

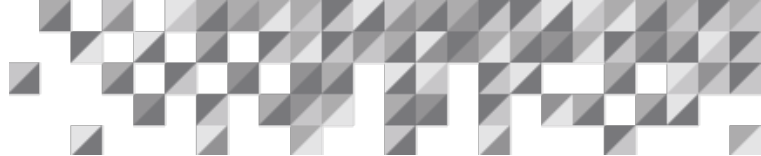
An Advanced Method for the Estimation of Reaction Stoichiometry and Rates from ARC Data ¹

An ioMosaic White Paper

G.A. Melhem

melhem@ioMosaic.com

¹ This paper appeared in the proceedings of the International Symposium on Runaway Reactions and Pressure Relief Design, August 1995, Boston, AIChE, Edited by G. A. Melhem and H. G. Fisher



ABSTRACT

Effective design of emergency relief systems requires accurate modeling. In particular, the PVT relation of such systems is fundamental and unique. This relation must be accurately represented during direct scale-up or computerized simulation. Variables which can significantly alter the PVT behavior of a system should be quantified, and included in the design.

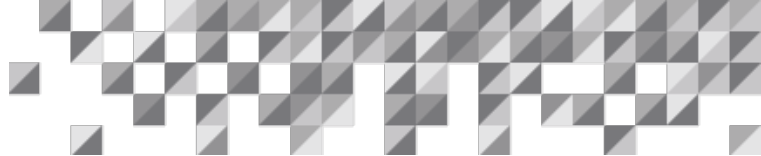
The pressure/temperature (PT) relation is a function of thermal inertia, liquid fill level (vessel void fraction), composition and chemical identity (vapor-liquid equilibrium, liquid/vapor density, heat of formation, etc.). For a specified relief device set pressure, there is a unique corresponding system temperature. For reactive systems, this temperature corresponds to a reaction rate. Small errors in estimating this temperature can lead to inadequate sizing and potential catastrophic vessel failure.

Estimation of fluid flow rates and their associated energy depletion rates is a strong function of chemical identity. Often, simple reaction models are used which ignore this fact. If the reaction model only fits the observed constant PVT relation and PT time histories, it will yield inaccurate predictions. The model may assume, for example, that the reaction products are made of a heavy and a light component. It may also specify a heat of reaction independently. However, these assumptions are often thermodynamically inconsistent and do not guarantee a unique solution, i.e. the chemical identities of the products are not unique. As a result, the estimated flow rates are often in error.

This paper presents a method that guarantees a thermodynamically consistent and unique solution. The method requires that the reaction stoichiometries and chemical identities of the products are thermochemically favorable. This is done by performing a constrained multiphase simultaneous physical and chemical equilibrium calculation. The calculation is performed at constant volume for a proposed stoichiometry and product list. These constraints are imposed as additional atom matrix constraints for the Gibbs free energy minimization; they reduce the search space for rate-limiting reaction steps.

This method yields a reaction stoichiometry that is used as input to a computer program. The program simulates the Accelerating Rate Calorimeter (ARC) test, in order to establish reaction rates— including pre-exponential factors, reaction orders, and activation energies.

We illustrate the use of this method in two cases. Both cases use closed volume data to find reaction stoichiometry and kinetic information. The first case considers the decomposition of di-*t*-butyl peroxide; the second looks at the esterification of methanol and acetic acid.



ESTABLISHING REACTION STOICHIOMETRY

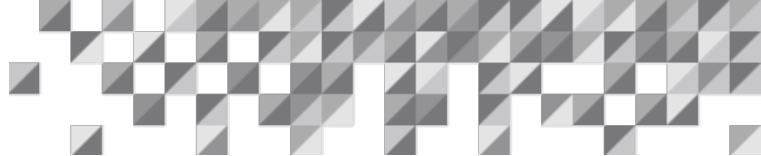
The Accelerating Rate Calorimeter (ARC) is an instrument that can provide adiabatic pressure and temperature-time data required for establishing reaction stoichiometry and pressure relief design. This instrument which was developed by Townsend and Tou (see [1] and [2]) is known to provide ample thermokinetic data that is applicable to the design and safety/performance evaluation of reactors and storage vessels. Such thermokinetic data includes:

- ² adiabatic rate of self-heating,
- ² adiabatic time to explosion,
- ² rate of pressure rise,
- ² maximum rate of reaction,
- ² kinetic data such as activation energy, reaction order and preexponential factor, and
- ² heat of reaction.

The ARC can also provide pressure-volume-temperature (PVT) data for pure components (vapor pressure) and mixtures (vapor-liquid equilibrium). Measured PVT data can be used with the aid of an equation of state to estimate liquid density, liquid heat capacity, latent heat of vaporization, nonideal solution thermodynamics, and most importantly vapor-liquid equilibrium data which is crucial for pressure relief design, especially for reactive systems.

For systems involving large numbers of degrees of freedom (reactions and species), obtaining the exact stoichiometry and species identity can be a formidable task. We can however, simplify and constrain the equilibrium calculation in order to narrow the search space as follows:

1. Volume, pressure and adiabatic temperature rise must match observed experimental values.
2. The final cooldown pressure/temperature conditions at constant volume yield a certain ratio of noncondensables / volatiles which must be reflected by the identity of any proposed reaction products.
3. Chemical analysis of the liquid phase and/or vapor phase can provide useful additional constraints. The amounts of the identified species do not need to be very accurate as long as the molar ratios (which serve as constraints) are.



These types of constraints can be imposed as additional atom matrix constraints for the Gibbs free energy minimization and will serve to reduce the search space for rate-limiting reaction steps.

Clearly, this type of analysis can be useful in obtaining global reaction rate models from constant volume adiabatic small-scale tests. The following assumptions are implicit in this methodology:

1. Slow reactions are the passive constraints that will retard the relaxation of the system from reaching complete equilibrium,
2. Fast reactions will equilibrate the system subject to the constraints imposed by the slow reactions and
3. The system will proceed to its final state through a sequence of constrained equilibrium states at a rate controlled by the slow reaction steps.

We have streamlined this analysis and linked the constrained minimization code with an extensive properties database. The stoichiometry/chemical identity program executes the following steps:

1. Select all species with similar atomic constituents from the database. For example if H₂O was a reactant, the program would select H₂, O₂, O₃, OH, H etc.
2. Rank species by increasing Gibbs free energy at the system temperature and pressure.
3. Select top 100 species.
4. Impose constraints using observed data.
5. Perform simultaneous physical/chemical equilibria.

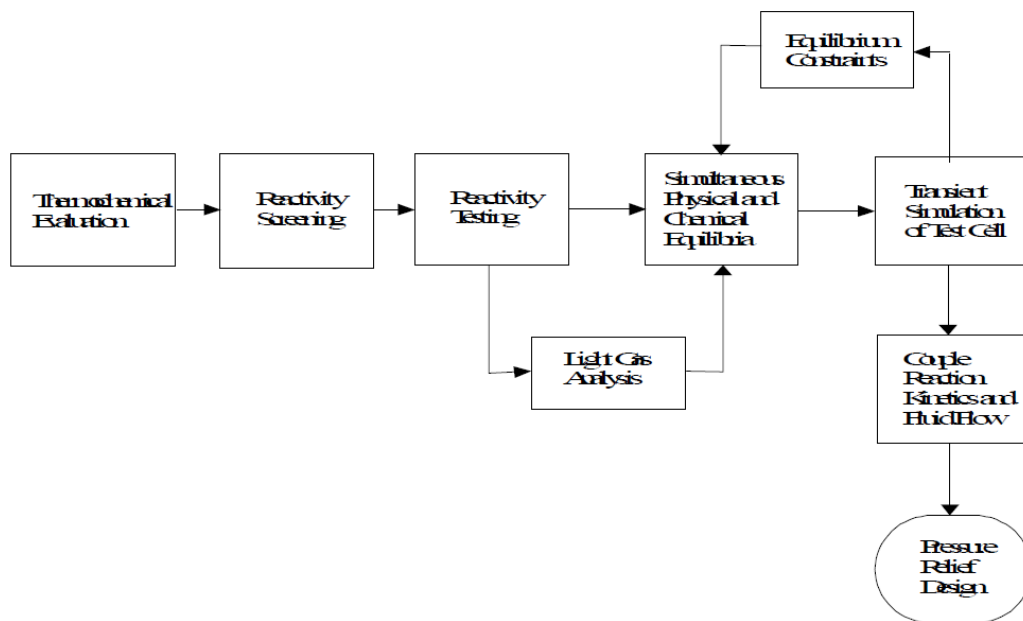
Once the global stoichiometry is identified, the detailed methods described by Melhem [4] for simulating reacting systems in vessels are used as follows to determine the reaction rates:

1. Guess reaction(s) order, preexponential factor(s) and activation energies.
2. Simulate test cell including heat-up period (heat/wait/search).
3. Calculate the sum of squares for T/P, T/time and P/time.
4. If minimum is not reached, go to step 1.

