

# INDEX

- A**
- additions of chemicals 113
  - accelerating rate calorimeters
    - (ARC) 42, 55, 86, (g)
  - acceptable level of safety 19
  - accumulation 7, 33, 34, 71, 75, 113, 163, 177, 184, (g)
  - activation energy 52, 68, (g)
    - decomposition 56
  - addition rate 33, 93
  - adiabatic (g)
    - calorimeters 41, 42, 71, 93
    - calorimetry 20, 84
    - conditions 29, 56
    - Dewar calorimetry 51, 86
    - induction time (g)
    - (pressure) Dewar calorimetry 41, 119
    - self-heat rate 57
    - temperature rise 6, 23, 84, (g)
  - ageing effects 28
  - agitation 10, 77, 108, 113, 161, 162, 178, 182, 183
    - failure 16, 18, 68, 75, 93
  - agitators
    - configuration 33
    - type 74
  - analysis of incidents 7
  - AND gates 100
  - apparent activation energy (g)
  - ARC (see accelerating rate calorimeter)
  - Arrhenius 47, 56, 79, 90, (g)
    - pre-exponential factor 49, 68, (g)
  - assessment
    - hazards 14, 46, 108, 112
    - procedure 14
  - strategy 13
- Association of the British Pharmaceutical Industry (ABPI) 20**
- autocatalysis 28, 34
  - autocatalytic reaction (g)
  - autoignition 127, 131
    - temperature 187, (g)
  - average bond energy summation 25
  - Avogadro's principle 58
- B**
- basic screening tests 20
  - basis of safety 52, 92, 161, 162, 172
    - selection and specification 106, 131
  - batch
    - operations 2, 64, 107, (g)
    - process (g)
    - reactions 33, 65
    - reactors 2, 33, 114, 126, (g)
  - bench scale (g)
  - bleve (g)
  - blowdown (g)
  - British Plastics Federation (BPF) 7, 101
  - bursting discs 120, 165, 167, 176, 185, 186, 192
    - rupture discs 187
- C**
- calorimetric techniques 35, 64
  - calorimetry 64, 72, 79
    - isoperibolic 36
    - isothermal 20
    - under reflux 64, 79
      - example 81
  - case histories 13, 161–195
  - checks of safety systems 125, 135, 139, 194

- chemical hazard assessment, example 196
- chemical manufacture 1, 108
- chemical processes involved in incidents 7
- chemical reaction hazards 1, 6, 25, 52, 106, 161, 207
- assessment 13, 15, 17, 46, 94
- control 1
- evaluation techniques 20
- CHETAH 26, 27
- CIMAH (see Control of Industrial Major Accident Hazards Regulations)
- combined probabilities 100
- condensed phase explosion (g)
- confined explosion (g)
- containment (g)
- loss of 12
- contamination 18
- continuous flow stirred tank reactor (CSTR) (g)
- continuous processes 2, 107, 114
- continuous reactors (g)
- Control of Industrial Major Accident Hazards (CIMAH) Regulations 4, 140
- Control of Substances Hazardous to Health (COSHH) Regulations 3, 4, 133
- control systems 3, 13
- convective inside film coefficient 64
- cooling capacity 2, 6, 75
- cooling, loss of 18, 75, 84
- COSHH (see Control of Substances Hazardous to Health Regulations)
- crash cooling 106
- critical
- diameter 163
- mass (g)
- steady-state temperature (CSST) (g)
- temperatures 54, (g)
- CSST (see critical steady-state temperature)
- CSTR (see continuous flow stirred tank reactor)
- D**
- Damkohler number 64
- data
- decomposition pressure test 56
- detonation 163
- Dewar calorimetry 66
- DSC and DTA 54
- evaluation 50, 52
- heat flow/power compensation calorimeters 70
- ICI 10 g sealed tube test 60
- insulated exotherm test 55
- interpreting 46, 84
- isoperibolic calorimetry 69
- literature 20
- pressure 61
- screening tests 52
- decomposition
- energy (g)
- kinetics 55
- temperature (g)
- decomposition pressure test (DPT) 28, 30
- data 58
- data trace 59
- defensive measures (g)
- deflagration 24, 27, 55, (g)
- delayed initiation of desired reaction 75
- Design Institute for Emergency Relief Systems (DIERS) 117, 119, (g)
- detonating explosives 24
- detonation 27, (g)
- Dewar calorimetry 35, 41, 55, 68, 79
- data 66
- Dewar flask 29
- differential scanning calorimetry (DSC) 28, 55, 85, 88, 179, (g)
- data 54, 92

