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Get the Most Out of Your ARC and APTAC Data

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Some of the best calorimeters that were developed out of need include the accelerating rate calorimeter (ARC[®])



Dow Chemical



Columbia Scientific



Arthur D. Little



TIAX



Netzsch



Tools developed by industry also included the automatic pressure tracking adiabatic calorimeter (APTAC™)



Union Carbide



Arthur D. Little



TIAX



Netzsch



The ARC is widely used and is considered a work horse for runaway reactions characterization

- ▶ Rate of self-heating
- ▶ Time to maximum rate
- ▶ Rate of pressure rise
- ▶ Maximum rate of reaction
- ▶ Kinetic data such as activation energy, reaction order and pre-exponential factor
- ▶ Heat of reaction, heat capacity, vapor pressure, and critical properties



The APTAC™ is a low thermal inertia calorimeter which provides direct scale up and additional capabilities

- ▶ Pressure balancing
- ▶ Larger test cell and lower thermal inertia
- ▶ Computer controlled reagent metering
- ▶ Isothermal and HWS modes
- ▶ Magnetic stirring
- ▶ Higher tracking; dT/dt (~400 C/min)
and dP/dt (~10,000 psi/min)
- ▶ Simple venting and controlled venting
- ▶ GC/IR hookups



Test cells used in the ARC and APTAC can be made from different metals

Test-Cell Name	Material of Construction	Typical Mass (g)	Volume at 25°C (ml)	Specific Heat [J/(kg °C)]	Specific Heat [cal/(g °C)]
ARC-FS-2-BC	Stainless Steel 316	3	9.5497	452.5	0.1082
APTAC-001	Titanium	33	136.4	519.7	0.1242
APTAC-001A	Titanium	55	136.4	519.7	0.1242
APTAC-002	Hastelloy C	118	136.4	365.0	0.0872
APTAC-003	Stainless Steel 316	94	136.4	452.5	0.1082
VSP2 VT2-304-SIL-SN-SN	Stainless Steel 304	24.9	110.7	469.2	0.1121
VSP2 VT2-316-SIL-SN-SN	Stainless Steel 316	24.8	110.7	452.5	0.1082
VSP2 VT2-HC-SIL-SN-SN	Hastelloy C-276	28	110.7	365.0	0.0872
VSP2 Special Order	Titanium	14	110.7	519.7	0.1242

Test cell volume should include additional volume of tubing and valve(s). For ARC this can be equivalent to 0.48 ml approximately.

Test cell volume may need to be corrected for expansion because of high pressures and temperatures

Overall Volume Balance:

$$\frac{dV_{excess}}{dt} = V_l \beta_l \frac{dT}{dt} - V_l \kappa_l \frac{dP}{dt} - 3\alpha V_s \frac{dT}{dt} - \left(\frac{D_i}{\delta} \right) \left(\frac{V_s}{E_{s,T}} \right) f(\nu) \frac{dP}{dt} = 0$$

$$\frac{dP}{dt} = \left[\frac{V_l \beta_l - 3\alpha V_s}{V_l \kappa_l + \left(\frac{D_i}{\delta} \right) \left(\frac{V_s}{E_{s,T}} \right) f(\nu)} \right] \frac{dT}{dt} = \left[\frac{(\beta_l - 3\alpha) E_{s,T}}{E_{s,T} \kappa_l + \left(\frac{D_i}{\delta} \right) f(\nu)} \right] \frac{dT}{dt}$$

Vessel Metal Volume:

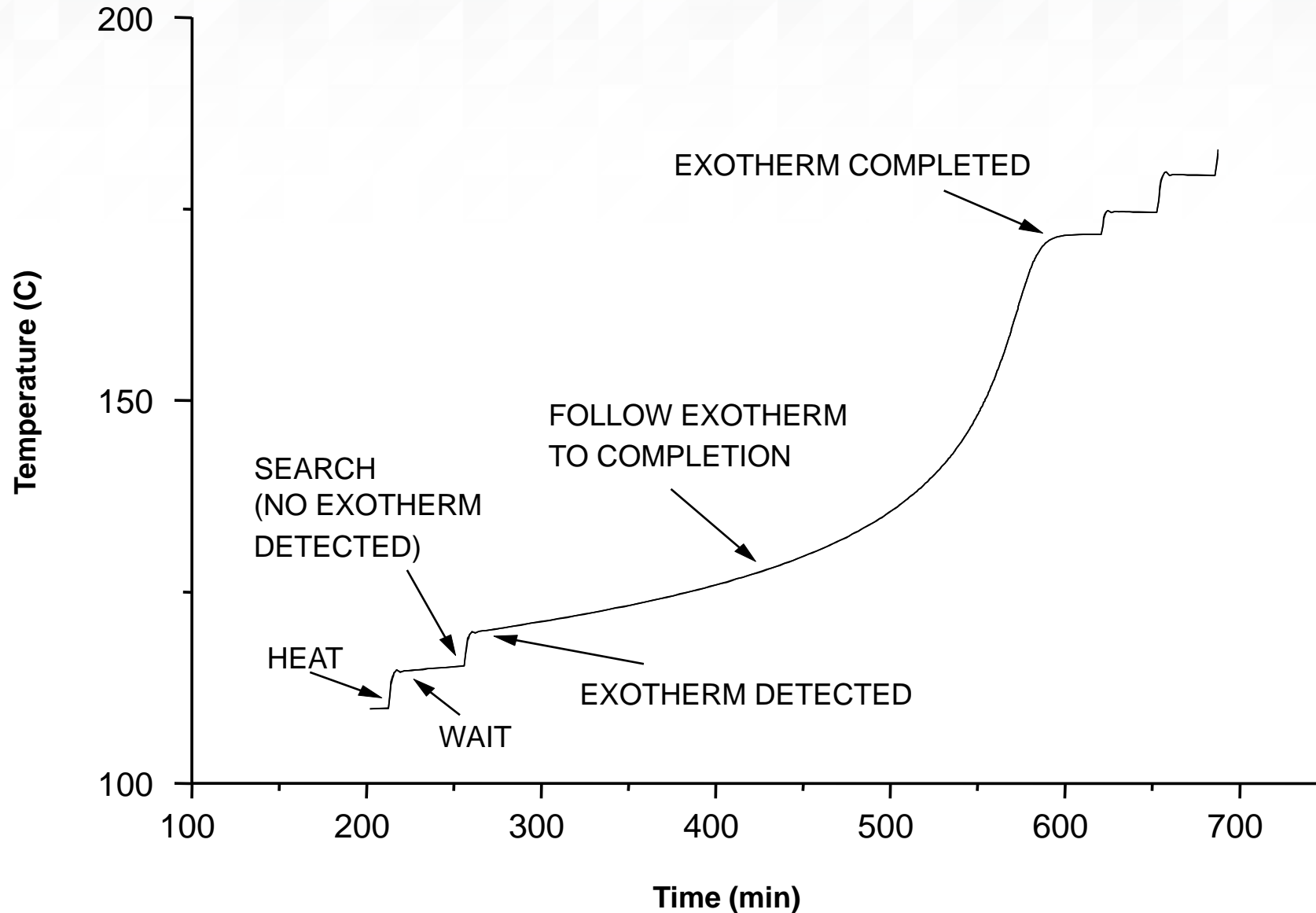
$$\frac{dV_s}{dt} = 3\alpha V_s \frac{dT}{dt} + \left(\frac{D_i}{\delta} \right) \left(\frac{V_s}{E_{s,T}} \right) f(\nu) \frac{dP}{dt}$$

$$f(\nu) = 1.25 - \nu \simeq 0.95 \quad \text{for a cylindrical vessel, and}$$

$$f(\nu) = \frac{3}{4}(1 - \nu) \simeq 0.53 \quad \text{for spherical vessel.}$$

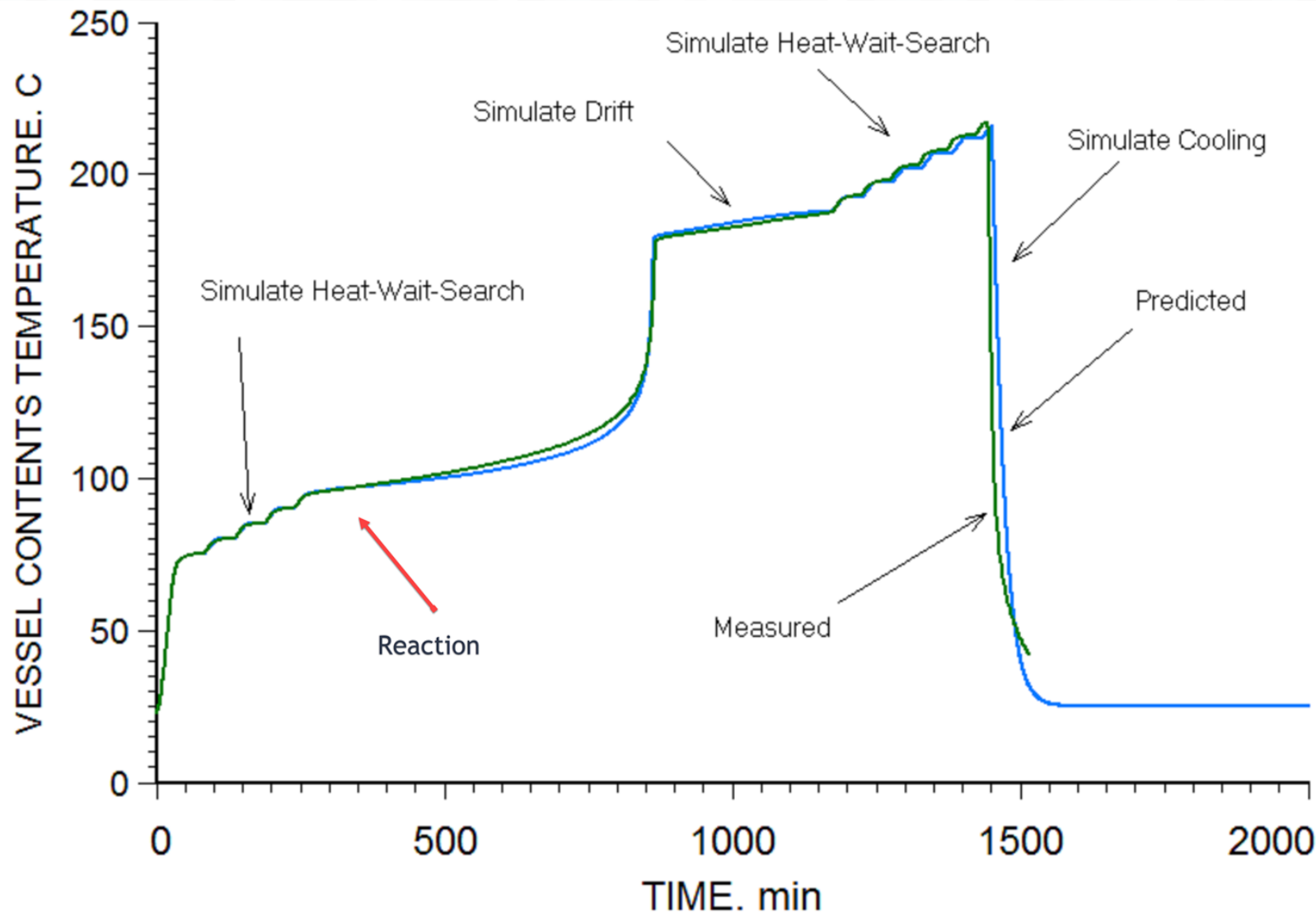
Source: G. A. Melhem, "Thermal Relief Requirement for Liquids", White Paper, ioMosaic Corporation, 2017

Using heat-wait-search method or isothermal aging, we can extract a myriad of useful data from both calorimeters