Scale-up is then achieved by using the same model for transient temperature, pressure and flow estimates for plant vessels under fire exposure or process upsets. This scale-up takes into account the size, configuration and operating conditions of the plant equipment, the extent of mixing, natural cooling losses and forced cooling capacity, vessel insulation, wall conductivity, etc. This integrated approach to ERS design for reactive systems is illustrated in Figure 1.



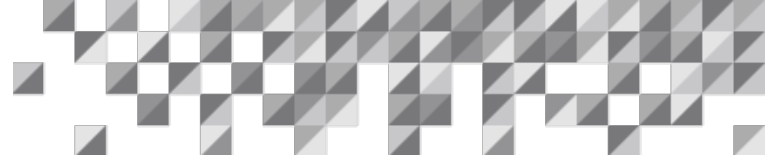
Figure 1: An integrated approach to emergency relief design for reactive systems



VAPOR-LIQUID EQUILIBRIUM DATA

In order for the proposed constrained minimization method to yield useful data for scaleup and ERS design, one must insure that the constant volume test can provide accurate vapor-liquid equilibrium data. This data is essential for accurate representation of the pressure/temperature relation and plays an important role for systems that are highly polar and/or asymmetric. The method used to simulate the test cell is equation of state based (see [4]). The binary interaction parameters are typically regressed from the same ARC data set after the constrained minimization is completed.

We illustrate the ARC's ability to measure vapor-liquid equilibrium by providing data for a 50/50 mixture (by weight) of acetone-water. The system acetone-water was selected as an illustration because of its nonideal behavior and because of the availability of ample experimental VLE data measured by other methods. A total of 6.560 grams of acetone-water mixture is placed in a titanium bomb at 303 K and 1 bar under a nitrogen gas pad. The titanium bomb mass is 8.854 grams and its volume is 9.8 ml. Figure 2 compares the measured pressure / temperature data from the ARC for the system nitrogen-acetone-water to model predictions using pre-established binary interaction parameters (BIPS) reported by Melhem et al. in 1989 [3]. The BIPS values estimated by Melhem et al. using VLE measurements by different investigators are as follows:



² acetone-water, $k_{ij} = -0.17643$, $\sigma_{ij} = 0.14203$,

² acetone-nitrogen, $k_{ij} = -0.16835$, $\sigma_{ij} = 0.002526$, and

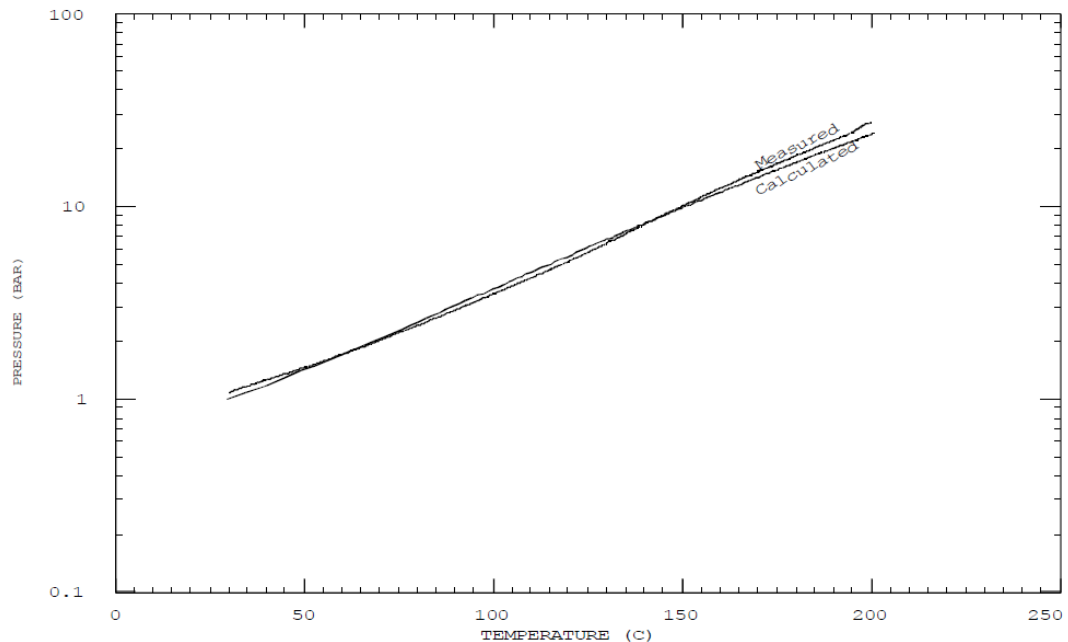
² water-nitrogen, $k_{ij} = -0.98224$, $\sigma_{ij} = 0.011908$.

As show by Figure 2, the agreement is excellent over a wide temperature range. The values of k_{ij} and σ_{ij} can be obtained using least squares minimization:

1. Guess k_{ij} and σ_{ij} .
2. Simulate test cell.
3. Minimize the sum of squares between measured and predicted P/T histories.
4. if minimum is not reached, go to 1.

This procedure can be used to verify or estimate PVT/VLE behavior using data collected during the heat-wait-search period.

Figure 2: Acetone-water-nitrogen vapor-liquid equilibrium ARC data





DI-T-BUTYL PEROXIDE/TOLUENE SYSTEM

In order to illustrate the use of the stoichiometry determination method outlined in this paper, we consider the system di-t-butyl peroxide and toluene. This system is selected because it is used by many ARC users as a test standard and because it is simple and will serve the purpose of illustrating how to apply the method.

The test used in this example involved the use of a sample which consisted of 4.0115 g of toluene and 1.0130 g of di-t-butyl peroxide in a titanium test cell. The measured ARC data and model predictions are illustrated in Figures 3, 4, 5 and 6.

Tables 1, 2 and 3 illustrate the results of the constrained Gibbs free energy minimization used to establish the overall stoichiometry of the decomposition.

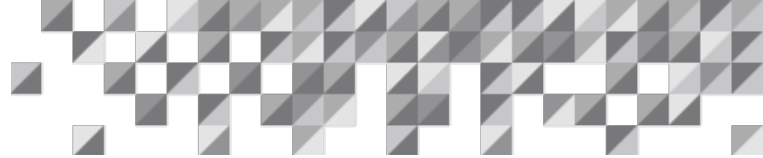
We considered 50 potential decomposition products to be present in both the liquid and vapor phase. Three cases were considered:

1. No additional constraints except for those implied by the atom matrix (base case).
2. Same as 1 but with one additional constraint that specifies that toluene does not participate in the reaction
3. Same as 2 but with three additional constraints that require that the final cooldown pressure must be matched and that the adiabatic temperature rise must also be matched. These three constraints are added incrementally. They are reported here as one case in order to simplify the tables. The cooldown pressure is easily matched by specifying a fixed ratio of all potential non-condensable gas products to the total number of moles. The adiabatic temperature rise is easily matched by specifying that the heat of reaction is equal to that measured in the ARC.

We note from Table 1 that the total Gibbs free energy has a global minimum when unconstrained and that it has a local minimum at the desired final state measured by the ARC. One should also note that the free energy minimization is sensitive to the presence of isomers. For example, the formation of tert-butanol is favored over the formation of sec-butanol and n-butanol.

For large molecules or decompositions involving more than one reaction, the identity of one or more of the reaction products may need to be experimentally determined by gas or liquid analysis before the system is completely specified.

