Property Measurement for Fuel Research: Physical Authenticity of Surrogates

Thomas J. Bruno

Physical and Chemical Properties Division

National Institute of Standards and Technology

Boulder, CO

Why Surrogates?

We all know the reasons-

- Aviation fuels are made of hundreds of components
  - Must meet general specifications,

    but an infinite number of combinations can do so

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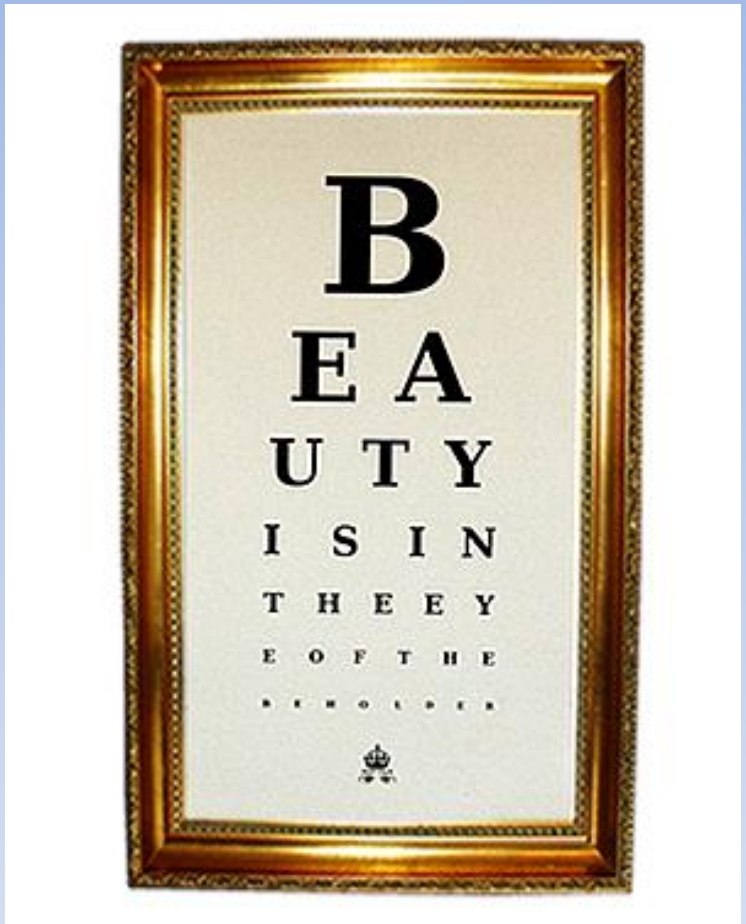
For well controlled measurements and modeling, a more defined composition is required.

-repeatability

-tractability

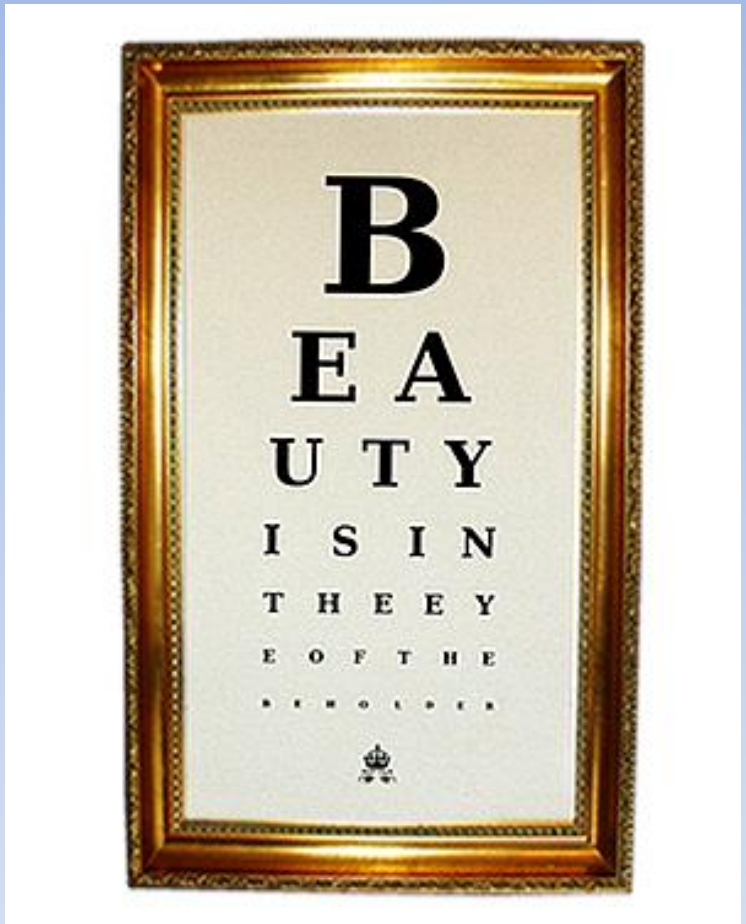
“Surrogate” means different things to different people



