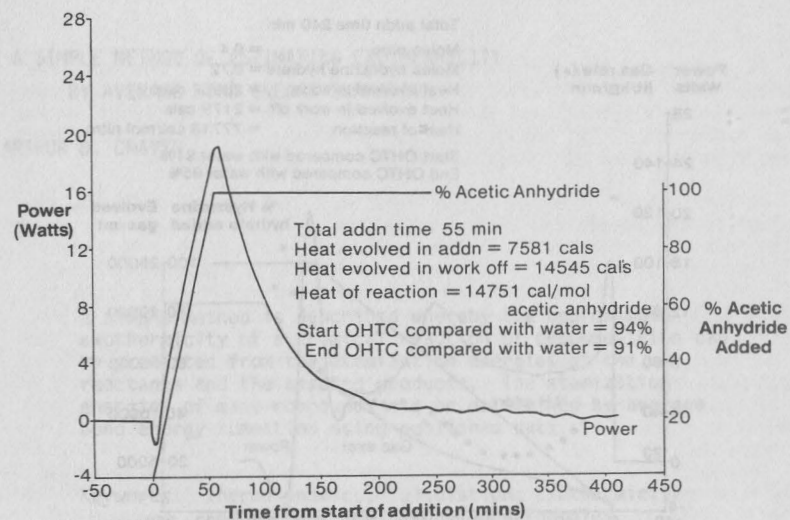


Fig 4 ISOTHERMAL REACTION CALORIMETER PROCESS POWER OUTPUT WITH TIME AT 60°C Addition of Acetic Anhydride (1.5 mol) to Methanol (3 mol)

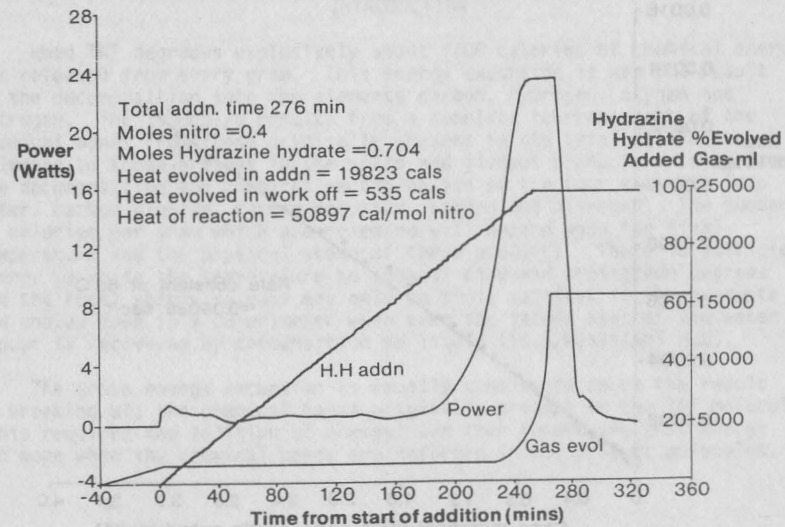


Fig 5 ISOTHERMAL REACTION CALORIMETER PROCESS POWER OUTPUT WITH TIME AT 77°C Nitro reduction by Hydrazine - catalyst in before Hydrazine