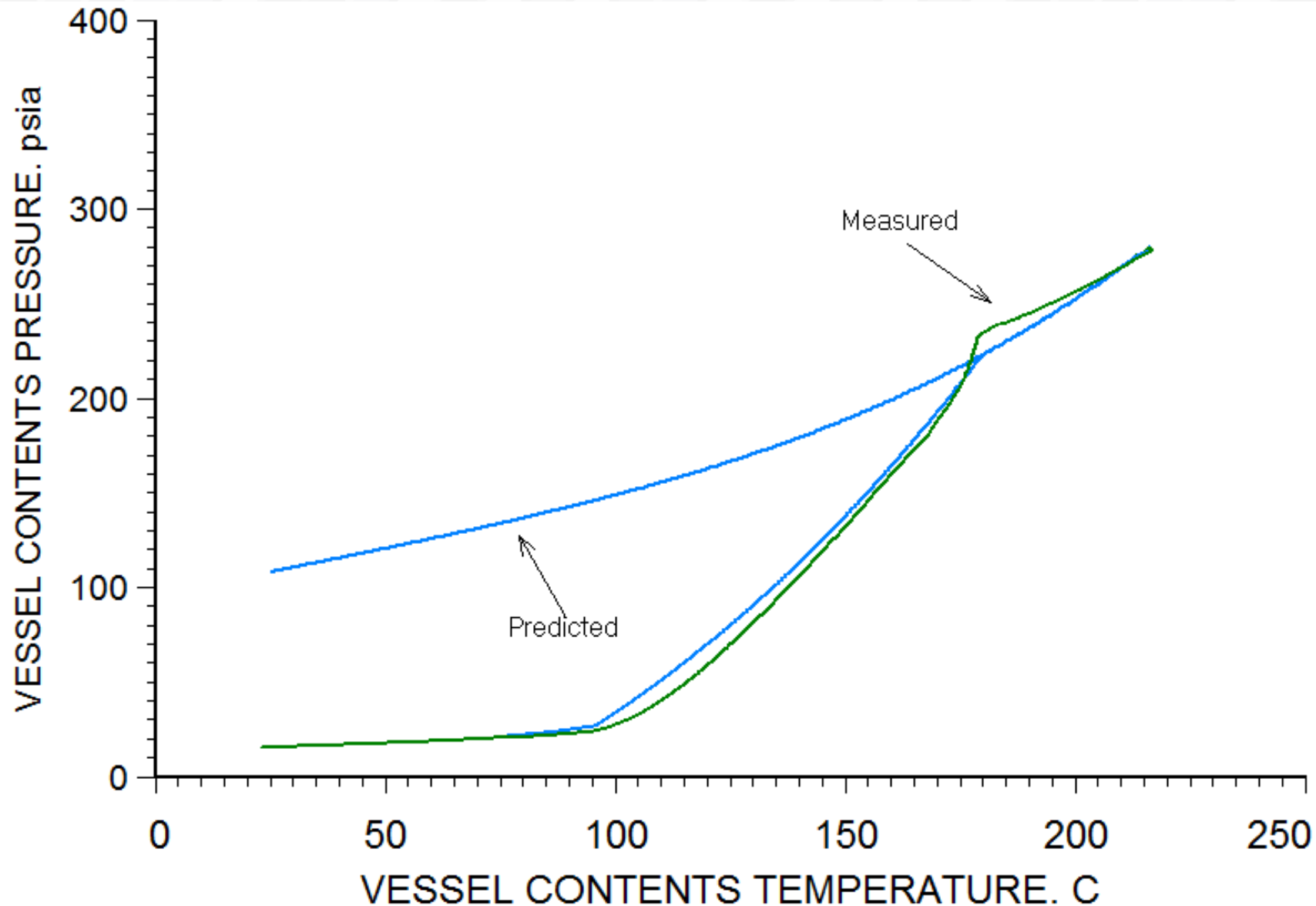


The initial non-reaction data collected is just as valuable as the exotherm data

50 %
dicumyl
peroxide in
toluene

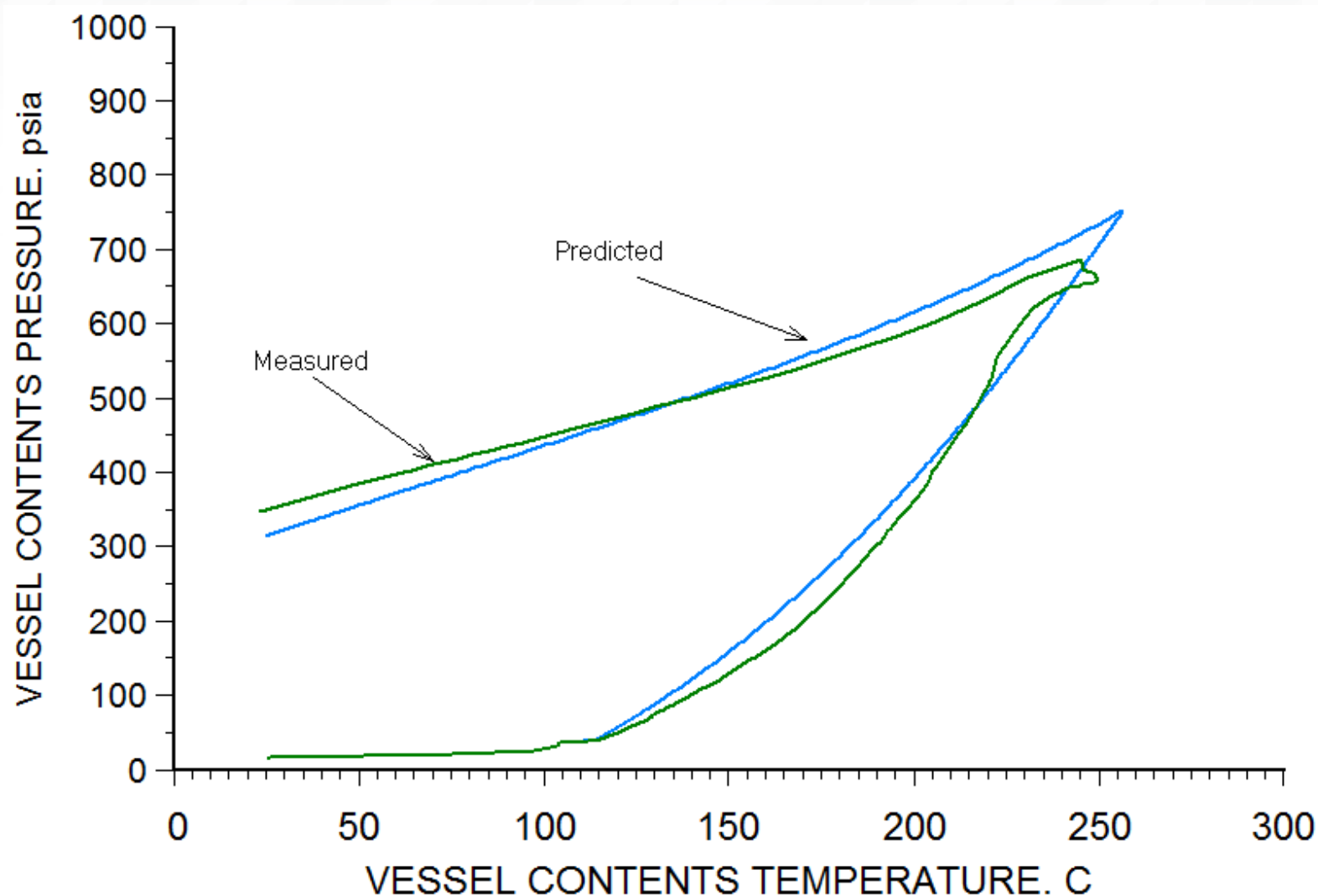


The initial non-reaction data represents valuable VLE data



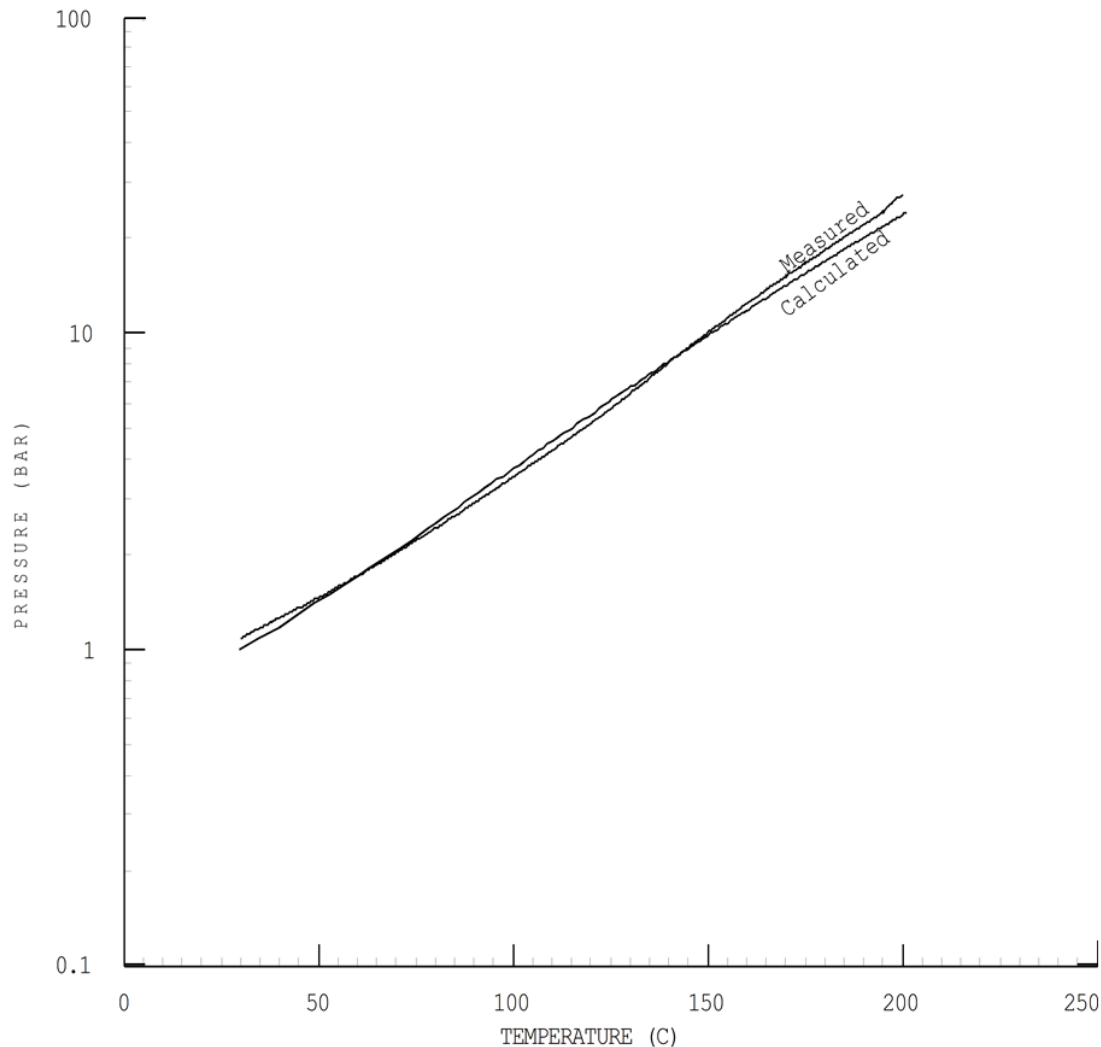
50 %
dicumyl
peroxide
in toluene

Both ARC and APTAC can produce valuable VLE and vapor pressure data



APTAC data
for 40 %
dicumyl
peroxide in
ethylbenzene

We have used the ARC and APTAC to develop and confirm VLE data, vapor pressure data, and critical properties