“Surrogate” means different things to different people

Physical surrogate-
property explicit

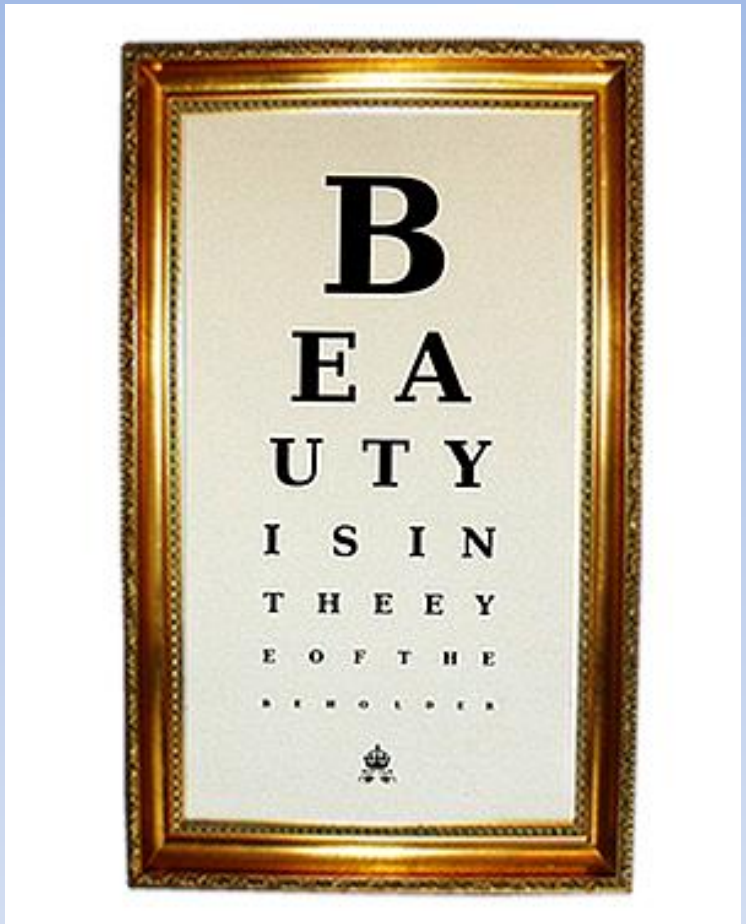
Chemical surrogate-
moiety explicit



“Surrogate” means different things to different people

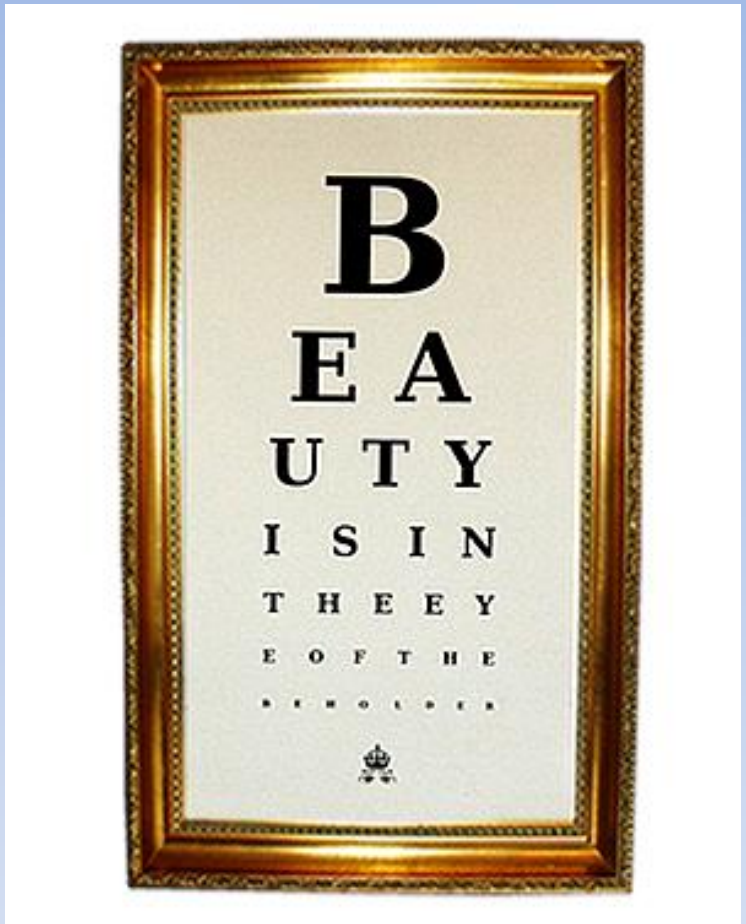
Operational Surrogates:

- kinetics
- flame characteristics
- safety characteristics

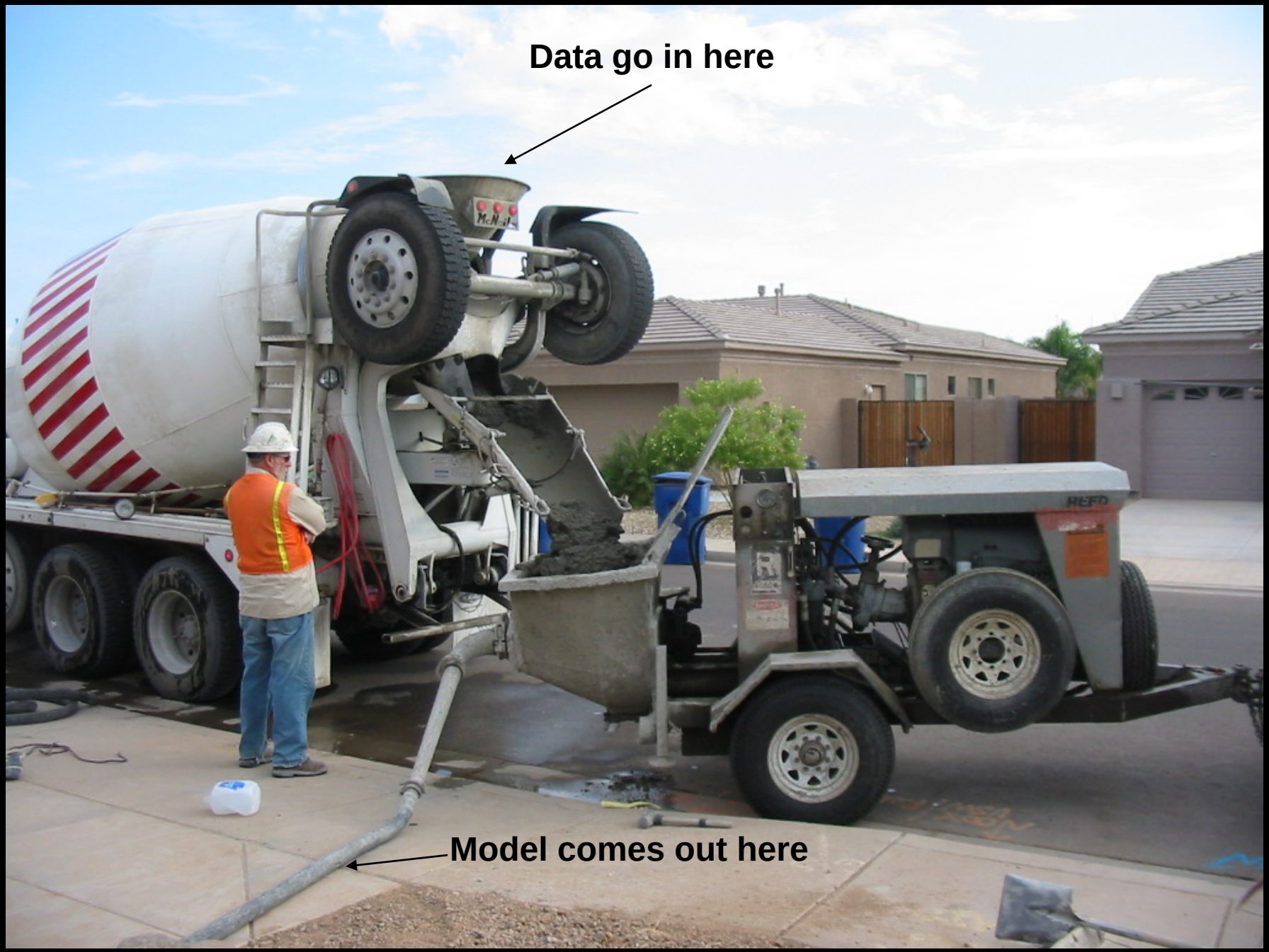


“Surrogate” means different things to different people

Thermophysical property predictive surrogates



The (un)Holy Matrimony of Measurement and Theory


Data go in here
Model comes out here

REFPROP - NIST Reference Fluid Properties

File Edit Options Substance Calculate Plot Window Help Cautions

3: Mixture 1: T = 300.0 K (0.0022...