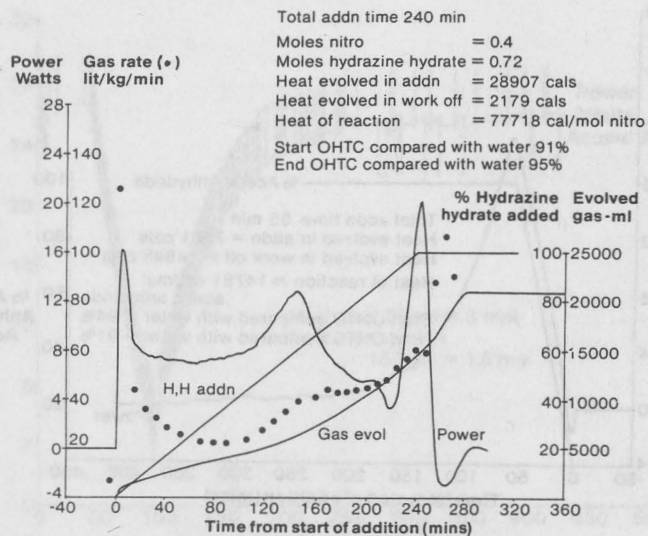


Fig 6 ISOTHERMAL REACTION CALORIMETER PROCESS POWER OUTPUT WITH TIME AT 77°C Nitro reduction by Hydrazine - Ni alloy added after 5% N₂H₄ added

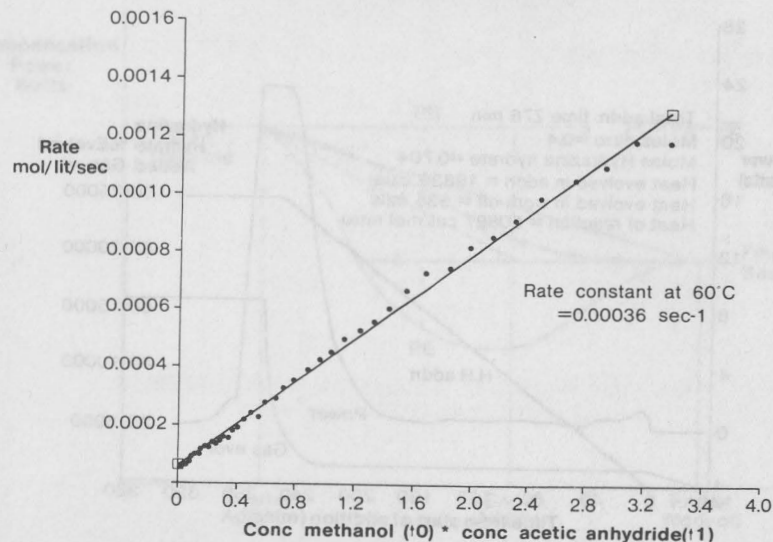


Fig 7 ISOTHERMAL REACTION CALORIMETER PLOT OF RATE AGAINST PRODUCT OF CONCENTRATIONS IN WORK-OFF Addition of Acetic Anhydride (1.5 mol) to Methanol (3 mol)

A SIMPLE METHOD OF ESTIMATING EXOTHERMICITY BY AVERAGE BOND ENERGY SUMMATION

ARTHUR D. CRAVEN

A simple method is described whereby the approximate exothermicity of a chemical reaction or decomposition can be predicted from the atomization energies of the reactants and the assumed products. The atomization energies of many compounds can be determined by average bond energy summation using published data.

Keywords: Thermodynamics; Calculation; Exothermicity; Combustion; Explosion; Bond Energies

1. INTRODUCTION

When TNT degrades explosively about 1100 calories of chemical energy are released from every gram. This energy excursion is not the result of the decomposition into the elements carbon, hydrogen, oxygen and nitrogen. The 1100cal/g results from a complete rearrangement of the chemical bonds from those originally present in the trinitrotoluene molecule to those present in the solid and gaseous products arising from the decomposition and chemical recombination of the four elements into water, carbon dioxide, carbon monoxide, carbon and nitrogen. The number of calories per gram which are released will depend upon the final temperature and the physical state of these products. There is sufficient energy to raise the temperature to several thousand centigrade degrees and the total energy release may only be truly manifest if the products are cooled down in a calorimeter when even the latent heat of the water vapour is recovered by condensation to liquid (10.52kcal/mol H₂O).

The gross energy excursion is usually considered to be the result of breaking all the chemical bonds originally present in the TNT molecule (this requires the addition of energy) and then recovering this energy and more when the chemical bonds are reformed in the product molecules.

Burgoyne Consultants Ltd., Burgoyne House, Chantry Drive, Ilkley, West Yorkshire, U.K.