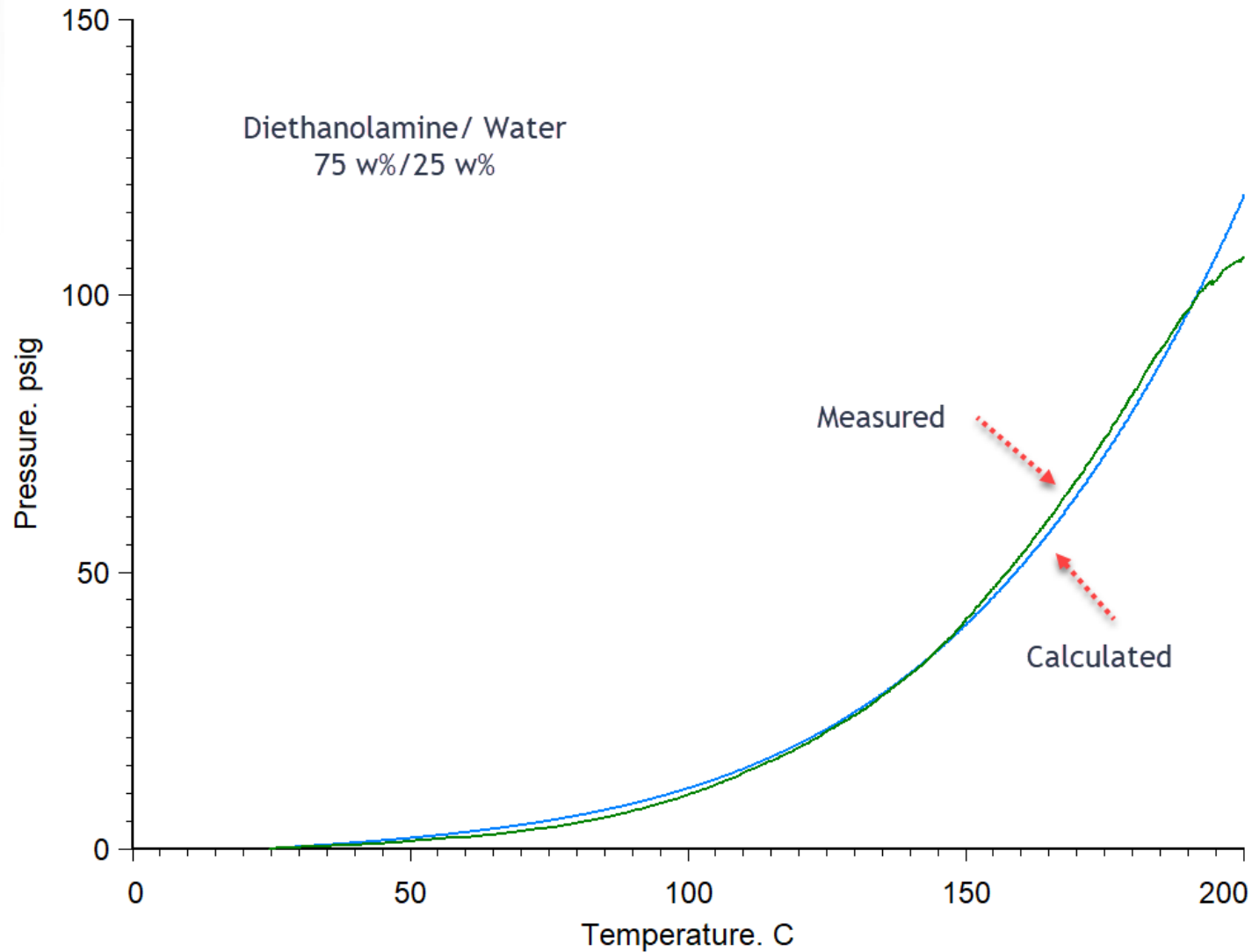


Acetone/Water
 $k_{ij} = -0.176$, $l_{ij} = -0.142$

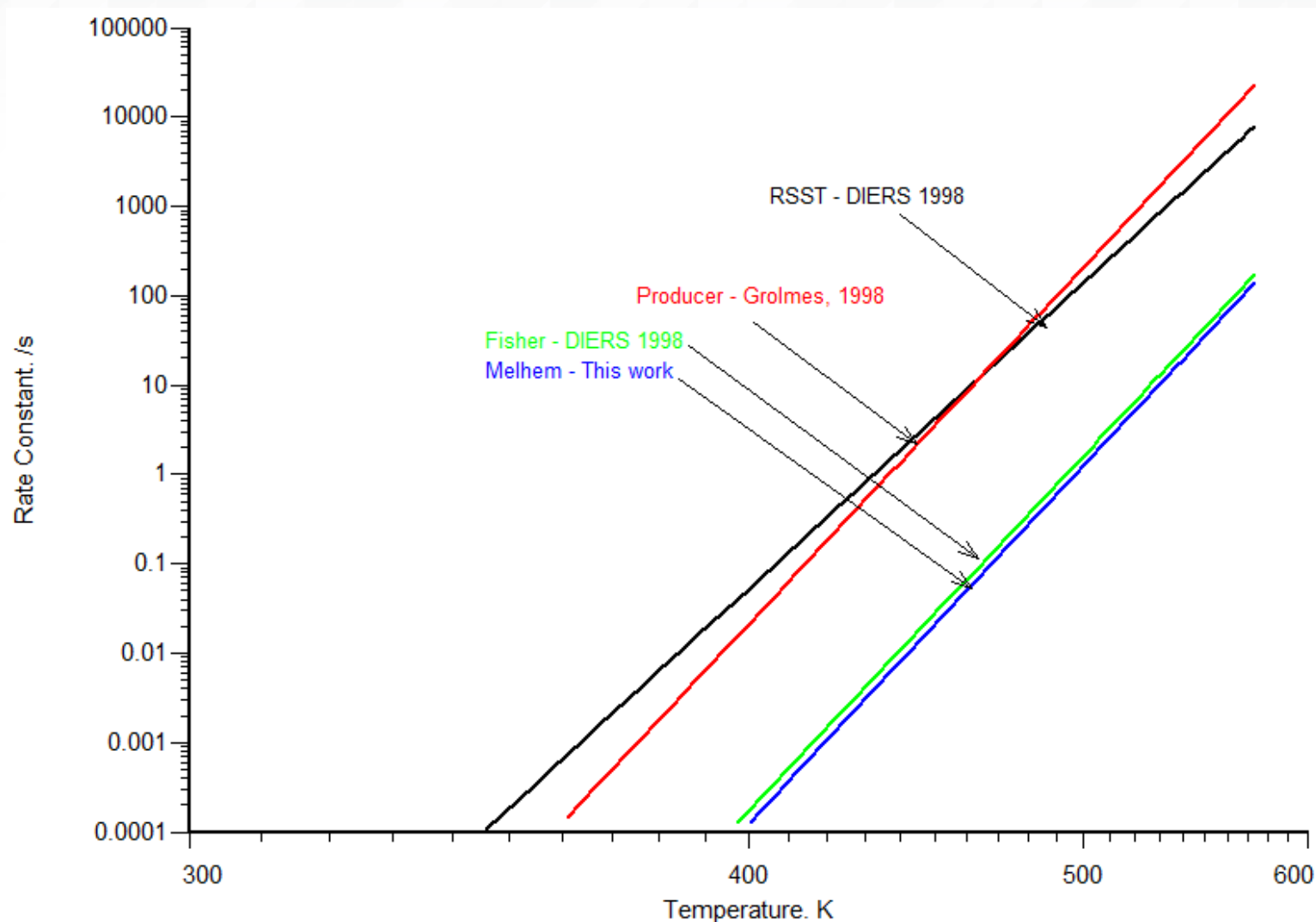
Water/Nitrogen
 $k_{ij} = -0.982$, $l_{ij} = -0.011$

Acetone/Nitrogen
 $k_{ij} = -0.168$, $l_{ij} = -0.002$

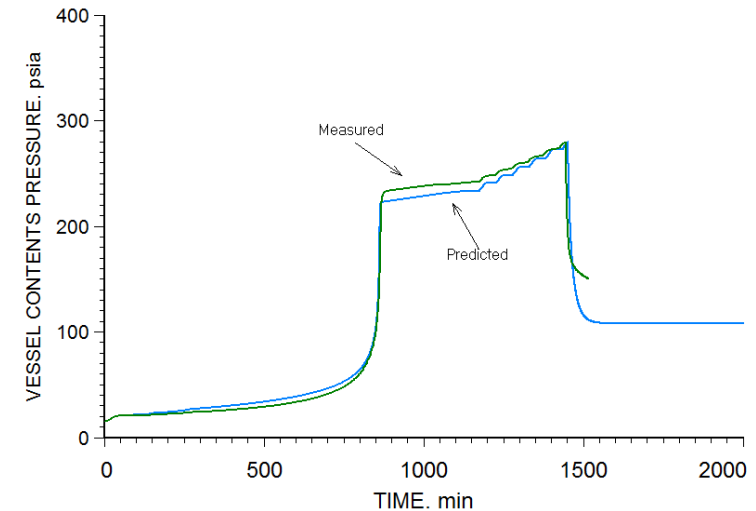
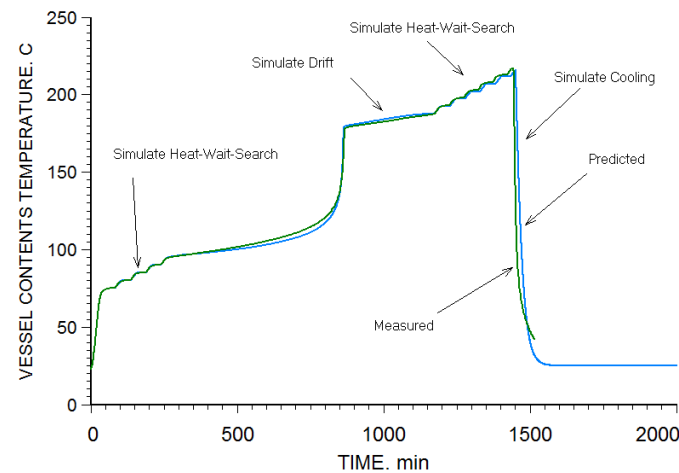
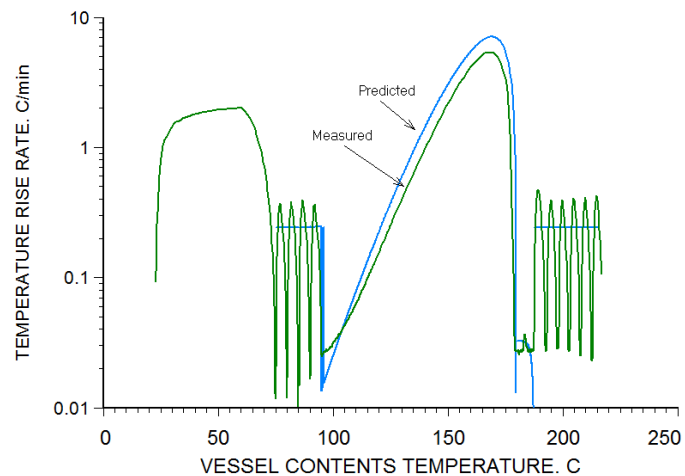
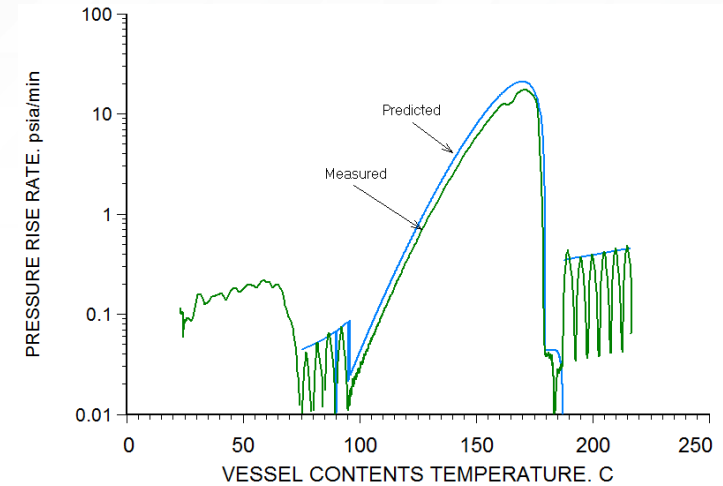
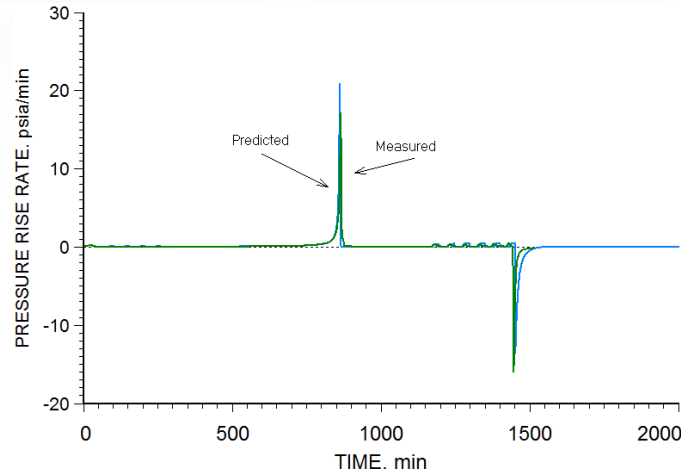
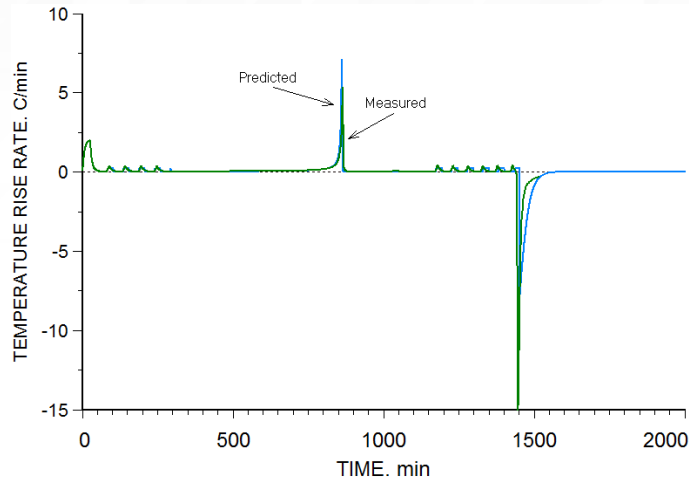
VLE is critically important for pressure relief systems design and evaluation, especially for non-ideal systems