Figure 3 compares the results of the test cell simulation (see [4]) using the stoichiometry determined by the free energy minimization. The equation of state is used without the specification



of binary interaction parameters (zero values were used). One of the many benefits of using computer simulations is the ability to extrapolate and correct the data. For example, Figure 3 illustrates what the temperature rise rate would be at a thermal inertia of 1 and for a mixture of different composition ². The calculated order of the reaction is 1 and the calculated activation energy is 18,954 /K. The pre-exponential factor is 1:05 £ 10¹⁶ where the units are kmol, m³ and seconds.

Figure 4 compares model predictions of pressure/temperature with measured values. Good agreement is shown. These predictions could have been refined to exact fits by also regressing, using the same computer code and based on the same ARC data, binary interaction parameters ³. The ARC collected data beyond the observed reaction and that part of the data was not replicated by the simulation. The cooldown curve, was duplicated and shows good agreement. This indicates that the selection of non-condensable products is appropriate.

Figures 5 and 6 compare model predictions of pressure/time and temperature/time data with experimental values. A good fit is evident. It is important to simulate the heat-wait-search period before the decomposition or reaction occurs, especially for gassy systems. The cooldown curve of pressure vs. time and temperature vs. time is not matched by the simulation since only the final point is used as a constraint.

We next test the method developed in this paper on a simple system that involves two reactants instead of a self-decomposition.

² One must confirm that there is no change in decomposition mechanism by running two or more experiments at different values of thermal inertia, say 1.5 and 2, for example

³ This is not necessary for this example, but should be done for actual designs. These parameters can also be estimated using group contribution methods

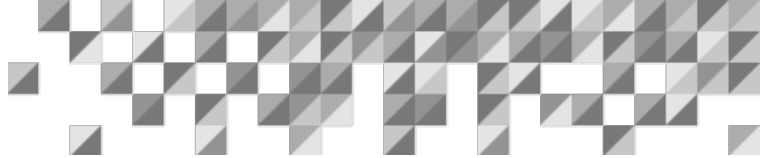


Figure 3: Comparison between model prediction and measured data for dT/dt

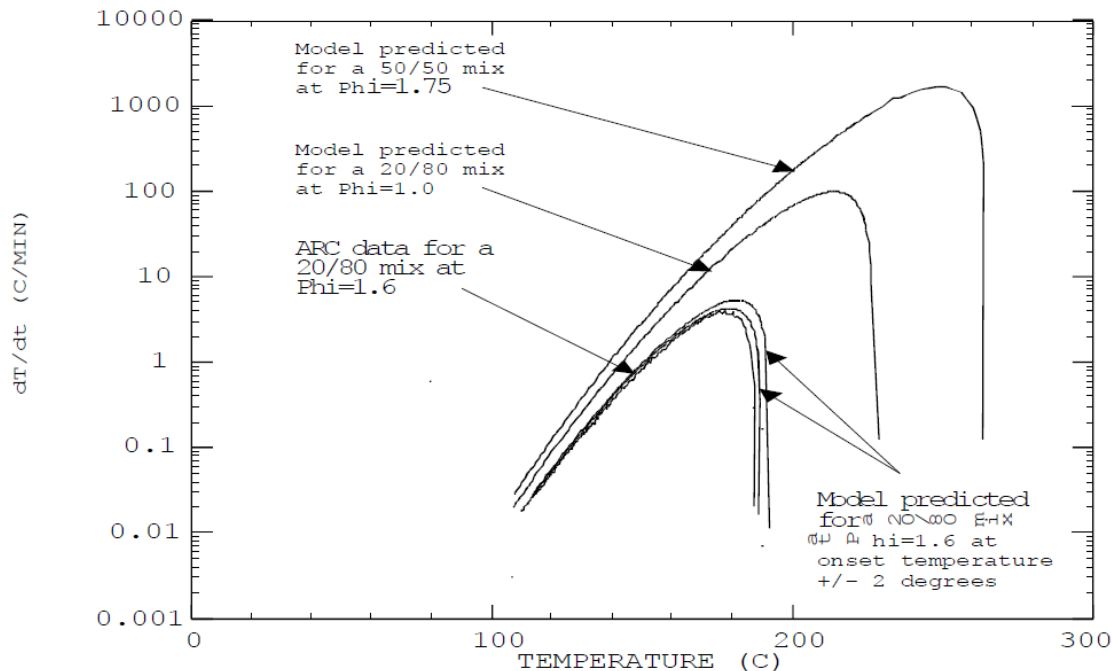
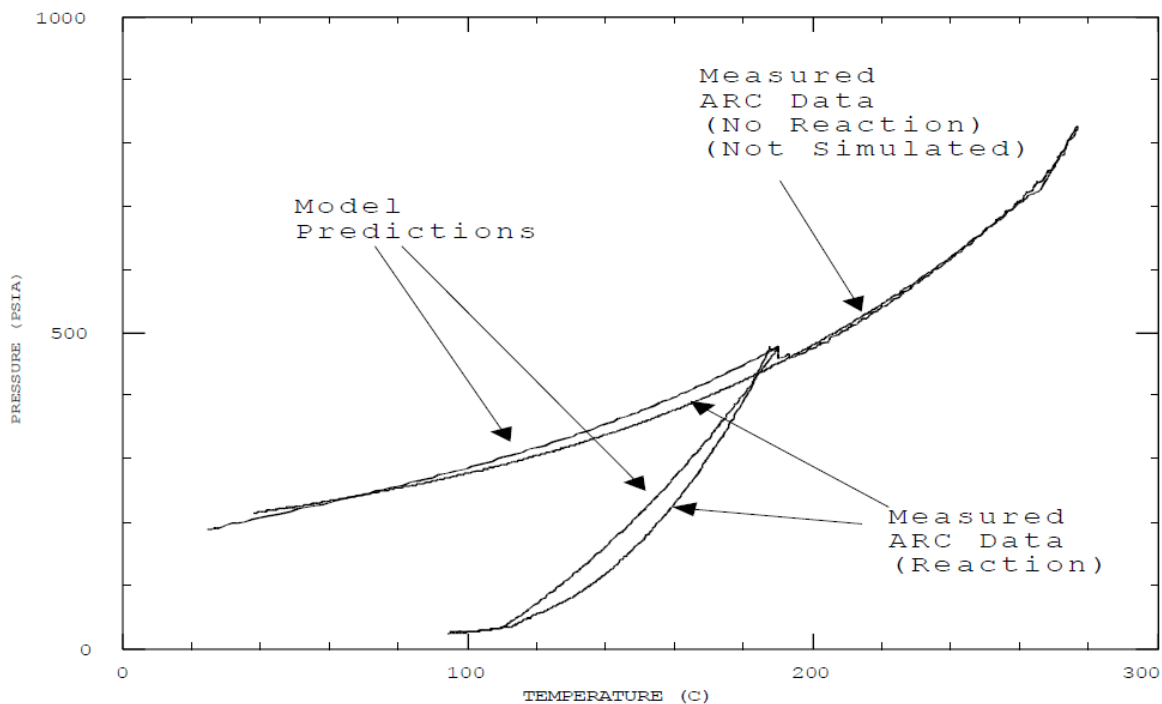


Figure 4: Comparison between model prediction and measured data for pressure vs. temperature



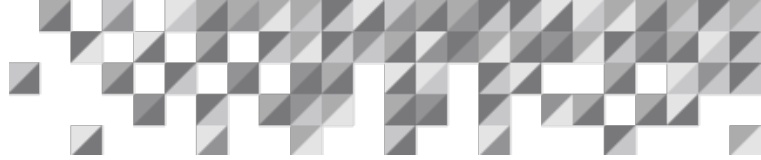


Figure 5: Comparison between model prediction and measured data for pressure vs. time