	Temperature (K)	Pressure (MPa)	Density (mol/dm³)	Enthalpy (J/mol)	Entropy (J/mol-K)
1	300.00	0.20000	0.080467	14728.	105.63
2	300.00	0.40000	0.16151	14696.	99.786
3	300.00	0.60000	0.24313	14663.	96.335
4	300.00	0.80000	0.32533	14631.	93.864
5	300.00	1.0000	0.40812	14598.	91.929
6	300.00	1.2000	0.49150	14565.	90.333
7	300.00	1.4000	0.57547	14532.	88.971
8	300.00	1.6000	0.66004	14499.	87.780
9	300.00	1.8000	0.74521	14466.	86.719
10	300.00	2.0000	0.83098	14433.	85.762
11	300.00	2.2000	0.91735	14400.	84.887
12	300.00	2.4000	1.0043	14366.	84.082
13	300.00	2.6000	1.0919	14333.	83.334

Select Properties to Display

Thermodynamic | Transport, Misc. | Derivative

- [x] Temperature
- [x] Pressure
- [x] Density
- [ ] Volume
- [ ] Int. Energy
- [x] Enthalpy
- [x] Entropy
- [ ] Cv
- [ ] Cp
- [ ] Cp0
- [ ] Cp/Cv
- [ ] Csat
- [ ] Sound Speed
- [ ] Comp. Factor
- [ ] Joule-Thom.
- [ ] Quality
- [ ] 2nd Virial Coef.
- [ ] 3rd Virial Coef.

(•) Bulk properties only
( ) Bulk, liquid, and vapor p

OK Cancel Select All Clear All

Estimated critical properties
Temperature: 196.19 K
Pressure: 5.0505 MPa
Density: 9.7532 mol/dm³

Components and composition

Mole Fraction

carbon dioxide	0.002202
nitrogen	0.021926
methane	0.95311
ethane	0.015123
propane	0.004471
isobutane	0.000495

Molar mass: 16.873 g/mol

OK Cancel

REFPROP

Reference Fluid Thermodynamic and Transport Properties

NIST Standard Reference Database 23, Version 8.1beta July 09, 2007
E.W. Lemmon, M.L. Huber, and M.O. McLinden
Physical and Chemical Properties Division
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Continue Information

Select Units

Dimension	Units
Temperature	K
Pressure	MPa
Volume	dm³
Mass/Mole	g/mol
Energy	J
Sound Speed	m/s
Viscosity	µPa-s
Thermal Conductivity	mW/m-K
Surface Tension	mN/m

Reset Units: SI, SI with Celsius, Molar SI, mks, cgs, Mixed, English, Unitless

Properties: ( ) Mass Basis (•) Molar Basis

Composition: ( ) Mass Basis (•) Molar Basis

OK Cancel

Pressure
[ ] Use Gage Pressure
(•) Barometric Pressure 0.101325 MPa
( ) Elevation m

Current Fluid: Mixture 1 Components: carbon dioxide/nitrogen/methane/ethane/propane/isobutane/butane/isopentane/pentane/heptane (0.002202/0.021926/0.95311/0.015123/0.004471/0.000495/0.001366/0

Clearly, the most important role of the surrogate mixture is to fulfill the intended purpose:

- TSI,
- Kinetics,
- Pool fires,
- Thermophysical properties,
- what have you

- Beyond this primary role, we all desire our surrogate mixtures to be authentic:

physicochemically

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physicochemically

Physical Properties

ρ, η, λ, vle, ss, …

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Physical Properties
ρ, η, λ, vle, ss, …

Chemical Properties:
group moieties-

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physicochemically

Physical Properties

ρ, η, λ, vle, ss, …

Chemical Properties:

group moieties-

For moiety family evaluation and analysis:

^{1}H, ^{13}C NMR

Happily, I have one on order!

Multinuclear probe

Cryoprobe: ^{1}H, ^{13}C, ^{19}F, ^{31}P

Cross polarization MAS solids probe

Diffusion probe

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physicochemically

Physical Properties
ρ, η, λ, vle, ss, …

Chemical Properties:
group moieties-

Can we use any of the thermophysical properties for this?

- Density, ρ (PVT surface), for a kerosene
  - write in 0.85 g/mL and you'll be close
- Speed of sound, heat capacities, etc., change by a few %
- viscosity and thermal conductivity change by 4 %
- In contrast, **volatility** changes appreciably with composition

The ADC:

–true thermodynamic state points

–consistent with historical data

–temperature, volume and pressure measurements of low uncertainty

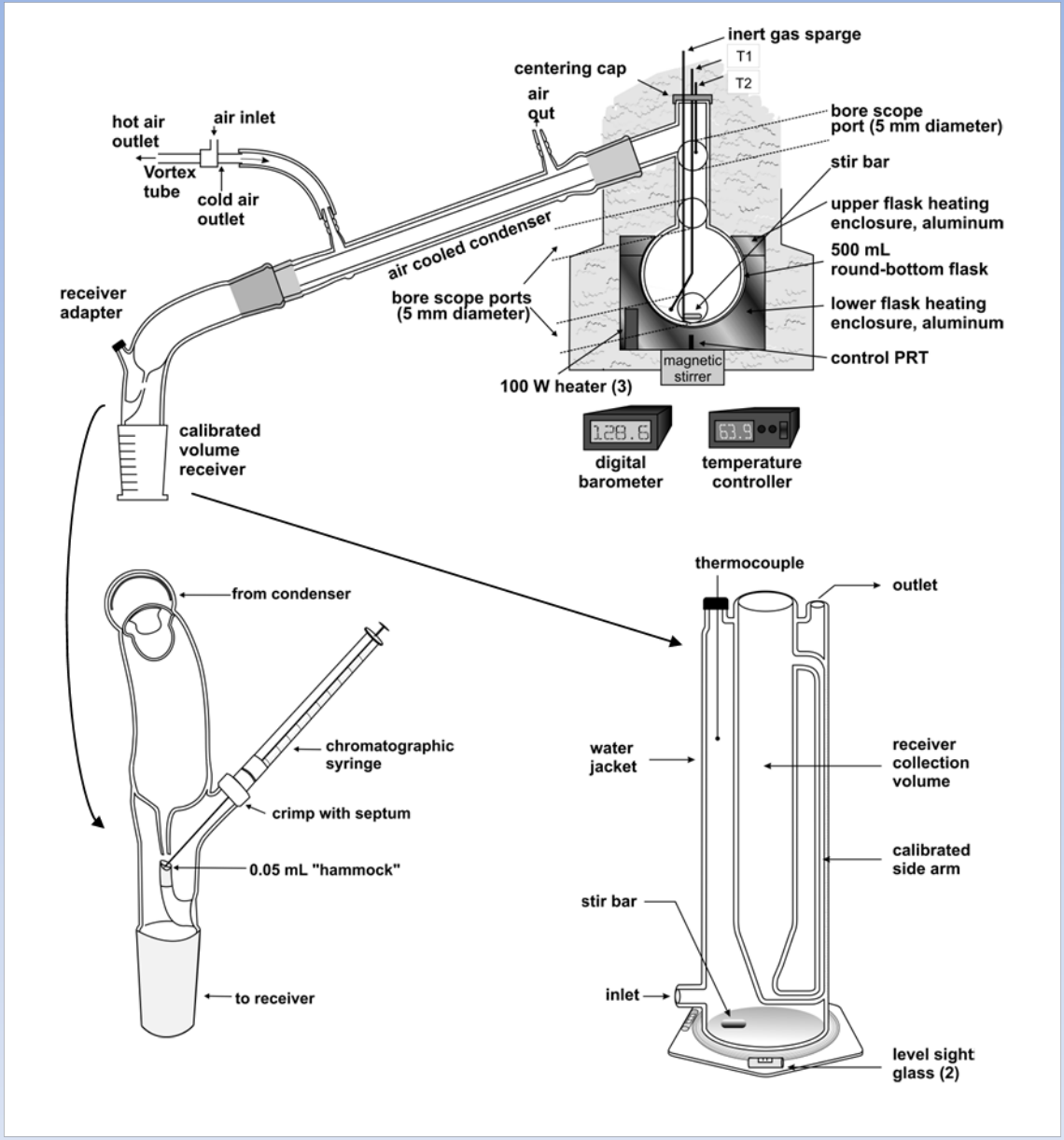
–qualitative, quantitative and trace analysis of fractions

–energy content of each fraction

–corrosivity of each fraction

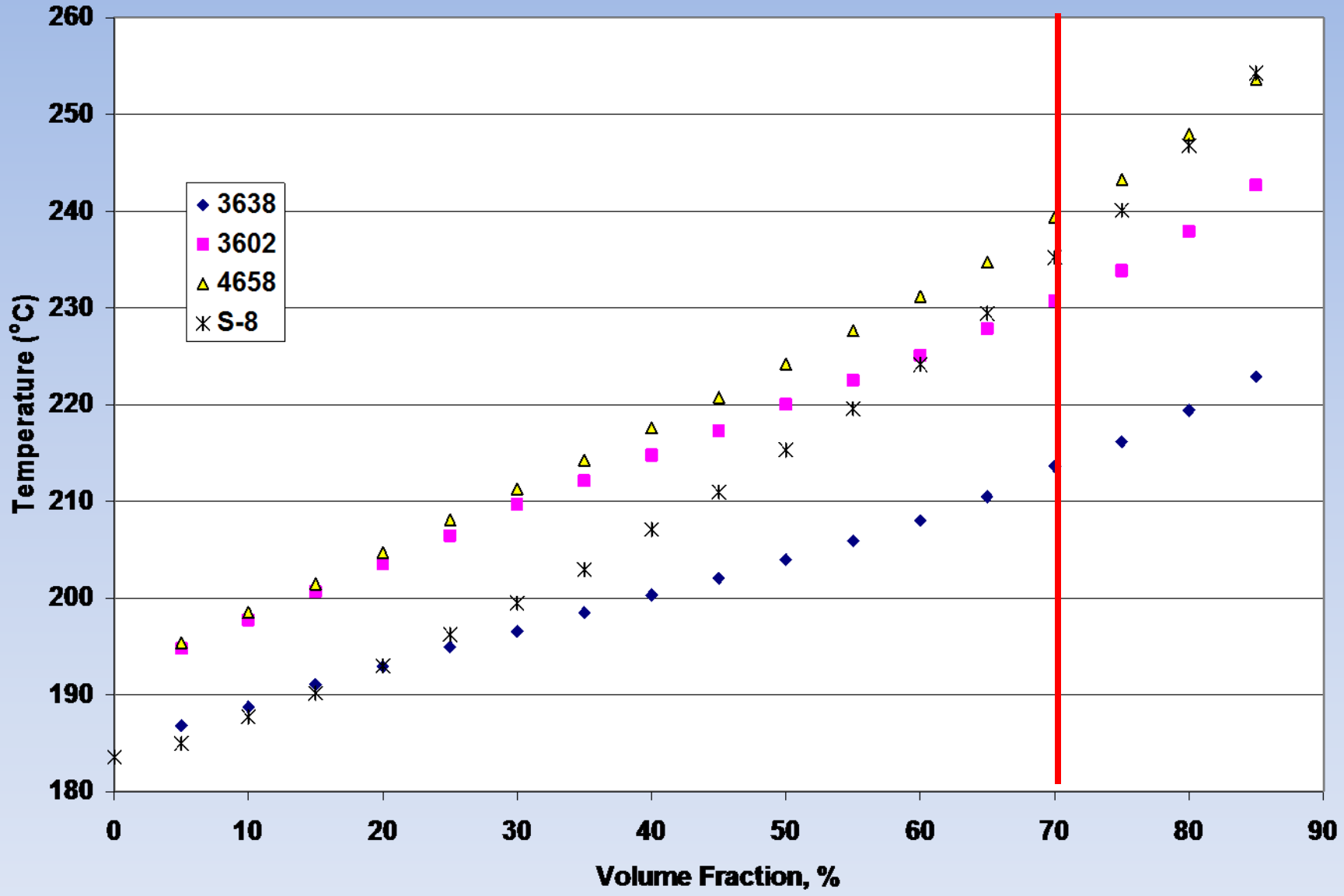
–greenhouse gas output of each fraction

–thermal and oxidative stability of the fluids



Apparatus for ADC.

Jet A, S-8


260
250
240
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220
210
200
190
180
Temperature (°C)
0
10
20
30
40
50
60
70
80
90
Volume Fraction, %
3638
3602
4658
S-8

So what will the ADC Provide (that's practical)?