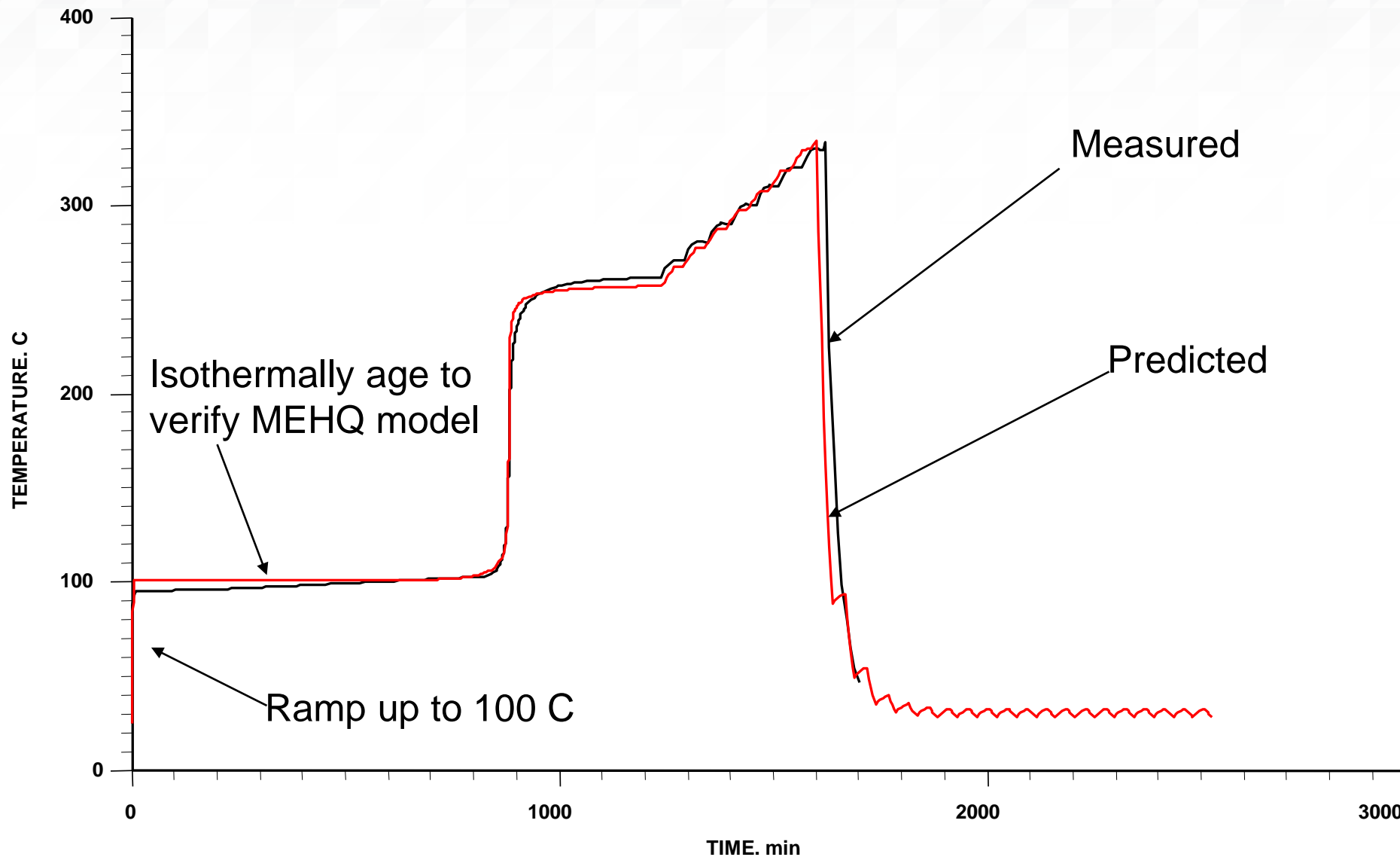
Once VLE is established for reactants, kinetic models can be developed for one or more reactions (dicumyl peroxide)



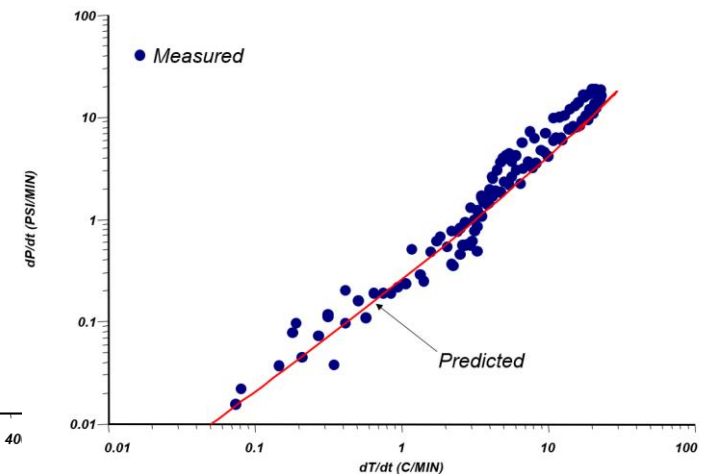
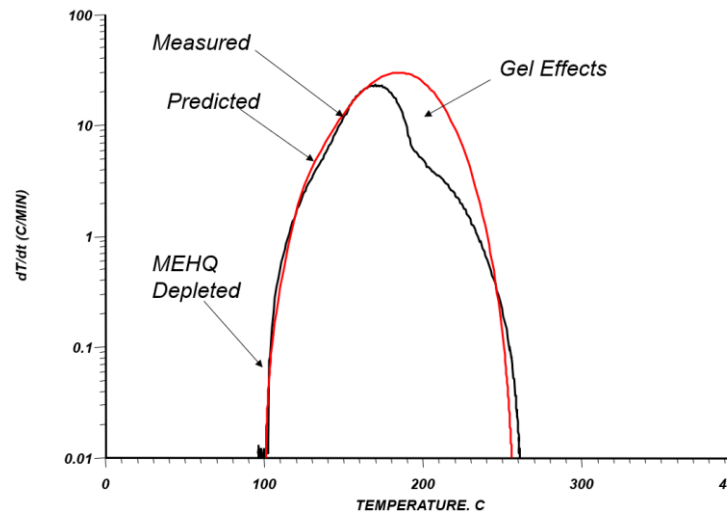
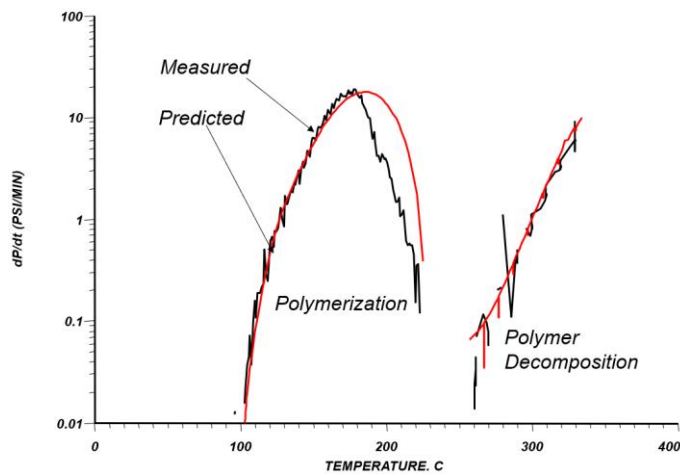
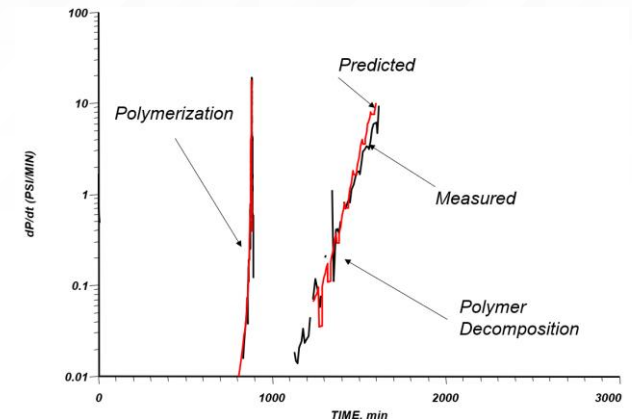
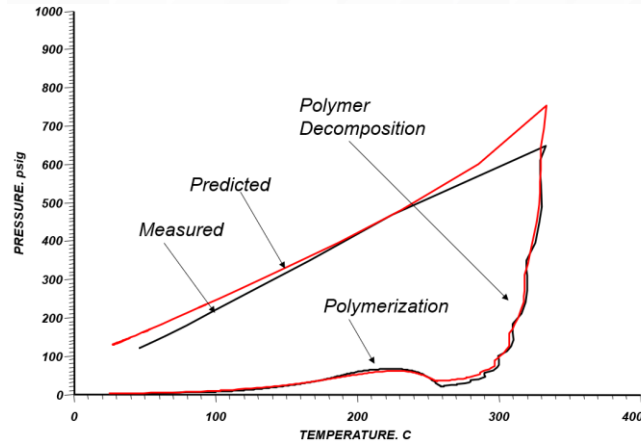
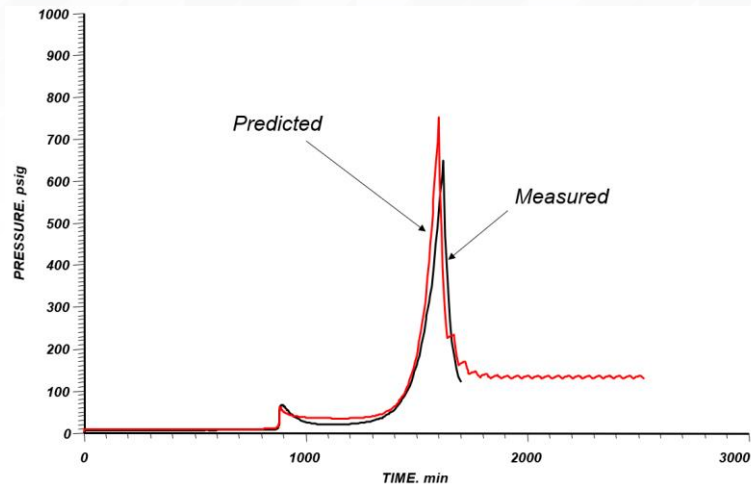
Multiple indicators are needed for a proper kinetic model (50 % dicumyl peroxide in toluene is shown below)