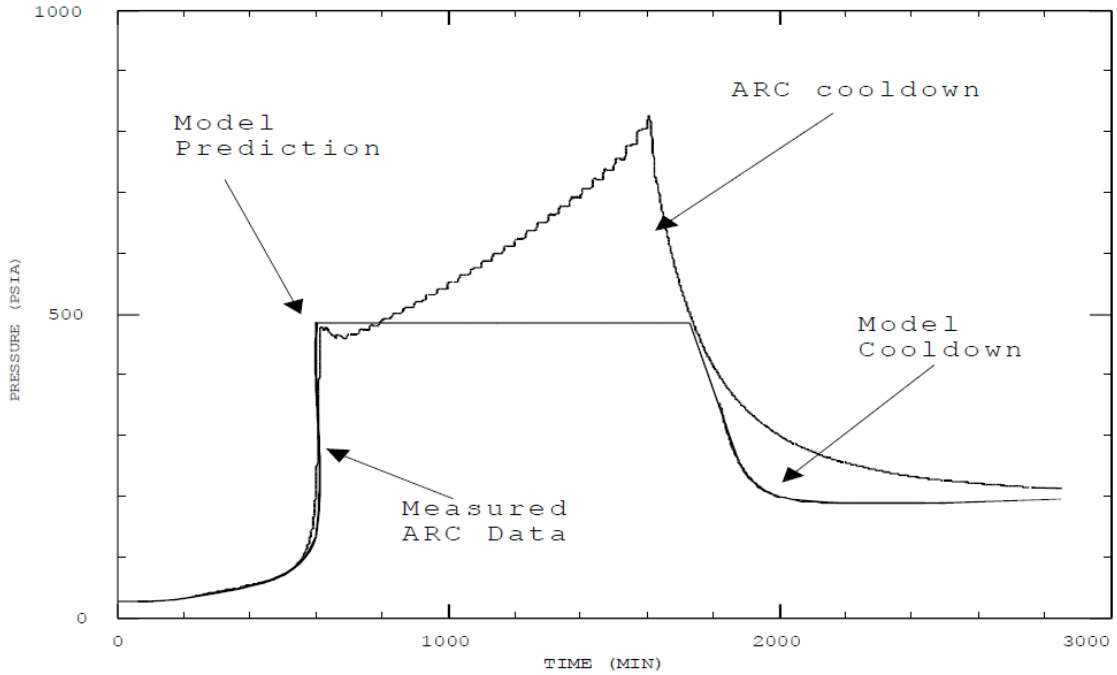
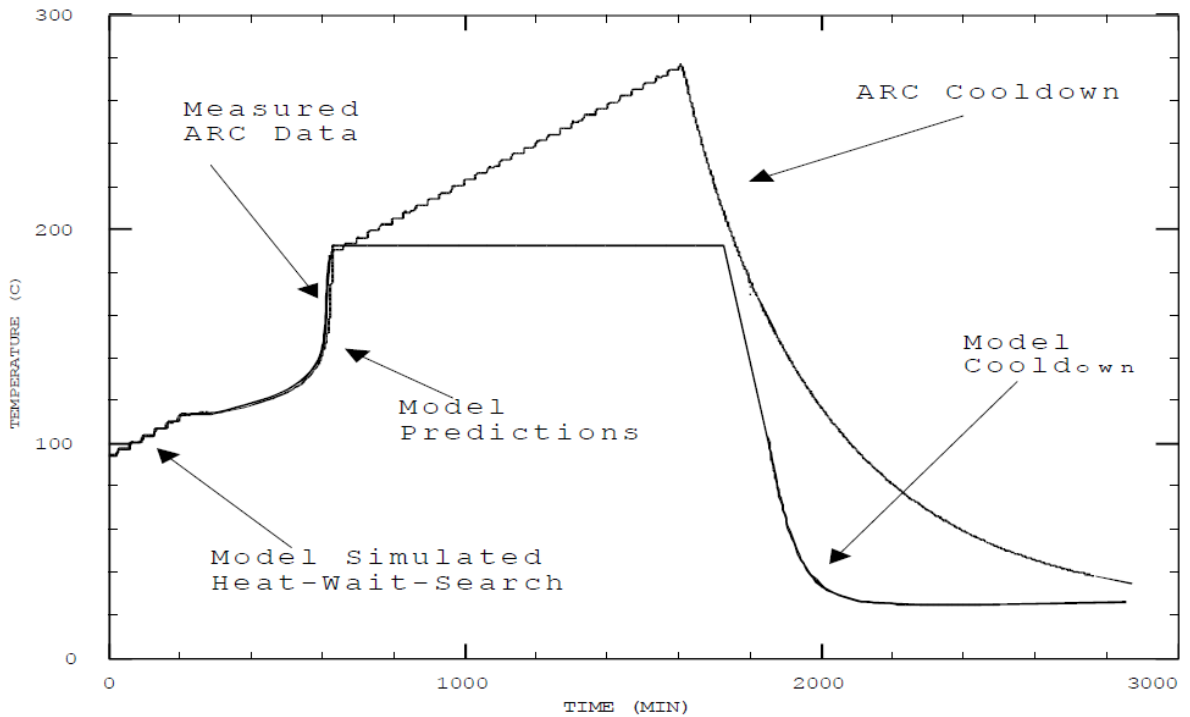


Figure 6: Comparison between model prediction and measured data for temperature vs. time





ESTERIFICATION OF METHANOL AND ACETIC ACID

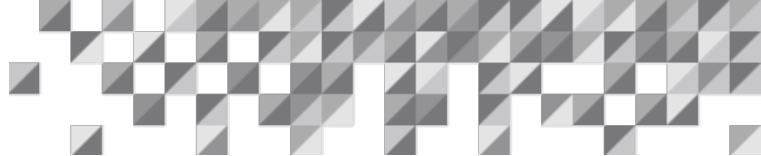
We will illustrate the use of closed volume data to find reaction stoichiometry and kinetic information for the esterification reaction of methanol and acetic anhydride. Figures 7, 8 and 9 illustrate the pressure-time, temperature-time, and temperature rise rate data observed experimentally using the ARC. The sample size used was five grams and consisted of 69.7 mole % acetic anhydride and 29.9 mole % methanol (acetic anhydride is in excess). The initial temperature and pressure were at 283 K and 101325 Pa with a nitrogen pad. The amount of nitrogen present in the bomb at the start is estimated at 0.415 mole %. The final cooldown pressure was measured to be slightly above atmospheric pressure at 298 K. Chemical analysis was not performed on the reaction products to determine their identity. The peak temperature was measured to be 377 K and the corresponding peak pressure was measured to be 299000 Pa. The bomb volume was 10 ml and has an equivalent thermal heat capacity of 15.3 g of iron.

We followed the constrained equilibrium method outlined in this paper and selected (for illustration purposes) 50 chemical species as potential reaction products. We then conducted three P/T simulations to match the peak temperature and pressure conditions measured in the experiment. These estimates are summarized in Table 4 with solid-vapor-liquid molar distributions reported in Tables 5 and 6. Iron was used to simulate the bomb thermal inertia and all quantities are scaled up to a kilomole and cubic meter basis to avoid numerical roundoff errors.

Case 1 represents an unconstrained simulation. All the reactants are consumed and no liquid phase is predicted for the reaction products. From Table 4 we note that to match the experimental peak temperature and pressure values, a volume change of 1550.4 m³ and an exothermic enthalpy change of -200 MJ are required. This clearly does not represent the measured constant volume data.

Case 2 is a repeat of case 1 with one additional constraint. This constraint specifies that all reaction products are volatiles, i.e. (with the exception of nitrogen) noncondensables are not present as products. This is in agreement with the reported final cooldown pressure. We note from Table 4 that the minimum Gibbs free energy calculated is larger than that of case 1 and that the maximum number of independent reactions has decreased by one degree of freedom. The calculated change in volume and enthalpy at 377 K and 299000 Pa still do not match the experimental data.

Case 3 is a repeat of case 2 with one additional constraint. This second constraint specifies (based on chemical grounds) that the total number of moles has to remain constant, i.e. the number of moles of reactants is equal to the number of moles of products. Table 4 shows a good agreement between predicted and reported constant volume data. Tables 5 and 6 show that



equimolar amounts of methyl acetate and acetic acid are formed and that all the methanol is converted. Small amounts of ethylene glycol, n-propionaldehyde and ethyl formate are also formed. The negative overall volume change is due to the absence of binary interaction parameters for the equation of state, i.e. zero values are used. BIPS values need to be estimated for systems which exhibit strong solution nonidealities.