- Initial boiling temperature, IBT
  - thermodynamically consistent
  - theoretically meaningful
- Distillation Curves
  - thermodynamically consistent
  - theoretically meaningful

Let's look at some surrogate mixtures, ignoring for the moment, the underlying motivation:

- Simple
  - 2 or 3 components
- Complex
  - More than 3 components

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- With the nomenclature used in the literature and at past Fuel Summits

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- Simple
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- Complex
  - More than 3 components

- With the nomenclature used in the literature and at past Fuel Summits
    - Older mixtures, to develop the methodology

Simple:

- **Surrogate A:**
  - 60% n-decane + 20% methylcyclohexane + 20% toluene
- **Surrogate B:**
  - 60% n-decane + 20% methylcyclohexane + 20% o-xylene
- **Surrogate C:**
  - 60% n-dodecane + 20% methylcyclohexane + 20% o-xylene
- **Surrogate F:**
  - 60% n-decane + 20% butylcyclohexane + 20% butylbenzene
- **Surrogate G:**
  - 60% n-decane + 40% isooctane
- **Aachen Surrogate:**
  - 80% n-decane + 20% 1,2,4-trimethylbenzene
- **Modified Aachen Surrogate:**
  - 80% n-dodecane + 20% 1,2,4-trimethylbenzene

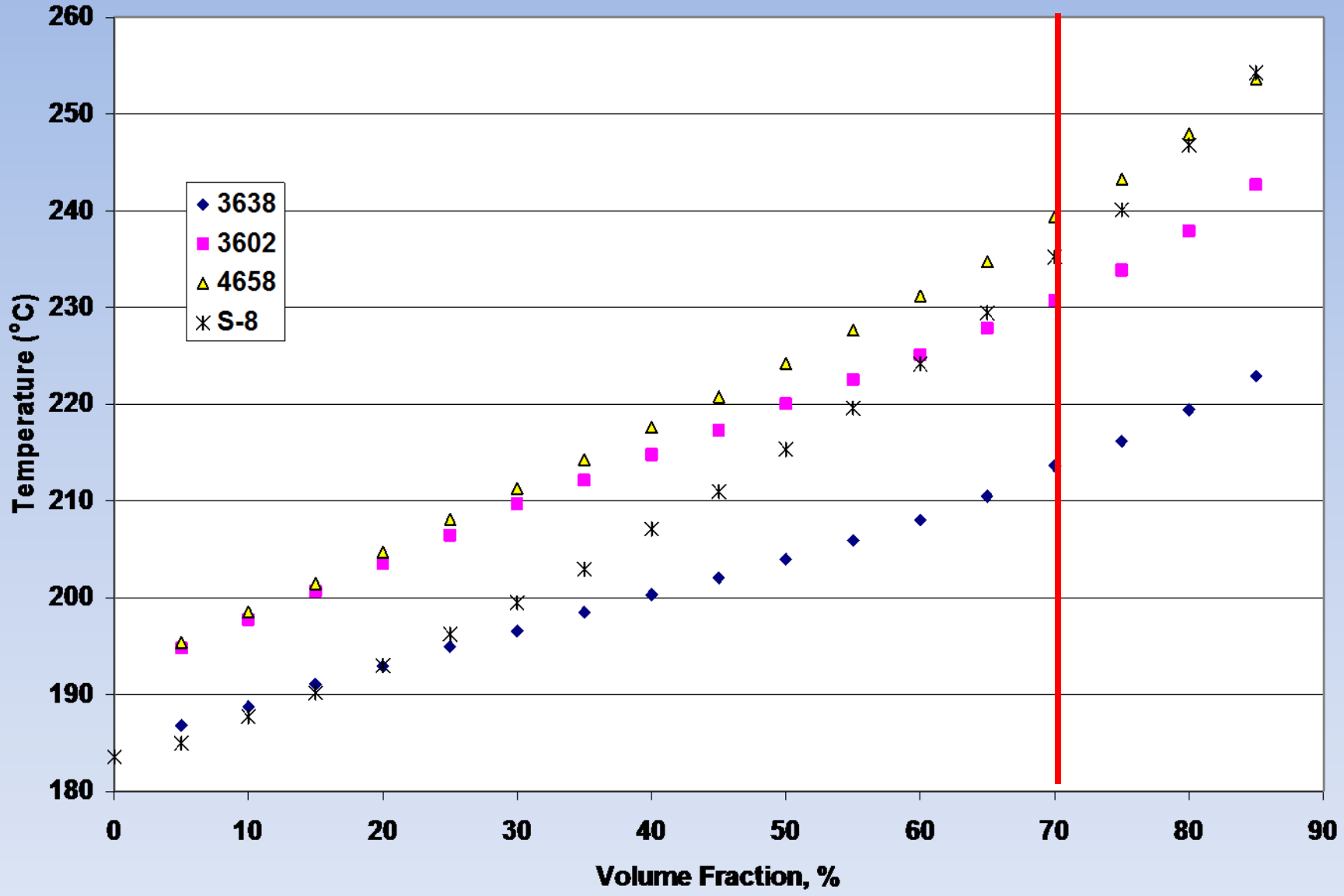
Complex:

- **Utah Surrogate:**
  - 30% n-dodecane + 20% n-tetradecane + 20% methylcyclohexane + 15% o-xylene + 10% isooctane + 5% tetralin
- **Drexel Surrogate 1:**
  - 36% isocetane + 26% n-dodecane + 14% methylcyclohexane + 18% 1-methylnaphthalene + 6% decalin
- **Drexel Surrogate 2:**
  - 43% n-dodecane + 27% isocetane + 15% methylcyclohexane + 15% 1-methylnapthalene
- **Schulz Surrogate:**
  - 21% n-dodecane + 16.2% n-decane + 15.6% n-tetradecane + 10.2% n-hexadecane + 5.7% isooctane + 5.1% methylcyclohexane + 4.7% cyclooctane + 4.6% butylbenzene + 4.5% m-xylene + 4.4% 1,2,4,5-tetramethylbenzene + 4.1% tetralin + 3.9 % 1-methylnaphthalene
- **Surrogate 1:**
  - 30% n-dodecane + 20% n-tetradecane + 20% methylcyclohexane + 15% m-xylene + 10% isooctane + 5% tetralin
- **Surrogate 3:**
  - 73.5% n-dodecane + 10% methylcyclohexane + 10% toluene + 5.5% isooctane+ 1% benzene
- **Violi Surrogate:**
  - 20% n-tetradecane + 25% n-dodecane + 25% n-decane + 20% toluene + 5% methylcyclohexane + 5% isooctane

Compare these with “real” fuel behavior

- IBT departure
  - But still, it’s only one point
  - The rest of the curve can do funny things
- Total curve departure
  - On the basis of objective, point by point metrics
- Total curve shape
  - Subjective and objective descriptors