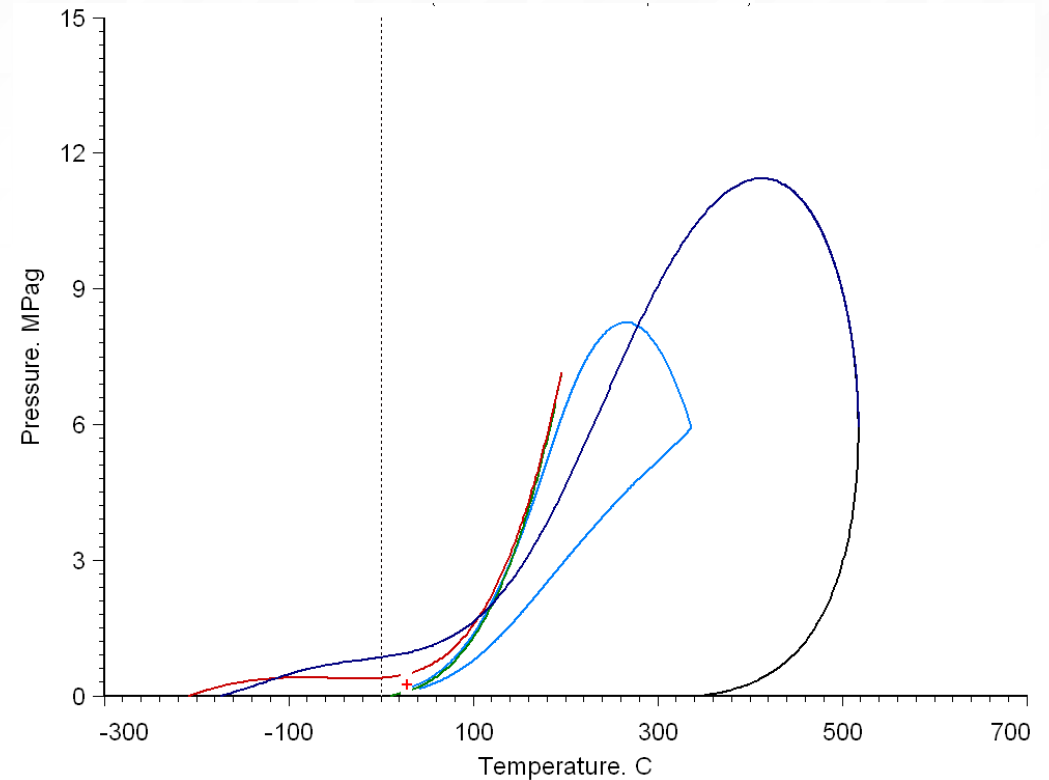
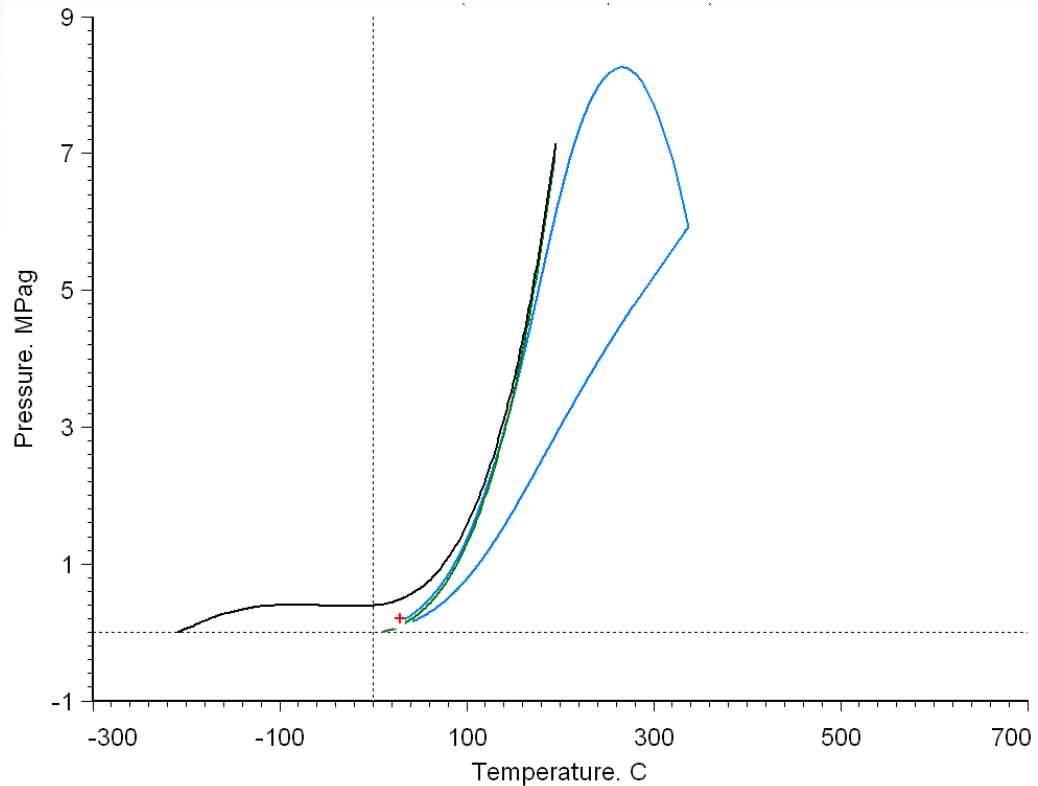
These type of estimates extend to all kinds of different chemistries such as polymerizations for example



The examples below shows kinetic and inhibitor model development for butyl acrylate

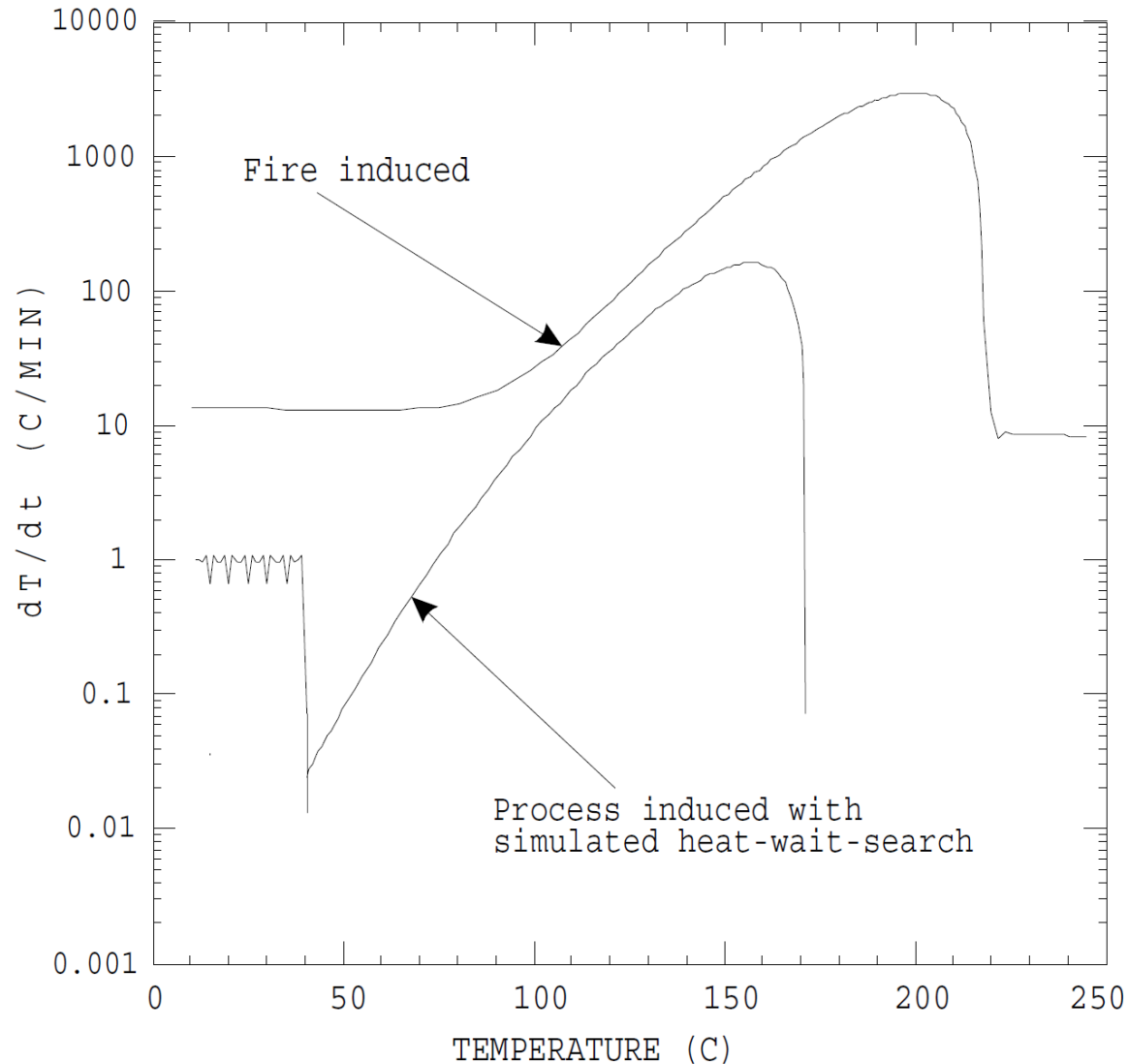


Note, the starting and final phases during HWS and runaway conditions change as does the phase envelope



It is possible for the ARC/APTAC test cells to become liquid full during runaway if large samples are used

The impact of external heating or fire exposure on reaction rates is highly non-linear and requires dynamic modeling

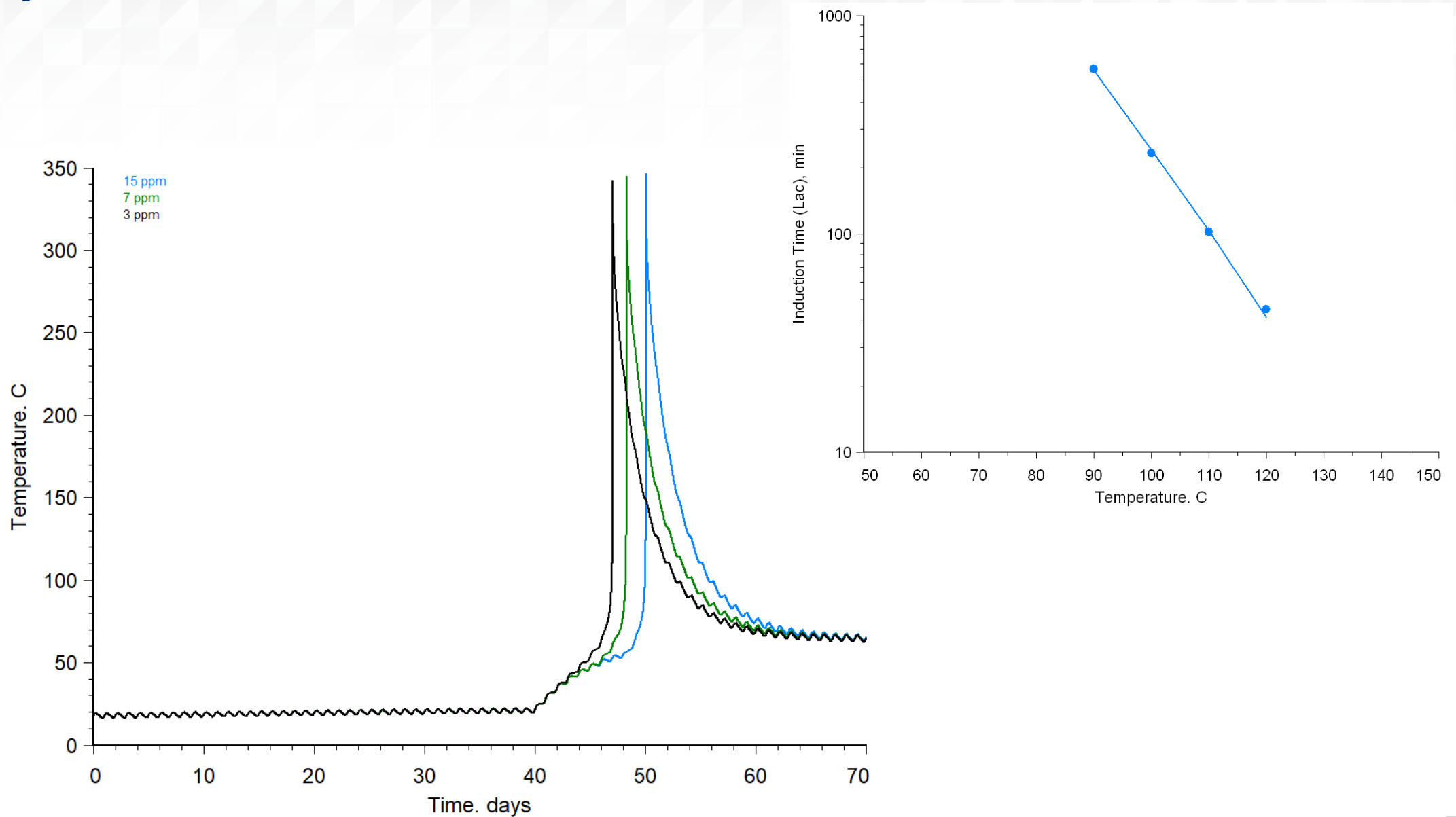


Data is for hydrogen peroxide / water system

In addition to VLE and kinetic models, many useful thermal stability indicators can be obtained from ARC/APTAC data

- ▶ Inhibitor induction time and Induction time for autocatalytic reactions
- ▶ Detected onset temperature
- ▶ Adiabatic temperature rise
- ▶ Heat of reaction
- ▶ Maximum adiabatic temperature due to reaction
- ▶ Maximum reaction pressure
- ▶ Time to maximum rate
- ▶ Power density
- ▶ Temperature of no return and self accelerating reaction temperature

The impact of inhibitors or autocatalytic behavior must be quantified and considered