The esterification of methanol / acetic anhydride is a well studied reaction which is known to yield methyl acetate and acetic acid. Using the reaction stoichiometry predicted by the equilibrium code and simulation of the test data yield an excellent agreement between the entire measured and predicted pressure temperature, pressure-time, temperature-time and temperature rise rate.

Chemical analysis of the liquid phase and/or vapor phase can provide useful additional constraints. The amounts of the identified species do not need to be very accurate as long as the molar ratios (which serve as constraints) are. This method can be applied to more complicated reaction schemes. A detailed and robust simultaneous chemical and physical equilibrium is required, however. Theoretically, we may need as many constraints as the number of the degrees of freedom in order to completely specify the system. We have, to date, applied this technique to more than thirty complex systems and used no-more than a total of six constraints.

SCALEUP OF ARC DATA

One of the most useful aspects of computer simulation is the ability of the user to perform sensitivity/what-if analysis. Once the reaction stoichiometry and rate model are established and validated, they are coupled with fluid mechanics to provide guidance for ERS design and many other useful process related operational and safety issues (see [4]).

We illustrate this using a simple example. Consider a spherical vessel that contains 6500 kg of a 50/50 mixture of di-t-butyl peroxide and toluene. The vessel has a total volume of 10.5 m³ and is being heated by a fire at the rate of 12 C/min approximately. A relief set pressure of 175000 Pa is desired. Determine what size rupture disk is required in order to protect the vessel from failing due to runaway conditions.

We used the kinetics data established in this paper as input to the detailed ERS design method outlined by Melhem in reference [4] and simulated the runaway reaction. Figures 10 and 11 illustrate the calculated pressure and vessel contents profiles as a function of time using different rupture disk sizes. A 12 inch rupture disk would be required. Other calculated data that is not shown here include the reaction force imparted to the vessel, the release rates, the molar composition of the effluent, etc.



These calculations assume a discharge coefficient of 0.62 for the rupture disks. The presence of additional piping/fittings can reduce the flow capacity of the rupture disks.

CONCLUSION

A new method is developed for identifying reaction stoichiometry, chemical identity for reaction products and reaction rates from closed volume ARC test data. The number of species considered is currently limited to a database of 1300 chemicals. This new method provides a reliable basis for the scaleup of ARC data for ERS design.

Finally, work is nearing completion on a variation of this scheme which will use group contribution concepts to generate all possible chemical structure permutations for reaction products.

Table 1: Constrained Gibbs free energy minimization data for di-t-butyl peroxide system

	Case 1	Case 2	Case 3
Atom and Constraints Matrix rank	5	6	9
Maximum number of independent reactions	96	95	92
Scaled Gibbs free energy	1232	1242	1564
Initial temperature (K)	383	383	383
Final temperature (K)	463	463	463
Initial pressure (Pa)	275000	275000	275000
Final pressure (Pa)	3290000	3290000	3290000
Initial number of moles (kmol)	254.815	254.815	254.815
Final number of moles (kmol)	277.98658	281.616	267.5
Change in number of moles (kmol)	23.17158	26.801	12.685
Initial volume (m3)	10.4	10.4	10.4
Final volume (m3)	51.6	46.8	10.8
Volume change (m3)	41.2	36.4	0.362
Initial enthalpy (MJ)	87000	87000	87000
Final enthalpy (MJ)	86400	86600	86900
Enthalpy change (MJ)	-516	-388	-69

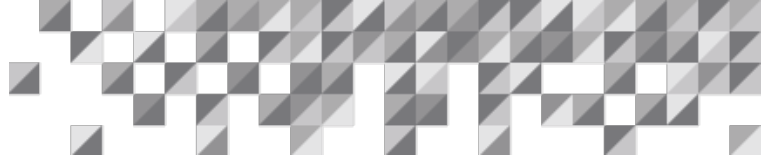


Figure 7: Constant volume pressure-time history for the acetic anhydride/methanol esterification reaction

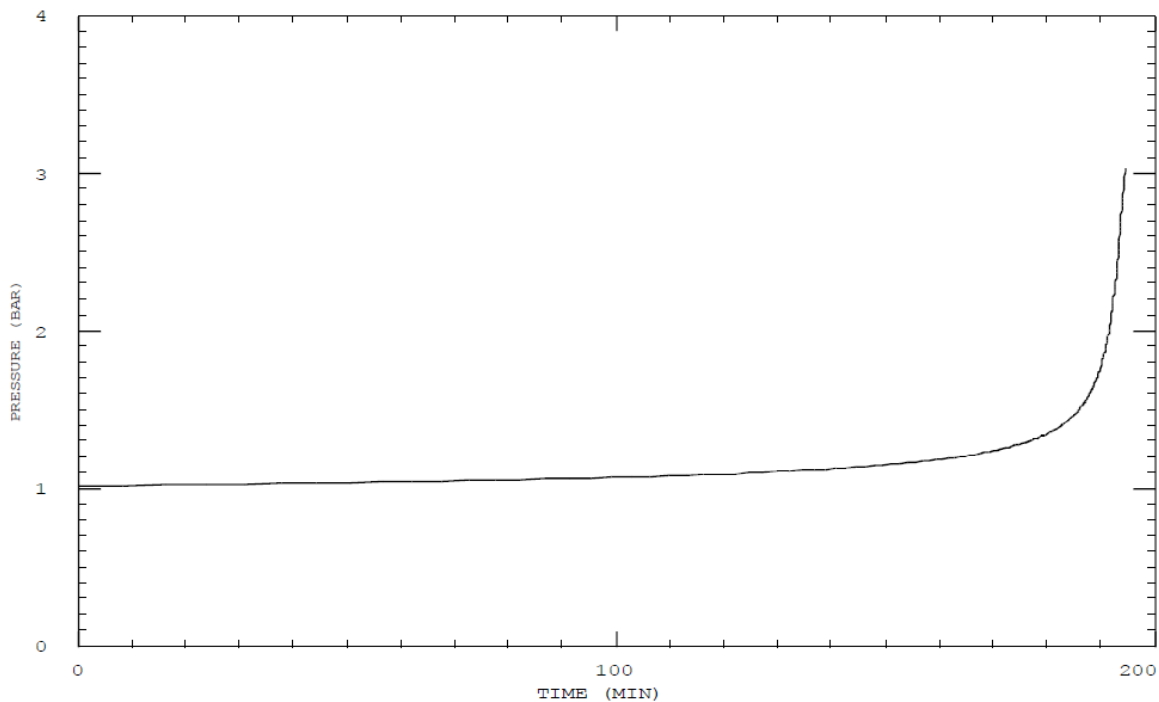
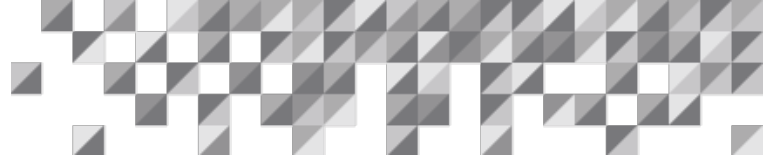


Table 2: Constrained Gibbs free energy minimization data for di-t-butyl peroxide. Solid/vapor molar distribution (kmol)

Component/Phase	Initial	Case 1	Case 2	Case 3
TITANIUM (S)	204	204	204	204
DI-t-BUTYL PEROXIDE (V)			9.19926	
TOLUENE (V)		6.28738	0.31842	0.60391
NITROGEN (V)	0.33000	0.01137		0.16703
FORMIC ACID (V)		0.00009		
WATER (V)		0.00296	0.00040	
ETHANOL (V)				
METHANOL (V)				
GLYOXAL (V)				
ACETONE (V)		0.00004	0.00002	0.37950
CARBON MONOXIDE (V)		0.01214	0.00504	
ACETALDEHYDE (V)				