Jet A, S-8


260
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Temperature (°C)
0
10
20
30
40
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60
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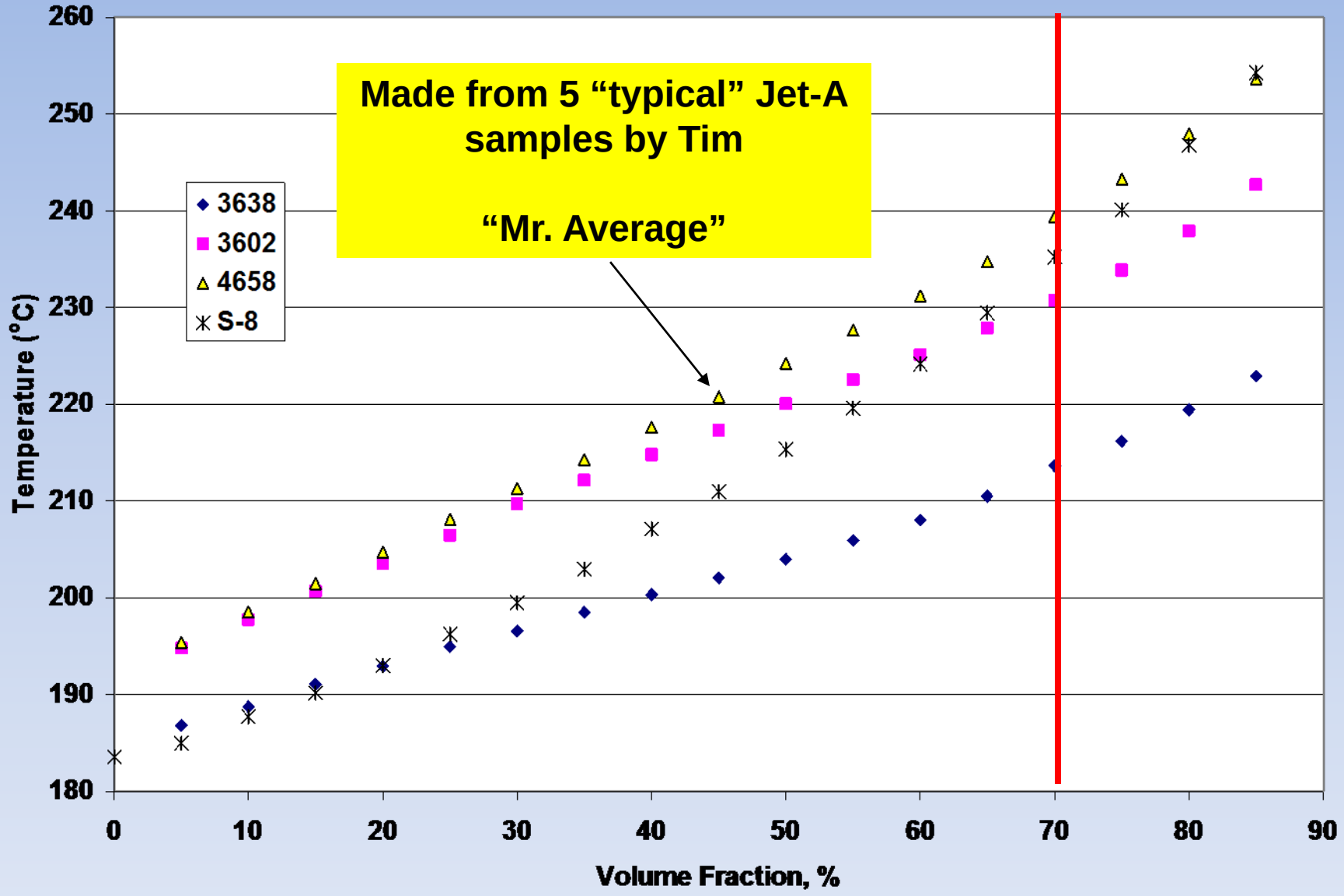
80
90
Volume Fraction, %
3638
3602
4658
S-8

Jet A, S-8


Made from 5 "typical" Jet-A samples by Tim
"Mr. Average"
3638
3602
4658
S-8
Temperature (°C)
Volume Fraction, %
260
250
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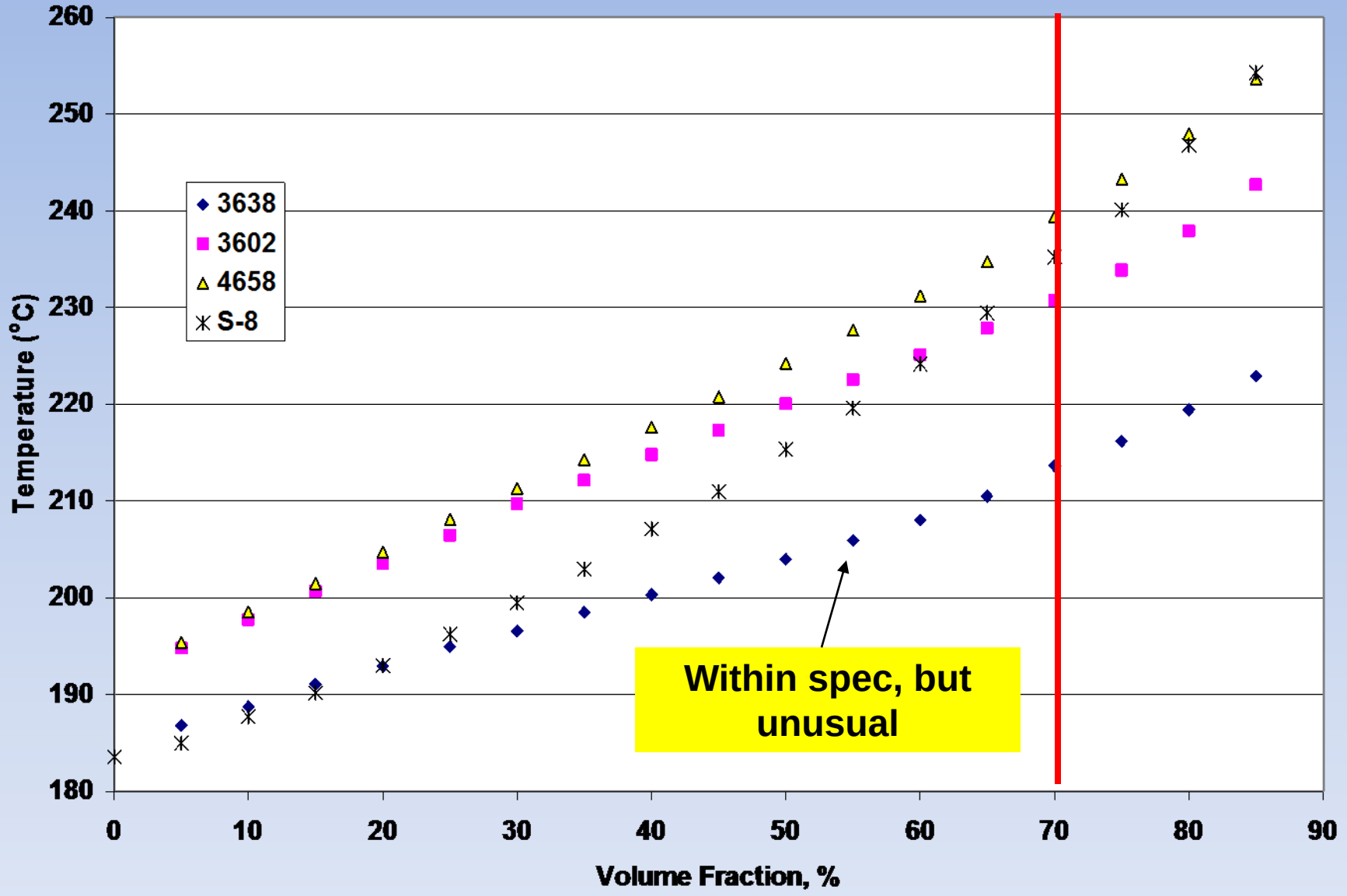
90