differential thermal analysis		explosibility testing	25
(DTA)	28, (g)	explosions	1, 4, 6, 12, 127, 131 (g)
data	54		
dimensionless concentration	67	<b>F</b>	
dimensionless numbers	64, 72	failure mode effect (and criticality)	
dimensionless rate	67	analysis (FME(C)A)	(g)
discharge		fault trees	94, 114, 209, (g)
nature of	115	analysis	99
safe disposal	123	batch reactors	101
single or two phase	117	BPF generic trees	102–104
three phase	118	demand tree	101
to atmosphere	4	ethoxylate reactor tree	105
disposal systems	115, 120	reactors	101
DPT (see decomposition pressure test)		structure	99
drown-out	106, 114	FIA method of vent sizing	119
DSC (see differential scanning calorimetry)		fire and explosion hazards	3, 126, 161, 175
DTA (see differential thermal analysis)		evaluation	126, 211
dumping	123, 186	example of evaluation	211
dump tanks	41, 76, 114, 118	flames and hot surfaces	130
<b>E</b>		flammable conditions	128, 211
EC 'Seveso' directive	5	avoidance	131
electrical equipment	135	flammable materials	1, 12
emergency procedures	135, 140, 161, 195	flare stacks	121
emergency relief systems	110, 114	FME(C)A (see failure mode effect (and criticality) analysis)	
emergency relief venting	2, 93, 106, 114, 120, 185	foaming	79, 117, 194
engineering design	3, 13, 161	foaming behaviour, testing	118
enthalpy of reaction	6	Frank-Kamenetskii	47, 49
environmental hazards	4, 14	frequency	209, (g)
equipment sensitivity	40	full scale production	16, 40, 43, 67, 94
evaluating chemical reaction		<b>G</b>	
hazards	20	gas evolution	20, 27, 32, 58, 64, 78
event tree	(g)	measurement	39, 78, 93
exotherm	(g)	gassy systems	93, 115
exothermic chemical reactions	2, 3, 16	general lessons from incidents	13
exothermic decomposition	209	geometric factor	74, 77
exothermicity	25, 27, 29, 43, 51, 53, 65	Grossel's method	121
experimental tests	15, 16, 20, 46	<b>H</b>	
explosibility screening	21, 23, 162	hazard analysis (Hazan)	94, 98
computer methods	26	example of use	206

- human error 101  
 hazard assessment 14, 108, 112, 176  
     procedures 161  
 Hazan (see hazard analysis)  
 hazard and operability study  
     (Hazop) 19, 94, 170, 171, (g)  
     batch process 98  
     guidewords 96  
     procedure 97  
     recording sheets 98  
     study co-ordination 95  
 hazardous chemical reactivity (g)  
 hazards (g)  
     assessment 14, 16, 52  
     consequences (g)  
     environmental 3, 14  
     fire and explosion 3, 126  
     general 1, 14  
     health 1, 3, 133  
     operational 1  
     plant operation 126  
     toxic 3, 14, 126, 133  
     types of 3  
 Hazop (see hazard and operability study)  
 Health and Safety at Work etc Act 1, 4  
 Health and Safety Executive 6, 140, 161  
 health hazards 1, 3  
     control 133  
 heat balance 50, 69  
 heat capacity 34, 35, 71  
 heat flow calorimeter 35, 38, 70, 71, (g)  
 heat flow/power compensation  
     calorimeters 69  
 heat generation 49  
 heat loss 49, 51, 67  
 heat of reaction 2, 20, 22, 28, 34, 47,  
     52, 67, 70, 84, 196, (g)  
 heat release 28  
 heat transfer 3, 13, 35, 47, 64,  
     77, 161, 167, 168  
 heat transfer/film coefficient 48, 53, 72  
 heat transfer mechanisms, influence  
     on data 46  
 hold times 33, 86  
 human factors 11  
 hybrid mixture (g)  
 hybrid system 116  
 hydrolysis 7, 168, 176, 178, 180  
**I**  
 ICI 10 g sealed tube test 28, 30  
     data 60  
 IET (see insulated exotherm test)  
 ignition  
     avoidance 131  
     external 127  
     source of 3, 129, 212  
 impact friction 130  
 incident (g)  
 incidents in batch reactors 1, 2, 126, 137  
     analysis 7  
     case histories 13  
     consequences 13  
     general lessons 13  
     industries involved 12  
     injuries and damage 12, 114  
     main causes 2, 8, 136  
 independent team (Hazop) 17  
 induction period/time (g)  
 induction time effects 31  
 inert gas blanketing 132  
 inherently safe 16, 106, 110, (g)  
 inherent safety 161  
 inhibiting runaway reaction 123, 161  
 inhibition 75, 115, 186, (g)  
 initial exotherm temperature 52, 55  
 initial screening 28  
     tests 22, 27  
 injuries and damage 12  
 instrumentation and control 114, 161, 184  
 insulated exotherm test (IET) 28, 29  
     data 55  
     data trace 57  
 interpreting data 46  
 interpreting runaway reaction data 84  
 isoperibolic calorimeter 69