Inhibitor induction time should be considered in the evaluation of potential reaction hazards

$$\frac{dC}{dt} = -A \exp\left[-\frac{E}{T}\right] C^n = -kC^n$$

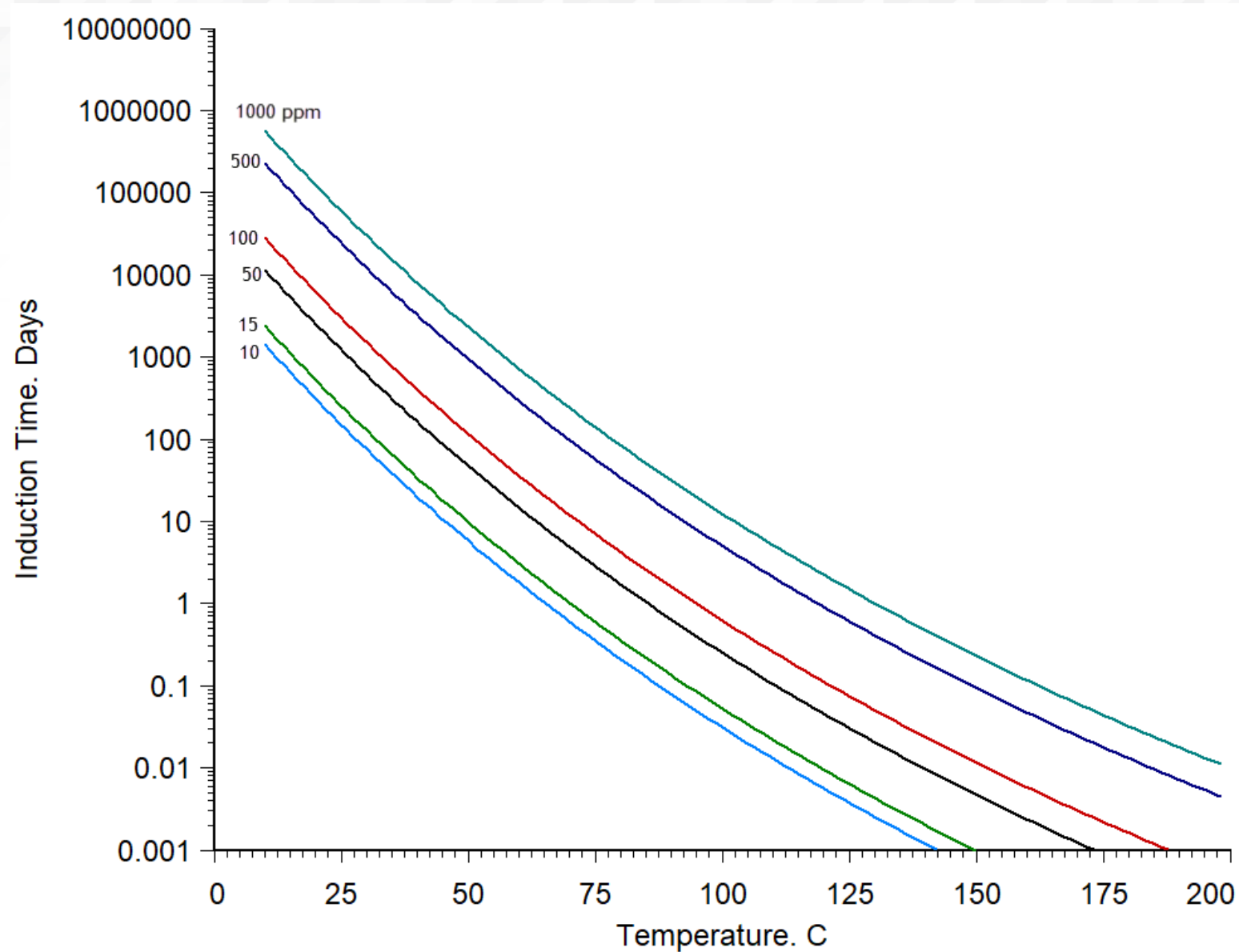
$$L_{ip} = \frac{1}{A^\bullet \exp\left[-\frac{E}{T}\right]} C_i^m = \frac{C_i^m}{k^\bullet}$$

Inhibitor	Monomer	Depletion Model			Effectiveness Model		
		A	E, K	n	A^\bullet	E, K	m
PTZ	Acrylic Acid	3.284×10^9	11747	0.25	1.975×10^9	11680	0.73
TBC	Styrene	2.400×10^{12}	12615	0	3.644×10^{12}	12615	1.308
MEHQ	Acrylic Acid	1.527×10^{21}	19100	0	1.975×10^{21}	19100	1.19
MEHQ	Ethyl Acrylate	3.992×10^{11}	13419	0.45	2.116×10^{11}	13403	0.55
MEHQ	Butyl Acrylate	3.515×10^{13}	14912	0.55	1.479×10^{13}	14880	0.45
MEHQ	Methyl Methacrylate	1.085×10^{11}	12450	0.1	0.822×10^{11}	12399	0.884
HQ	Vinyl Acetate *	1.733×10^8	10620	0.5	9.341×10^7	10620	0.54
HQ	Vinyl Acetate**	3.869×10^7	10963	0.15	2.981×10^7	10963	0.777

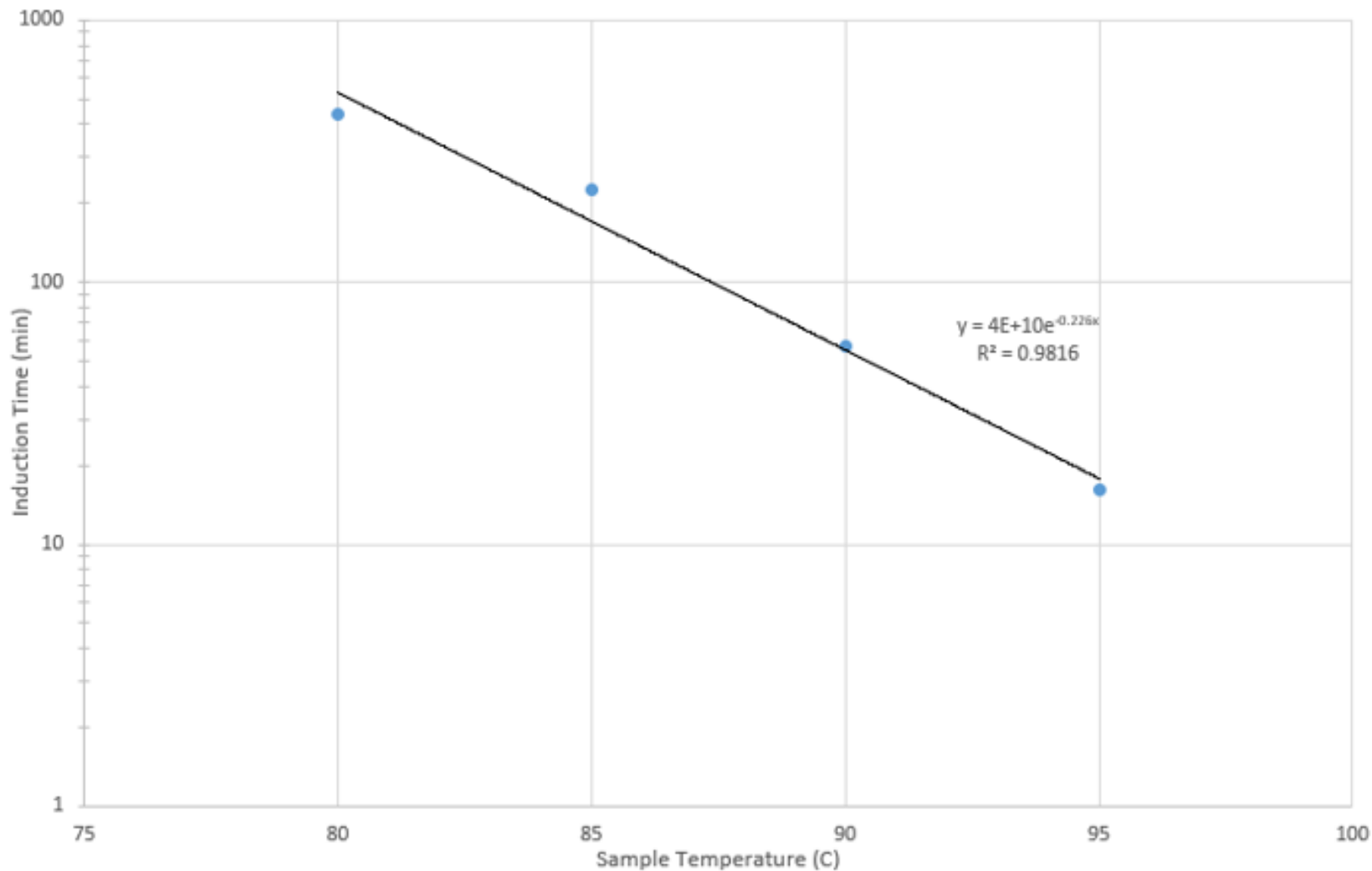
A and A^\bullet are expressed in SI units (s, kmol, m³). For a 1st order reaction, A and A^\bullet will be in s⁻¹.

* Air atmosphere. ** Low Oxygen atmosphere.

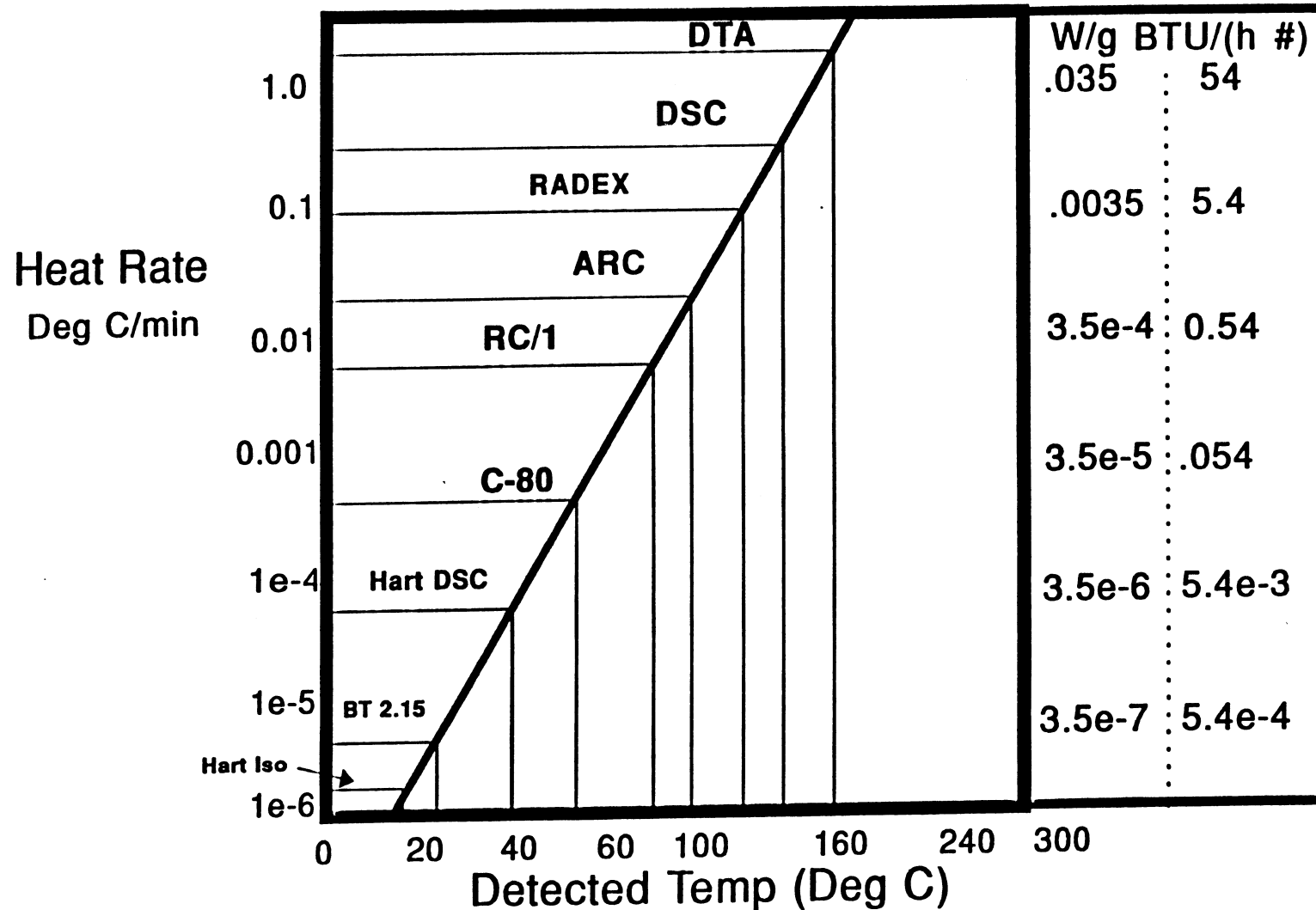
Impact of TBC concentration on styrene monomer stability