Jet A, S-8


260
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Temperature (°C)
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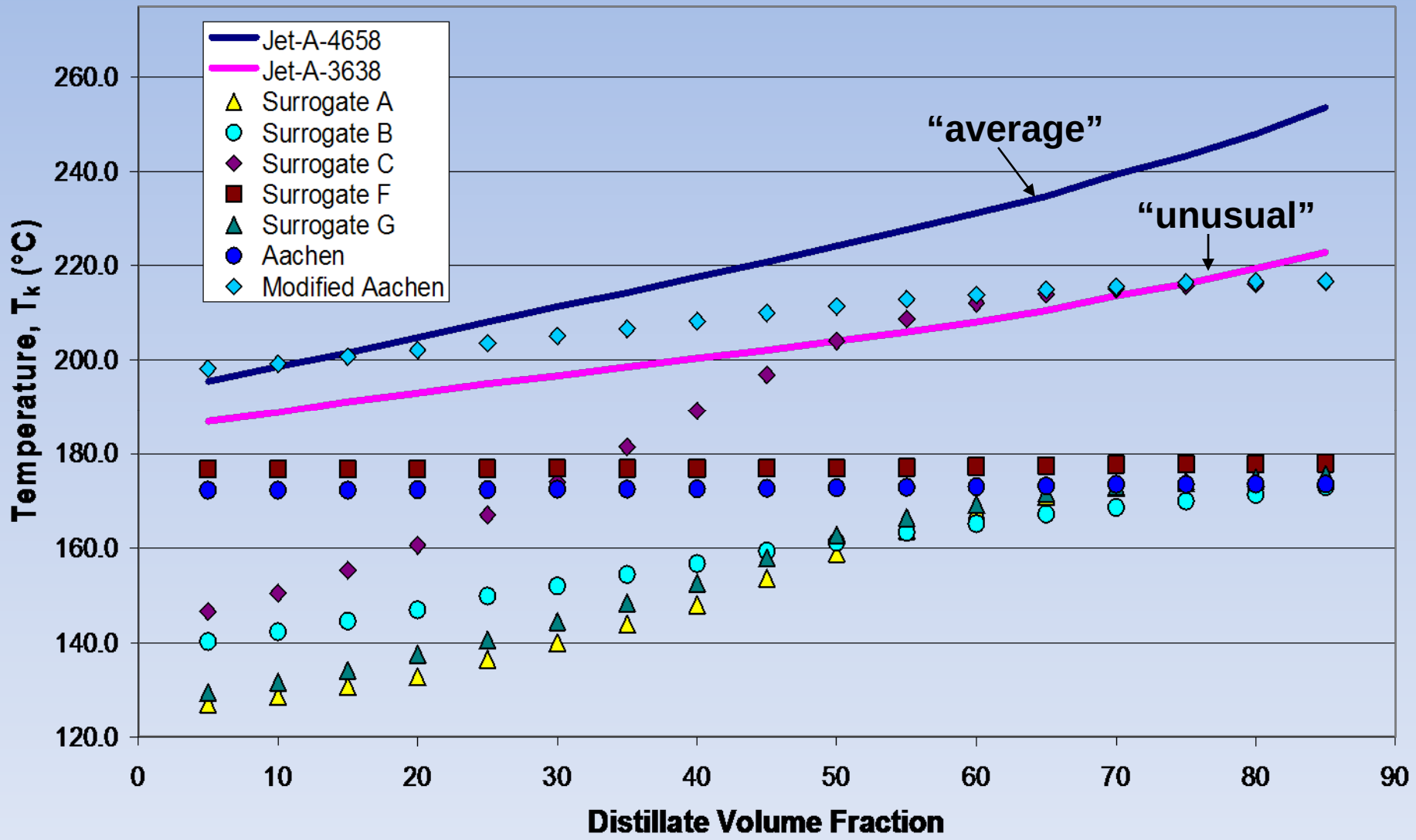
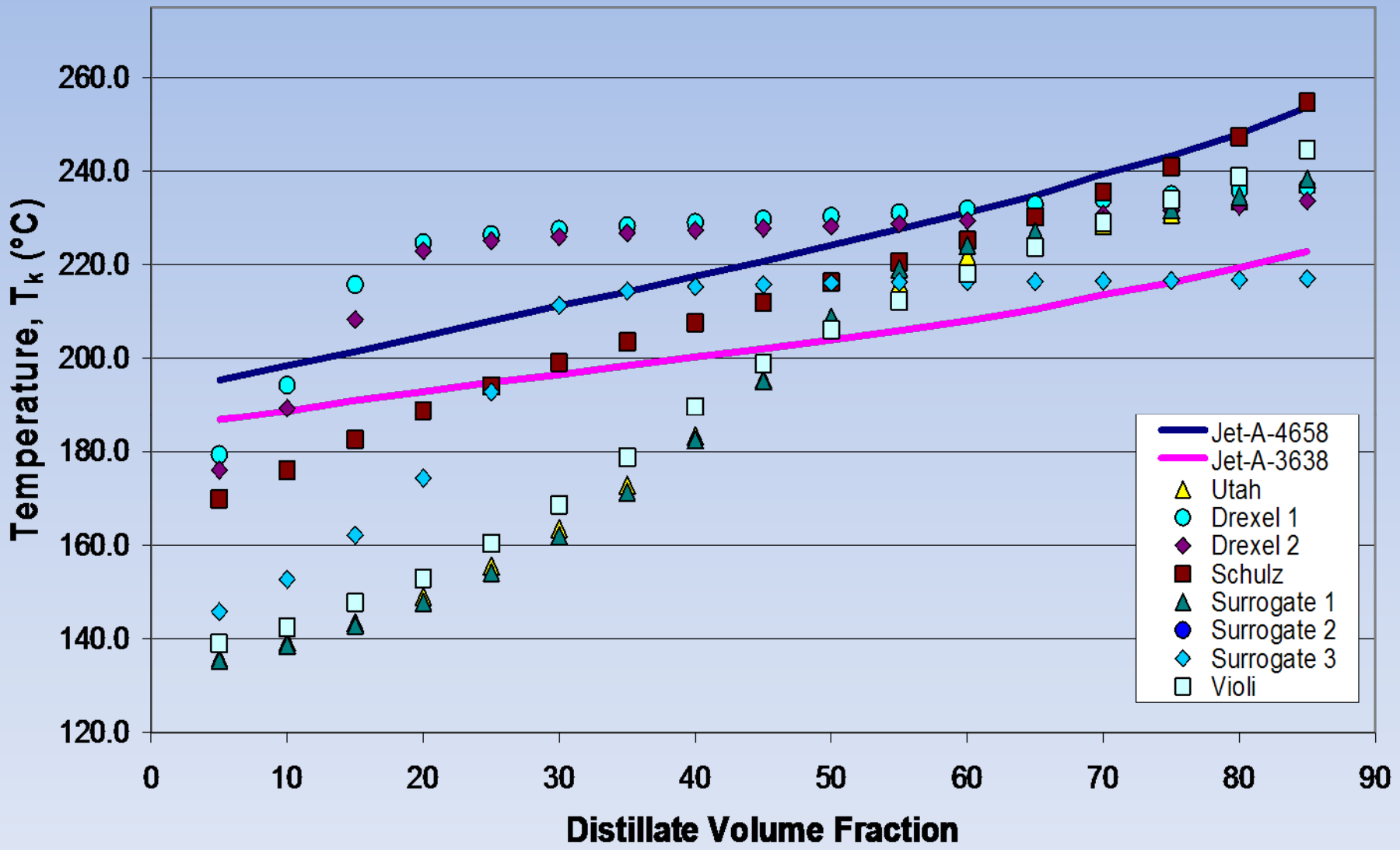
90
Volume Fraction, %
3638
3602
4658
S-8
Within spec, but unusual