isoperibolic calorimetry	36	maximum pressure after	
isoperibolic system	(g)	decomposition	(g)
isothermal	(g)	microcalorimeter	(g)
calorimetry	20, 71	mischarging of reactants	11, 28, 34,
conditions	28		180, 182
DSC experiments	45, 92	modifications	107, 112
heat flow calorimeters	38	control	112
semi-batch reactions	35, 68	multi-purpose plant	2, 115
<b>K</b>			
kinetic data	(g)	<b>N</b>	
kinetics	85	naturally-foaming system	117
decomposition	55	near adiabatic	(g)
desired reaction	71	NIHHS (see Notification of Installations	
knock-out drums	122	Handling Hazardous Substances	
design	121	Regulations)	
worked example of sizing	122	nitration	7, 162, 182, 183, 194
<b>L</b>			
laboratory scale, hazards at	16	of toluene	60
law of 'conservation of energy'	(g)	non-foaming system	118
legislation	4	non-specific faults	18, 64, 77
levels of process definition	17	normal reaction, characterizing	32, 64
level swell	117	Notification of Installations	
liquid swell	79	Handling Hazardous Substances	
literature data	20, 22, 24	(NIHHS) Regulations	4
literature search	21	Nusselt number	72
logic gates	99	<b>O</b>	
loop reactors	(g)	100 degree rule	52
loss of containment	12	onset temperature	28, 30, 40, 53,
loss of cooling	15, 18		85, 90, 92, (g)
<b>M</b>			
main causes of incidents	3, 8	operating	
maintenance of plant	11, 135, 138,	conditions	46
	161, 182, 193	instructions	114, 136, 178, 192
accidents	138	procedures	13, 114, 135,
preventive	(g)		161, 162, 188
maloperations	16, 18, 46, 52, 68, 93,	operational hazards	1
	95, 107, 173, 189	operator training	114, 135, 137,
examples	108		161, 192
manufacture of chemicals	1	OR gates	100
materials of construction	28, 33	over-adiabatic mode	(g)
		overheating	2
		oxygen balance	24

- P**
- P&ID (see piping and instrumentation diagram)
- permit-to-work systems 138
- PFD (see process flowsheet diagram)
- PFR (see plug flow reactor)
- phenol-formaldehyde 185  
condensations 7
- Phi 40, 43, 50, 52, 57, 87, 93, (g)
- Phi-Tec adiabatic calorimeter 44
- pilot plant 16, 94
- piping and instrumentation diagram (P&ID) 95
- plant design and operation 9, 46, 162, 165
- plant maintenance 161, 193
- plug flow reactor (PFR) (g)
- polymerization reactions 7, 123, 181
- power compensation calorimetry 36
- Prandtl number 72
- precipitation 77
- pre-exponential factor (g)
- pressure data 61
- prevention of runaway reactions 92
- preventive maintenance (g)
- preventive measures 161, 175, (g)
- preventive safety measures 106, 112
- probability 209, (g)  
prediction 100
- process  
changes 46, 135, 136, 161, 189  
chemistry 3, 9, 13, 14, 161, 162  
definition 17, 165  
documentation 127, 215  
instructions 135, 161, 175, 187, 188  
maloperations 18, 33, 46  
modifications 15, 115  
risk analysis 94  
safety 14
- process flowsheet diagram (PFD) 95
- processing reactive chemicals 1
- product (and personnel)  
changeovers 135, 137, 161, 191
- products (g)
- protection from runaway reactions 93, 120
- protection methods, vented and unvented 110
- protective safety measures 106, 114, 161, 185
- protective systems 16
- pyrophoric ignition 187
- pyrophoric material 126, 130, (g)
- Q**
- quasi-adiabatic (g)
- quenching 76, 115, 123, 186, (g)
- R**
- rate of  
chemical addition 113  
heat loss 6, 40, 46, 85  
heat production 2, 6, 33, 38, 71, 93  
heat removal 33, 34, 48  
gas evolution 32, 34, 39, 78, 93  
reaction 2, 6, 56, (g)
- raw materials 108, 161, 179
- quality 9, 18
- reactants (g)  
accumulation 33  
concentration 33
- reaction (g)  
chemistry 9, 78  
inhibition 106  
kinetics 20, 33, 34, 36, 67, (g)  
unwanted or unexpected 46
- reaction rate constant (g)
- reactive chemical groups 23
- reactive substances/materials (g)
- reactive systems screening tool (RSST) 44
- reflux (g)
- reflux calorimeter 79
- relief device set pressure 115, 118