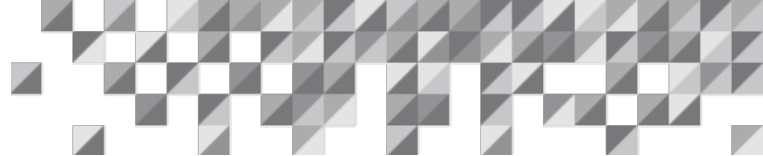
Component/Phase	Initial	Case 1	Case 2	Case 3
n-PROPIONALDEHYDE (V)				
DIMETHYL ETHER (V)				
FORMALDEHYDE (V)				
HYDROGEN PEROXIDE (V)				
ALLYL ALCOHOL (V)				
KETENE (V)				
ACROLEIN (V)				
METHANE (V)		29.1621	23.13736	1.57906
METHYL VINYL ETHER (V)				
ETHANE (V)		0.04681	0.02017	0.18280
1,2-PROPYLENE OXIDE (V)				
n-BUTANOL (V)				
ETHYLENE OXIDE (V)				
1,3-PROPYLENE OXIDE (V)				
HYDROGEN (V)		0.00171	0.00011	
OXYGEN (V)				
PROPYLENE (V)		0.00004	0.00010	
ETHYLENE (V)		0.00004		
PROPARGYL ALCOHOL (V)				
CYCLOPROPANE (V)				
OZONE (V)				
METHYLACETYLENE (V)				
PROPADIENE (V)				
ACETYLENE (V)				
ETHYLBENZENE (V)		0.14401	0.04780	0.00464
1,2-DIPHENYLETHANE (V)		0.12910	0.00835	
n-BUTANOL (V)				
sec-BUTANOL (V)				
tert-BUTANOL (V)				0.05288
ISOBUTANOL (V)				



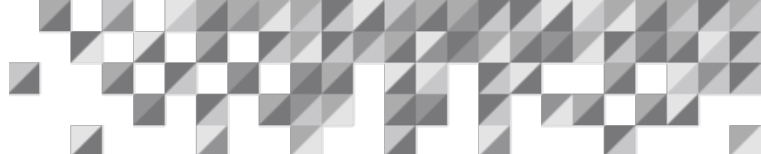
Component/Phase	Initial	Case 1	Case 2	Case 3
DIETHYL ETHER (V)				
C4H10O (V)				
C4H10O2 (V)				
1,3-BUTANEDIOL (V)				
1,4-BUTANEDIOL (V)				
1,2-DIMETHOXYETHANE (V)				
2-ETHOXYETHANOL (V)				
ACETIC ANHYDRIDE (V)				
CARBON DIOXIDE (V)		6.20060	5.87675	

Table 3: Constrained Gibbs free energy minimization data for di-t-butyl peroxide. Liquid molar distribution (kmol)

Component/Phase	Initial	Case 1	Case 2	Case 3
DI-t-BUTYL PEROXIDE (L1)	6.87900			
TOLUENE (L1)	43.60600	18.8614	34.40074	43.00209
NITROGEN (L1)		0.31863	0.01158	0.16297
FORMIC ACID (L1)			0.00002	
WATER (L1)		0.00043	0.00060	
ETHANOL (L1)				
METHANOL (L1)				
GLYOXAL (L1)				
ACETONE (L1)		0.00003	0.00002	10.14767
CARBON MONOXIDE (L1)		0.00003	0.00033	
ACETALDEHYDE (L1)				
n-PROPIONALDEHYDE (L1)				
DIMETHYL ETHER (L1)				
FORMALDEHYDE (L1)				
HYDROGEN PEROXIDE (L1)				
ALLYL ALCOHOL (L1)				
KETENE (L1)				



Component/Phase	Initial	Case 1	Case 2	Case 3
ACROLEIN (L1)				
METHANE (L1)		1.57721	1.87412	2.74251
METHYL VINYL ETHER (L1)				
ETHANE (L1)		0.01748	0.00161	0.76217
1,2-PROPYLENE OXIDE (L1)				
n-BUTANOL (L1)				
ETHYLENE OXIDE (L1)				
1,3-PROPYLENE OXIDE (L1)				
HYDROGEN (L1)		0.00034	0.00001	
OXYGEN (L1)				
PROPYLENE (L1)		0.00001	0.00001	
ETHYLENE (L1)		0.00001	0.00001	
PROPARGYL ALCOHOL (L1)				
CYCLOPROPANE (L1)				
OZONE (L1)				
METHYLACETYLENE (L1)				
PROPADIENE (L1)				
ACETYLENE (L1)				
ETHYLBENZENE (L1)		0.67787	0.22861	0.53482
1,2-DIPHENYLETHANE (L1)		9.86413	1.48636	
n-BUTANOL (L1)				
sec-BUTANOL (L1)				
tert-BUTANOL (L1)				3.17794
ISOBUTANOL (L1)				
DIETHYL ETHER (L1)				
C4H10O (L1)				
C4H10O2 (L1)				
1,3-BUTANEDIOL (L1)				
1,4-BUTANEDIOL (L1)				
1,2-DIMETHOXYETHANE (L1)				



Component/Phase	Initial	Case 1	Case 2	Case 3
2-ETHOXYETHANOL (L1)				
ACETIC ANHYDRIDE (L1)				
CARBON DIOXIDE (L1)		0.67050	0.99902	

Table 4: Constrained Gibbs free energy minimization data for methanol/acetic acid esterification

	Case 1	Case 2	Case 3
Atom and Constraints Matrix rank	5	6	7
Maximum number of independent reactions	98	97	96
Scaled Gibbs free energy	-9493	-7688	-7469
Initial temperature (K)	283	283	283
Final temperature (K)	377	377	377
Initial pressure (Pa)	101325	101325	101325
Final pressure (Pa)	299000	299000	299000
Initial number of moles (kmol)	335.798	335.798	335.798
Final number of moles (kmol)	422.917	343.440	335.798
Change in number of moles (kmol)	87.119	7.642	0
Initial volume (m3)	10.6	10.6	10.6
Final volume (m3)	1561	37.2	10.3
Volume change (m3)	1550.4	26.4	-0.3
Initial enthalpy (MJ)	82800	82800	82800
Final enthalpy (MJ)	82600	81972	82860
Enthalpy change (MJ)	-200	-828	-60

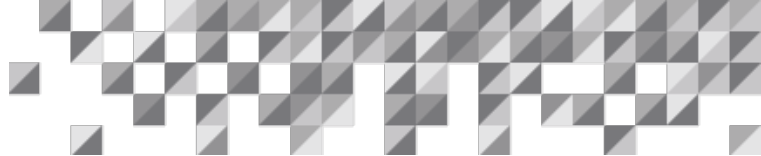


Figure 8: Constant volume temperature-time history for the acetic anhydride/methanol esterification reaction

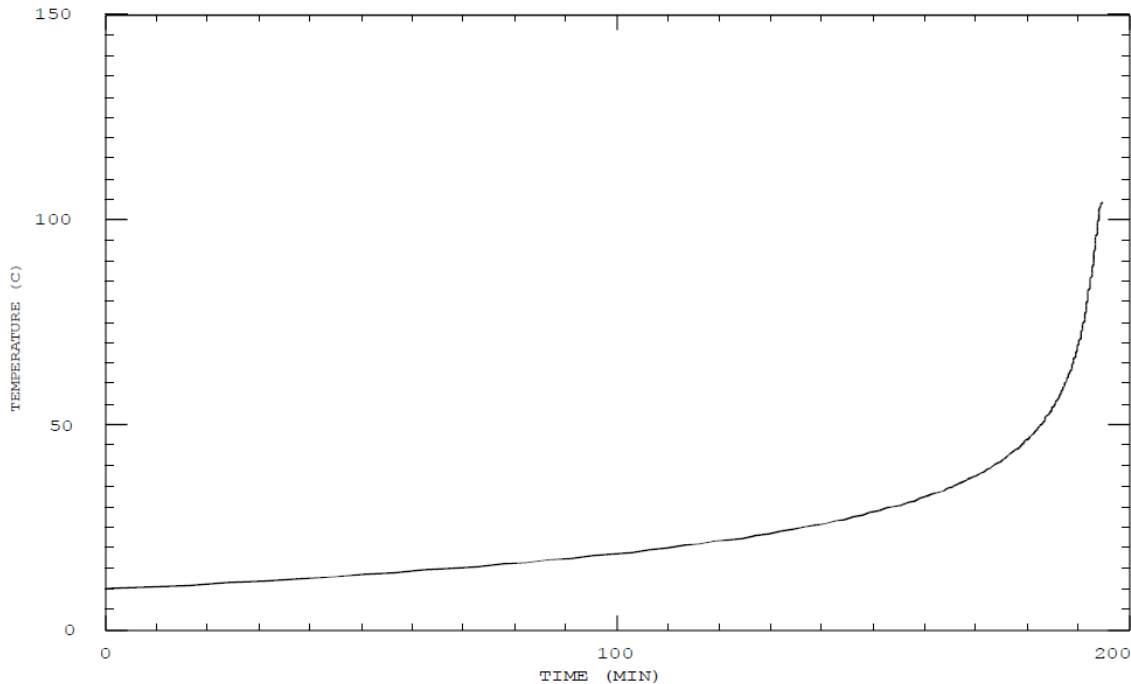
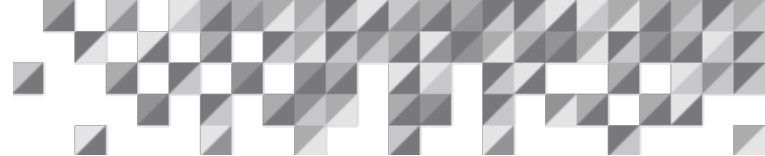