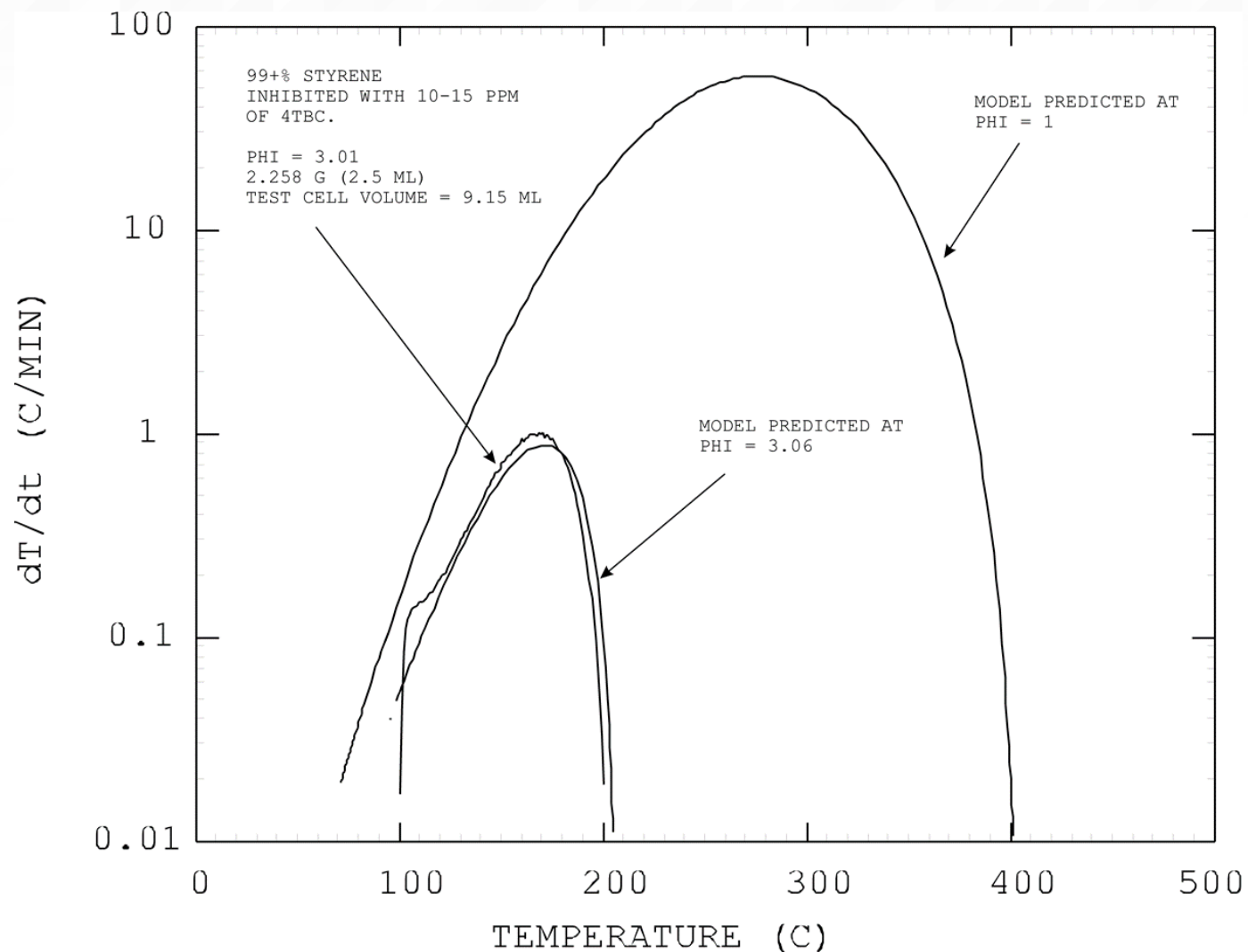
Autocatalytic reactions can only be thermally stable for a specific time duration depending on temperature



The detected onset temperature cannot be used directly and should be corrected for thermal inertia



The thermal inertia and test apparatus sensitivity can have a significant impact on measured reaction data



The detected onset temperature can be quickly corrected for thermal inertia for single stage reactions

$$\phi = 1 + \frac{m_c c_{p,c}}{m_s c_{p,s}} = \frac{\Delta T_{\text{adiabatic}}}{\Delta T_{\text{measured}}}$$

ϕ values for ARC can range from 1.5 to 5. T_{do} can be corrected for thermal inertia using the following expression:

$$\underbrace{\frac{1}{T_{doc}}}_{\phi=1} = \underbrace{\frac{1}{T_{do}}}_{\phi>1} + \frac{\ln \phi}{E}$$

where E is the reaction activation energy in Kelvin. Note that a detection sensitivity of 0.02 °C/min translates into 29 °C/day. It is recommended that T_{doc} is further reduced by 50 C before applying directly to plant scale equipment [4]. T_{do} data obtained by DSC should be reduced by 75 C [4]. Even with a reduction of 50 or 75 C there can be numerous scenarios that can provide the needed temperature increase to start a runaway reaction including fire exposure, excessive steam or oil heating, contamination, failure of process controls, etc.

Measured data can also be corrected for thermal inertia for simple single stage reactions

1. Correct the measured temperature using the corrected onset temperature T_{doc} :

$$T(t)_{\text{corrected}} = T_{doc} + \phi [T(t)_{\text{measured}} - T_{do}]$$

2. Correct the measured temperature rise rate, $\frac{dT}{dt}(t)$, data:

$$\frac{dT}{dt}(t)_{\text{corrected}} = \phi \frac{dT}{dt}(t)_{\text{measured}} \exp \left[E \left(\frac{1}{T(t)_{\text{measured}}} - \frac{1}{T(t)_{\text{corrected}}} \right) \right]$$

3. Sequentially update the measured time data:

$$t_{\text{corrected}} = \int_{T_{doc}}^{T(t)_{\text{corrected}}} \left[\frac{1}{\frac{dT}{dt}(t)_{\text{corrected}}} \right] dT$$

where $t_{\text{corrected}}$ is the adjusted reaction time at a thermal inertia of 1.

It is always prudent to calculate the expected adiabatic temperature rise

This is calculated from the thermal inertia multiplied by the difference between the measured final temperature, T_{mf} at the detection sensitivity of the instrument, minus the measured detected onset temperature, T_{do} :

$$\Delta T_{\text{adiabatic}} = \phi \Delta T_{\text{measured}} = \phi (T_{mf} - T_{do})$$

The heat of reaction can easily be corrected for thermal inertia

Heat of reaction data are necessary to establish the maximum potential temperature rise due to reaction and cooling requirements. ΔH_{rxn} is typically a weak function of temperature. It is best obtained by measurement although reasonable values can be approximated from group contribution or published literature data. If adiabatic calorimetry data are available, the heat of reaction can be calculated from the measured overall temperature rise:

$$\Delta H_{\text{rxn}} = \phi c_{p,s} \Delta T_{\text{measured}}$$

The maximum adiabatic temperature due to reaction should be calculated for desired and undesired reactions

This value can be calculated from the heat of reaction and heat capacity of the reacting mixture. For complex systems where solution effects and temperature dependencies are important, it is better calculated using dynamic simulation using computer software such as SuperChems Expert™ .

$$T_{\max} = T_0 + \frac{\Delta H_{\text{rxn}}}{c_{p,s}}$$

where T_0 is the starting reaction temperature.

The maximum reaction pressure without venting can also be estimated from measured calorimetry data

The maximum reaction pressure $P_{\max}(T)$ at a specific temperature in a storage or process vessel that is reached due to a runaway reaction can be established by dynamic simulation where cooling and/or venting can be considered during the runaway. Alternatively, P_{\max} can be approximated using this simple equation:

$$P_{\max}(T) = P_{nci} \left(\frac{T}{T_i} \right) + P_{bub}(T) + \kappa R_g T \left(\frac{V_l}{V_v} \right)$$

where T is the temperature of interest, T_i is the starting temperature in K, P_{nci} is initial pressure of non-condensable gases in the vapor space of the vessel in Pa at T_i , $P_{bub}(T)$ is the liquid bubble point or vapor pressure at temperature T , R_g is the universal gas constant, 8314 J/kmol/K, V_l is the liquid volume in m^3 , V_v is the vapor space volume in m^3 , and κ is the measured moles of gas produced per cubic meter of liquid.

The time to maximum rate is needed to establish safe operating limits

$$t_{mr} = \frac{T_i^2}{E} \frac{1}{q(T_i)} \quad \frac{1}{V_l} \frac{dN}{dt} = - \underbrace{A \exp\left(-\frac{E}{T}\right)}_{k(T)} \prod_{j=1}^{j=m} C_j^{n_j}$$

$$q(T_i) = \frac{\Delta H_{rxn} k(T_i) M_w \prod_{j=1}^{j=m} C_j^{n_j}}{c_p \rho l}$$

$$q(T_i) = \frac{\Delta H_{rxn} k(T_i) M_w}{c_p \rho l} \quad \text{and} \quad t_{mr} = \left(\frac{T_i^2}{E}\right) \left(\frac{c_p \rho l}{\Delta H_{rxn} k(T_i) M_w}\right)$$

Zero Order

$$T_{t_{mr}24} = 0.65 \times T_{do} + 50$$

A rule of thumb

Another useful thermal stability indicator is power density

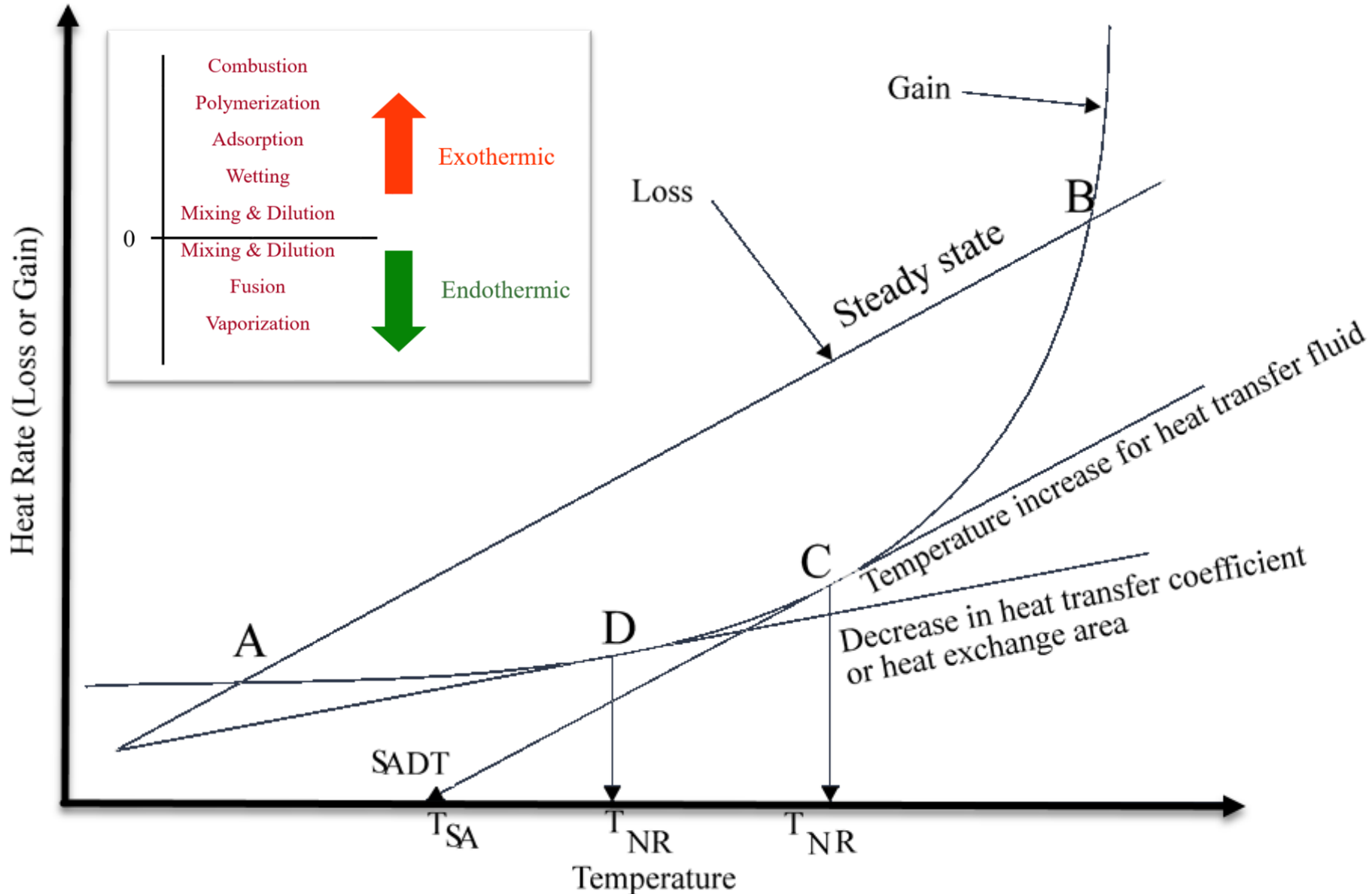
$$w(T) = c_p q(T)$$
$$W(T) = c_p \rho q(T)$$