Reynolds number	72	data	52
risk	(g)	disadvantage	27
risk analysis	94, 161, (g)	scrubbing systems and vents	39, 113, 118, 122
RSST (see reactive systems screening tool)		selectivity	(g)
runaway reactions	2, (g)	self-accelerating decomposition temperature (SADT)	(g)
accelerating	48	self-heating	29, 67, 84
characterization	40, 117	Siemenov	46, 53, 65
consequences	40, 92, 101, 107, 114	semi-batch	
containment	93, 106, 115, 124	operations	2, 64, 107, 114, (g)
decision tree	124	reactions	33, 68
interpreting data	84	reactors	33, (g)
kinetics	45	'Seveso' directive	5
onset	49	sources of hazard	1
prevention	40, 92, 161, 175	sources of ignition	3, 129, 212
protection	93, 161, 185	avoidance	131
		external	127
<b>S</b>		Soxhlet assembly	80
SADT (see self-accelerating decomposition temperature)		stages of a process	14, 20
safe operating conditions	34	Stanton number	65
safe operating temperature		static electricity	130
calculation	85	stationary conditions	(g)
simulation	85	storage	161, 163, 173, 175, 179, 180, 181, 183
safe process envelope	113	sulphonation	7, 182, 188
safe storage times	32	system	
safe time	113, 161, 183	classification	115
safety		gassy	115
acceptable level	19	hybrid	115
audits	140	naturally-foaming	117
back-up systems	3, 13	non-foaming	118
based on containment	124	vapour pressure	115
based on inhibiting runaway reaction	123	venting	39
control systems	117	systems with non-uniform temperature distribution	47
factors	84, 120	systems with uniform temperature distribution	48
measures	14, 17, 106, 110		
preventive	106		
protective	106		
selecting basis of system	172		
system	108		
scale-up	6, 33, 64, 71, 78, 167	<b>T</b>	
screening tests	20, 27, 52, 84, 162, 197	technical documentation	135
		example of manual	215

- |                                   |                                       |  |  |
|-----------------------------------|---------------------------------------|--|--|
| temperature control               | 10, 108, 161,<br>175, 178, 179        | <b>V</b>                                     |  |
| temperature of no return          | (g)                                   | vapour cloud explosion (VCE)                 | 181, (g)   |
| tempered systems                  | 118                                   | vapour pressure system                       | 115, 119   |
| tempering reactions               | 41, 116                               | vapour systems                               | 93   |
| <i>tert</i> -butyl peroxybenzoate | 55, 59                                | VCE (see vapour cloud explosion)             |  |
| testing foaming behaviour         | 118                                   | vented and unvented methods of<br>protection | 110  |
| thermal decomposition             | 28                                    | venting                                      | 13, 39, 76, 161, 172, 173,<br>181, 182, 185, (g) |
| temperature                       | 23                                    | vent sizing                                  | 20, 43, 118                                      |
| thermal reaction number           | 65                                    | correction for effects of                    |  |
| thermal stability                 | 50, 179, 202                          | downstream equipment                         | 120  |
| thermally unstable                | 163, 183, (g)                         | Fauske method                                | 119  |
| thermochemistry                   | 3, 9, 13                              | FIA method                                   | 119  |
| calculations                      | 22, 24                                | gassy systems                                | 119  |
| thermodynamic data                | (g)                                   | hybrid systems                               | 120  |
| time to maximum rate (TMR)        | 85, (g)                               | Leung method                                 | 119  |
| using adiabatic calorimeters      | 86                                    | nomogram                                     | 119  |
| using DSC                         | 88                                    | safety factors                               | 120  |
| TMR (see time to maximum rate)    |                                       | vent sizing package (VSP)                    | 43   |
| top event                         | (g)                                   | video  | 13   |
| toxic hazards                     | 3, 14, 126, 133, 161, 186             | viscosity factor                             | 72, 73   |
| toxic materials                   | 12                                    | VSP (see vent sizing package)                |  |
| training                          | 3, 13, 21, 114, 134,<br>137, 141, 161 | <b>W</b>                                     |  |
| true inhibition                   | 123                                   | Wilson plot                                  | 73   |
| two-phase system                  | 77, 119                               | worst case scenario                          | 86, 107, 115                                     |
| typical testing procedure         | 21                                    |  |  |
| <b>U</b>                          |                                       |  |  |
| unstable substance/material       | (g)                                   |  |  |

(g) indicates an entry in the Glossary, page 142