Table 5: Constrained Gibbs free energy minimization data for methanol/acetic anhydride esterification. Solid/vapor molar distribution (kmol)

Component/Phase	Initial	Case 1	Case 2	Case 3
IRON (S)	273.950	273.950	273.95	273.95
ACETIC ANHYDRIDE (V)			0.05035	0.01970
METHANOL (V)				
NITROGEN (V)	0.25664	0.25664	0.24848	0.20925
CARBON DIOXIDE (V)		71.6930	0.00381	
ACETIC ACID (V)			0.36491	0.02940
FORMIC ACID (V)			0.00121	
METHYL ACETATE (V)				0.18591
ETHYLENE GLYCOL (V)				
METHYL FORMATE (V)			0.00022	
ETHYL FORMATE (V)				0.00046



Component/Phase	Initial	Case 1	Case 2	Case 3
METHYL ACRYLATE (V)			0.04029	
WATER (V)			0.00068	
beta-PROPIOLACTONE (V)				
VINYL ACETATE (V)				
VINYL FORMATE (V)				
CARBON MONOXIDE (V)		4.41002		
GLYOXAL (V)				
DIKETENE (V)			0.00040	
ACETALDEHYDE (V)			0.00092	
FORMALDEHYDE (V)				
n-PROPIONALDEHYDE (V)			0.00432	0.00103
HYDROGEN PEROXIDE (V)				
DIMETHYL ETHER (V)				
KETENE (V)			0.00093	
ALLYL ALCOHOL (V)				
ACROLEIN (V)			0.03141	
METHANE (V)		51.5319		
METHACROLEIN (V)		0.00007	0.27799	
trans-CROTONALDEHYDE (V)			0.01838	
METHYL VINYL ETHER (V)				
2,5-DIHYDROFURAN (V)			0.00027	
ETHANE (V)		7.83576		
1,2-PROPYLENE OXIDE (V)				
HYDROGEN (V)				
OXYGEN (V)				
ETHYLENE OXIDE (V)				
1,3-PROPYLENE OXIDE (V)				
DIVINYL ETHER (V)				
ETHYLENE (V)		0.00549		
PROPARGYL ALCOHOL (V)				



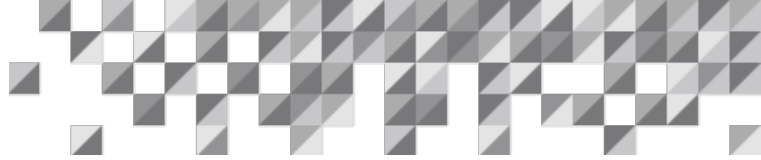
Component/Phase	Initial	Case 1	Case 2	Case 3
PROPYLENE (V)		5.35822	1.65796	
CYCLOPROPANE (V)				
1,3-BUTADIENE (V)		7.87622	0.30041	
METHYLACETYLENE (V)				
DIMETHYLACETYLENE (V)		0.00020	0.00002	
ACETYLENE (V)				
PROPADIENE (V)				
1,2-BUTADIENE (V)				
ETHYLACETYLENE (V)			0.00089	
VINYLCACETYLENE (V)				

Table 6: Constrained Gibbs free energy minimization data for methanol/acetic acid esterification. Liquidmolar distribution (kmol)

Component/Phase	Initial	Case 1	Case 2	Case 3
ACETIC ANHYDRIDE (L)	43.10200		20.62222	24.67269
METHANOL (L)	18.49016			
NITROGEN (L)			0.00815	0.04739
CARBON DIOXIDE (L)			0.00312	
ACETIC ACID (L)			40.9804	18.46073
FORMIC ACID (L)			0.00277	
METHYL ACETATE (L)			0.00196	18.02022
ETHYLENE GLYCOL (L)				0.08052
METHYL FORMATE (L)			0.00037	
ETHYL FORMATE (L)				0.04255
METHYL ACRYLATE (L)			0.14814	
WATER (L)			0.00081	
beta-PROPIOLACTONE (L)			0.00139	
VINYL ACETATE (L)				
VINYL FORMATE (L)				
CARBON MONOXIDE (L)				

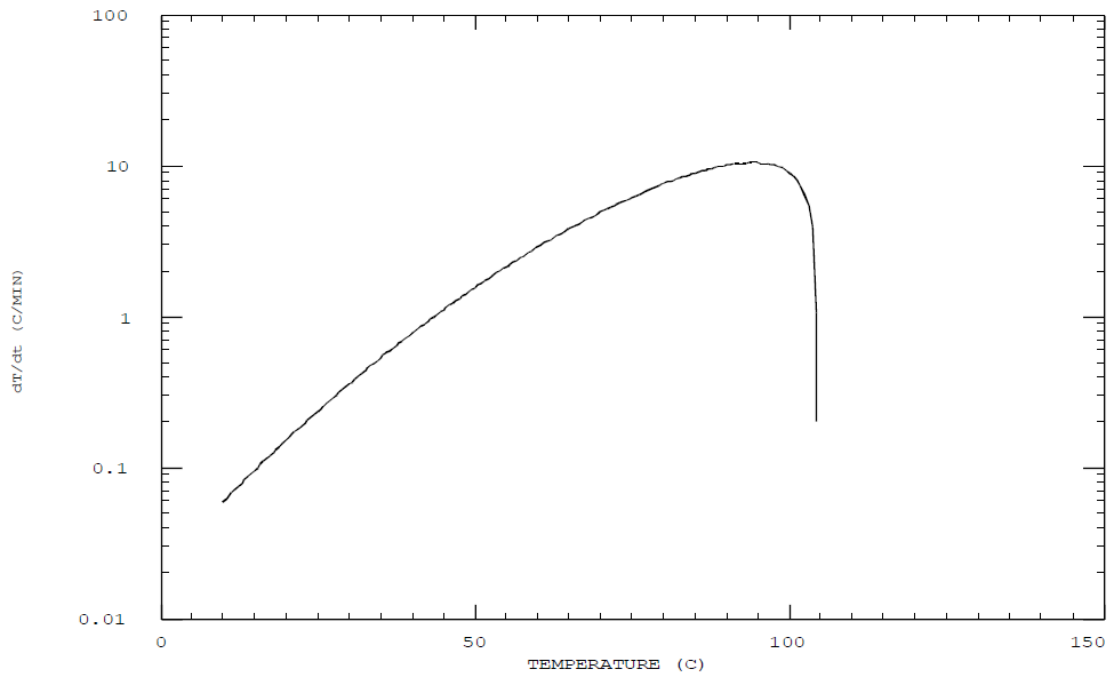


Component/Phase	Initial	Case 1	Case 2	Case 3
GLYOXAL (L)				
DIKETENE (L)				
ACETALDEHYDE (L)			0.00126	
FORMALDEHYDE (L)			0.00038	
n-PROPIONALDEHYDE (L)			0.02116	0.07831
HYDROGEN PEROXIDE (L)				
DIMETHYL ETHER (L)				
KETENE (L)				
ALLYL ALCOHOL (L)			0.00031	
2-BUTYNE-1,4-DIOL (L)				
ACROLEIN (L)			0.00035	
METHANE (L)				
METHACROLEIN (L)			0.68495	
trans-CROTONALDEHYDE(L)			1.61204	
METHYL VINYL ETHER (L)				
2,5-DIHYDROFURAN (L)			0.02429	
ETHANE (L)				
1,2-PROPYLENE OXIDE (L)				
HYDROGEN (L)				
OXYGEN (L)				
ETHYLENE OXIDE (L)				
1,3-PROPYLENE OXIDE (L)				
DIVINYL ETHER (L)				
ETHYLENE (L)				
PROPARGYL ALCOHOL (L)				
PROPYLENE (L)			1.58132	
CYCLOPROPANE (L)			0.00038	
1,3-BUTADIENE (L)			0.78737	
METHYLACETYLENE (L)				
DIMETHYLACETYLENE (L)			0.00184	