$$IPD = W(250 \text{ }^\circ\text{C}) = W(523.15 \text{ K})$$

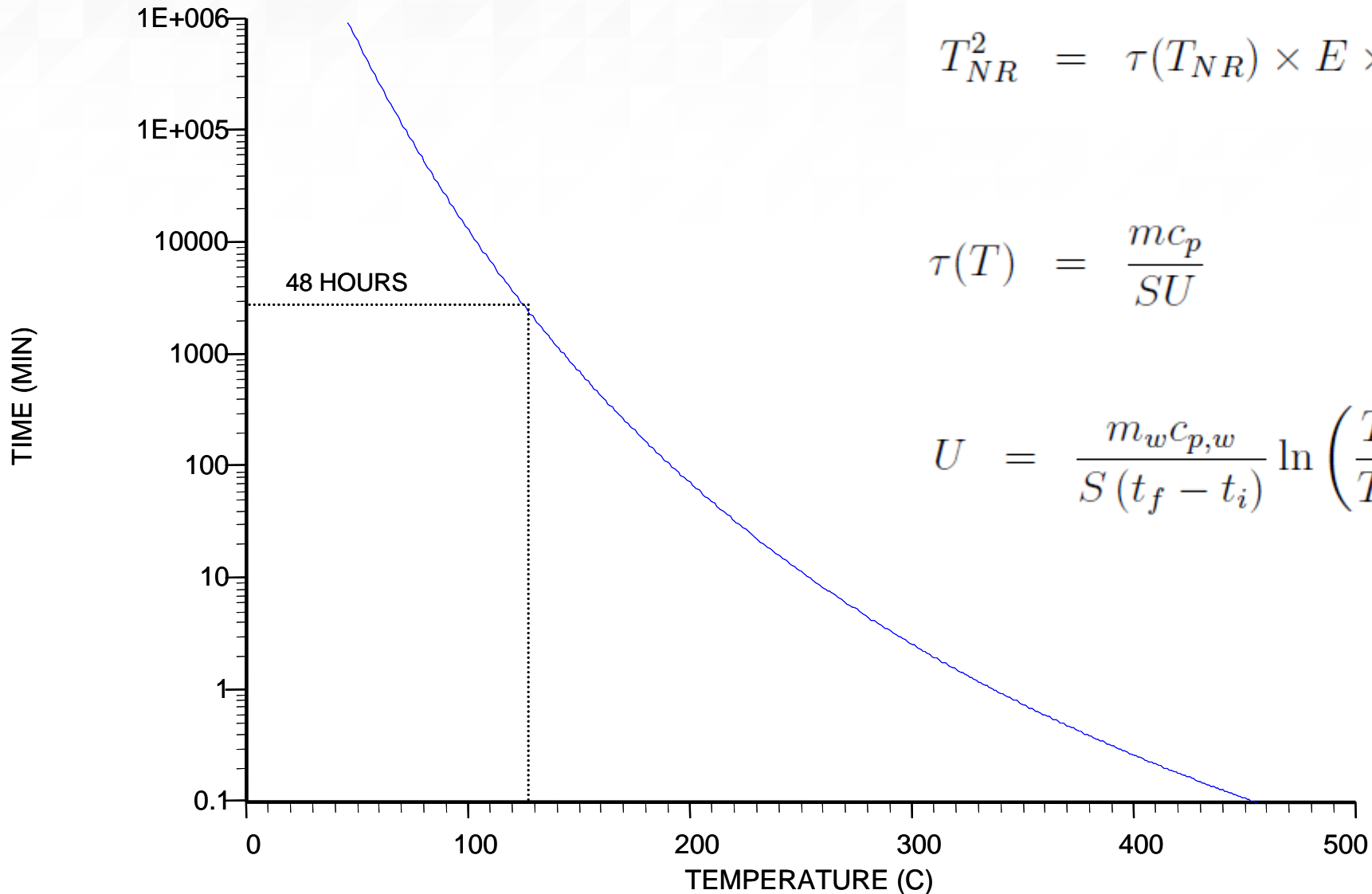
NFPA 704 Chemical instability rating system based on IPD

Rating	IPD, W/ml	Description
4	$IPD \geq 1000$	Materials that in themselves are readily capable of detonation or explosive decomposition or explosive reaction at normal temperatures and pressures
3	$100 \leq IPD < 1000$	Materials that in themselves are capable of detonation or explosive decomposition or explosive reaction but that require a strong initiating source or must be heated under confinement before initiation
2	$10 \leq IPD < 100$	Materials that readily undergo violent chemical change at elevated temperatures and pressures
1	$0.01 \leq IPD < 10$	Materials that in themselves are normally stable but that can become unstable at elevated temperatures and pressures
0	$IPD < 0.01$	Materials that in themselves are normally stable, even under fire conditions

The temperature of no return is the absolute maximum safe operating limit



The temperature of no return can be estimated from adiabatic calorimetry data



$$T_{NR}^2 = \tau(T_{NR}) \times E \times q(T_{NR})$$

$$\tau(T) = \frac{mc_p}{SU}$$

$$U = \frac{m_w c_{p,w}}{S(t_f - t_i)} \ln \left(\frac{T_{w,i} - T_s}{T_{w,f} - T_s} \right)$$

The self accelerating reaction temperature is the lowest ambient or heat transfer fluid temperature above which equilibrium is lost

Kamenetskii

$$T_{SA}^2 = \underbrace{c_p \rho \left(\frac{r^2}{\lambda \delta_c} \right)}_{\text{time constant}} \times E \times q(T_{SA})$$

$$\delta_c = \frac{K + 1}{e \left[\frac{1}{B_{i\infty}} + \frac{1}{B_i} \right]}$$

Geometry or shape	K	$B_{i,\infty}$
Infinite slab	0	2.39
Infinite cylinder	1	2.72
Sphere	2	3.01
Right cylinder ($l = d$)	1.78	2.72
Finite cylinder ($l > d$) with heat loss at both ends	$1 + 0.78(d/l)^2$	2.72
Finite cylinder ($l > d$) with heat loss at one end	$1 + 0.195(d/l)^2$	2.72
Finite cylinder ($d > l$) with heat loss at both ends	$-0.12 + 1.9(l/d)^2$	2.72
Cube	1.52	2.72
Box	$0.825 [1.067 + (x/y)^2 + (x/z)^2] - 1$	2.72

$$T_{SA} = T_{NR} - \frac{1}{\frac{E}{T_{NR}^2} - \frac{n}{T_f - T_{NR}} + \frac{d \ln[\tau(T_v)]}{dT_v}} \Big|_{@T_v = T_{NR}}$$

Semenov

$$T_{SA} = T_{NR} - \frac{T_{NR}^2}{E}$$

Zero Order

Simple reaction models (isoconversion), assume that conversion of reactants is only a function of temperature

$$\frac{C}{C_0} = \frac{T_{mf} - T}{\underbrace{T_{mf} - T_{do}}_{\Delta T}} \text{ or } C = \left(\frac{T_{mf} - T}{\Delta T} \right) C_0$$

$$\frac{dC}{dt} = -\frac{C_0}{\Delta T} \frac{dT}{dt}$$

$$\frac{dC}{dt} = -KC^n = -A \exp\left(-\frac{E}{T}\right) C^n$$

$$\frac{dT}{dt} = A \exp\left(-\frac{E}{T}\right) C_0^{n-1} \left[\frac{(T_{mf} - T)^n}{\Delta T^{n-1}} \right]$$

$$\ln \left[\frac{\Delta T^{n-1}}{(T_{mf} - T)^n} \frac{dT}{dt} \right] = \ln (AC_0^{n-1}) - \frac{E}{T}$$

$$\alpha = 1 - \frac{C}{C_0} \text{ where } 0 \leq \alpha \leq 1$$

$$\frac{dT}{dt} = \Delta T \frac{d\alpha}{dt}$$

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{T}\right) \underbrace{C_0^{n-1} \left[\frac{(T_{mf} - T)^n}{\Delta T} \right]^n}_{f(\alpha)} = A \exp\left(-\frac{E}{T}\right) f(\alpha)$$

$$q(T) = \Delta T \frac{d\alpha}{dt} = \frac{\Delta H_{rxn}}{c_v} \frac{d\alpha}{dt}$$

Differential scanning calorimetry can also be used to develop simple isoconversion kinetic models

$$\alpha = \frac{Q}{\Delta H_{rxn}} \text{ or}$$

$$\frac{d\alpha}{dt} = \frac{\dot{Q}}{\Delta H_{rxn}}$$

and

$$\ln \left(\frac{d\alpha}{dt} \right) = \ln [A(\alpha)f(\alpha)] - \frac{E(\alpha)}{T(t)}$$

$$T(t) = T_0 + \beta t$$

$$t = \int_0^t dt = \int_0^\alpha \frac{d\alpha}{A(\alpha) \exp \left(-\frac{E(\alpha)}{T(t)} \right) f(\alpha)}$$

$$\frac{\partial T}{\partial t} = \frac{\lambda}{\rho c_v} \left[\frac{\partial^2 T}{\partial r^2} + \frac{J}{r} \frac{\partial T}{\partial r} \right] + \underbrace{\Delta T \frac{d\alpha}{dt}}_{\text{Heat Generation by Reaction}}$$

$$\frac{d\alpha}{dt} = \sum_{i=1}^{i=N_{\text{steps}}} K_i (1 - \alpha^{n_i}) \alpha^{m_i}$$

If the number of steps is two and we set $n_1 = 1, m_1 = 0, n_2 = 1, m_2 = 1$ then:

$$\frac{d\alpha}{dt} = K_2 (1 - \alpha) \left(\frac{K_1}{K_2} + \alpha \right)$$

When $K_1 \ll K_2$ the implied reaction become autocatalytic:

$$\frac{d\alpha}{dt} \simeq K_2 (1 - \alpha) \alpha$$

When $K_1 \gg K_2$:

$$\frac{d\alpha}{dt} \simeq K_1 (1 - \alpha)$$

The ARC / APTAC calorimeters provide critical thermal stability and kinetic rate data for compliance, design, and process optimization

- ▶ Required process safety information (PSI) for PSM regulated facilities
- ▶ Safe operating limits
- ▶ Process optimization
- ▶ Emergency relief systems design and evaluation
- ▶ Vent containment design and evaluation
- ▶ Chemical compatibility information
- ▶ Safe storage and transport

Some additional resources are available upon request

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- J. Sharkey, G. Gruber and D. Muzzio, "Prediction of the flammability range for chemical systems using Aspen", Paper presented at the AIChE DIERS User's Group Meeting, October 2, 2002.

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About ioMosaic Corporation

Through innovation and dedication to continual improvement, ioMosaic has become a leading provider of integrated process safety and risk management solutions. ioMosaic has expertise in a wide variety of areas, including pressure relief systems design, process safety management, expert litigation support, laboratory services, training, and software development.

ioMosaic offers integrated process safety and risk management services to help you manage and reduce episodic risk. Because when safety, efficiency, and compliance are improved, you can sleep better at night. Our extensive expertise allows us the flexibility, resources, and capabilities to determine what you need to reduce and manage episodic risk, maintain compliance, and prevent injuries and catastrophic incidents.

Our mission is to help you protect your people, plant, stakeholder value, and our planet.

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