Component/Phase	Initial	Case 1	Case 2	Case 3
ACETYLENE (L)				
PROPADIENE (L)			0.00073	
1,2-BUTADIENE (L)			0.00118	
ETHYLACETYLENE (L)			0.00015	
VINYLACETYLENE (L)				

Figure 9: Constant volume temperature rise rate history for the acetic anhydride/methanol esterification reaction



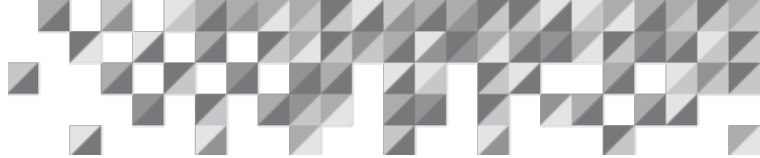


Figure 10: Computed pressure profiles for 4, 8, and 12 in rupture disks

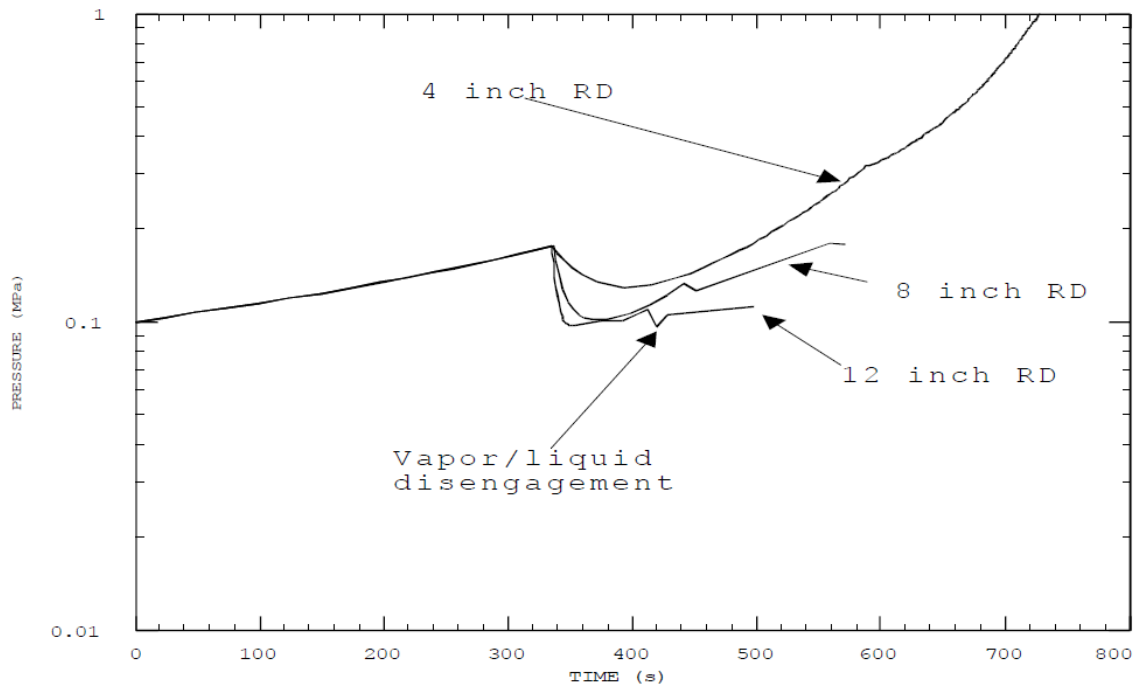
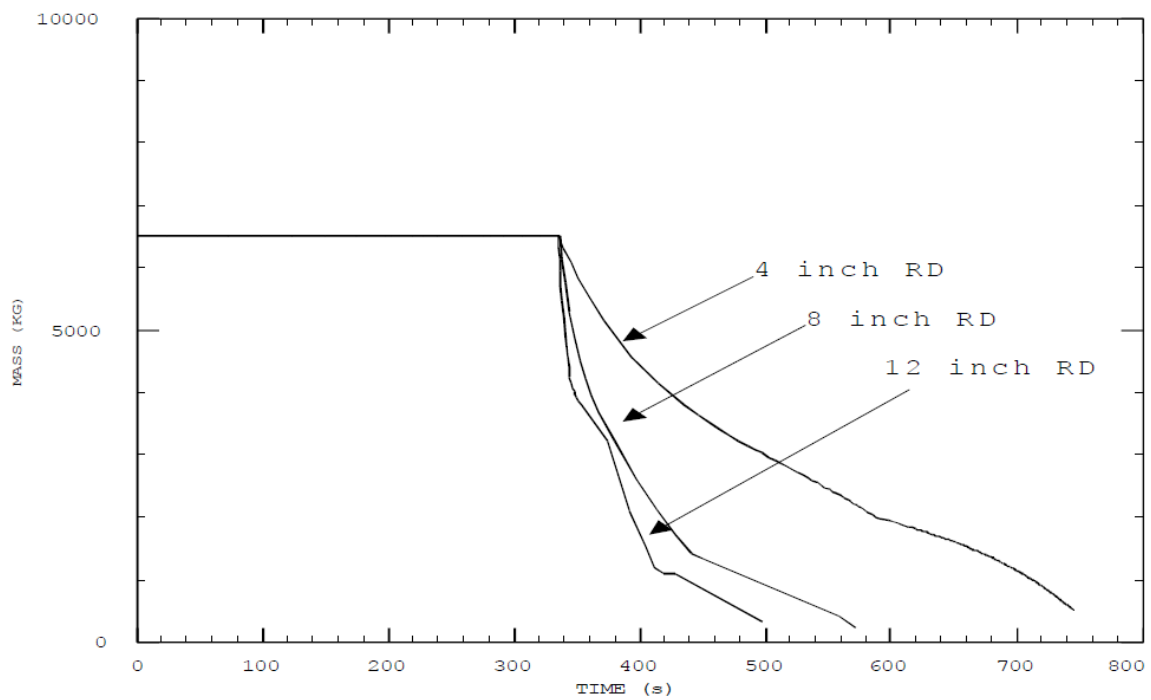
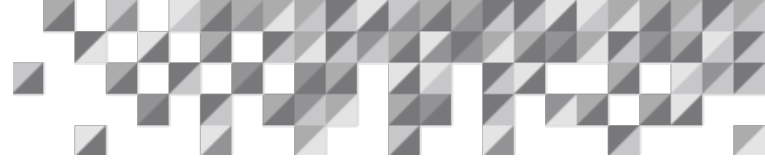


Figure 11: Computed mass profiles for 4, 8, and 12 in rupture disks





REFERENCES

D. I. Townsend. *Chem. Eng. Prog.*, 73(80), 1977.

D. I. Townsend and J. C. Tou. *Thermochim. Acta.*, 37(1), 1980.

G. A. Melhem, R. Saini, and B. M. Goodwin. A modified Peng-Robinson equation of state. *Fluid Phase Equilibria*, 47:189–237, 1989.

G. A. Melhem. Advanced ERS design using computer simulation. In *International Symposium on Runaway Reactions and Pressure Relief Design*, AIChE, 1995.