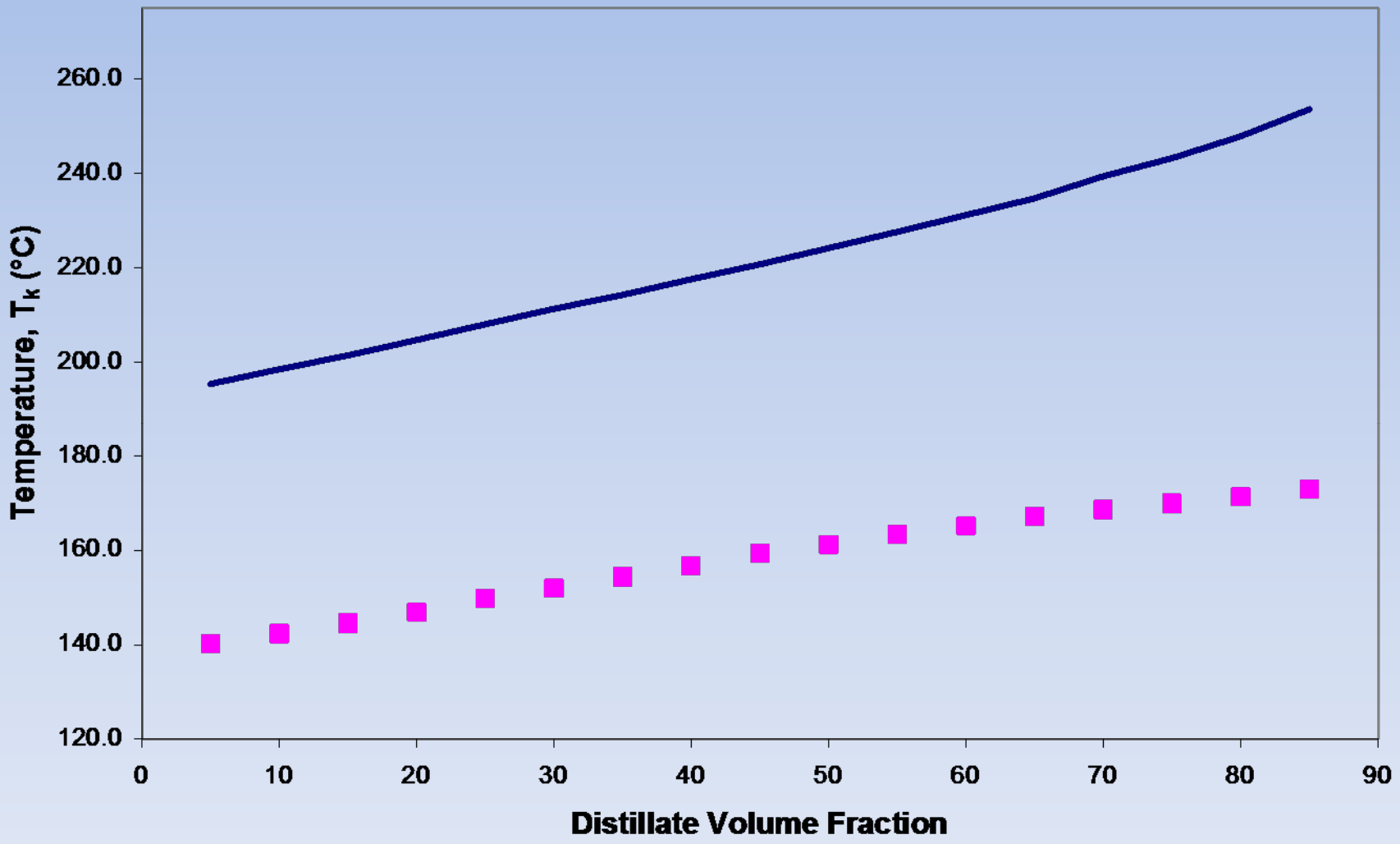
The Simple Surrogates:

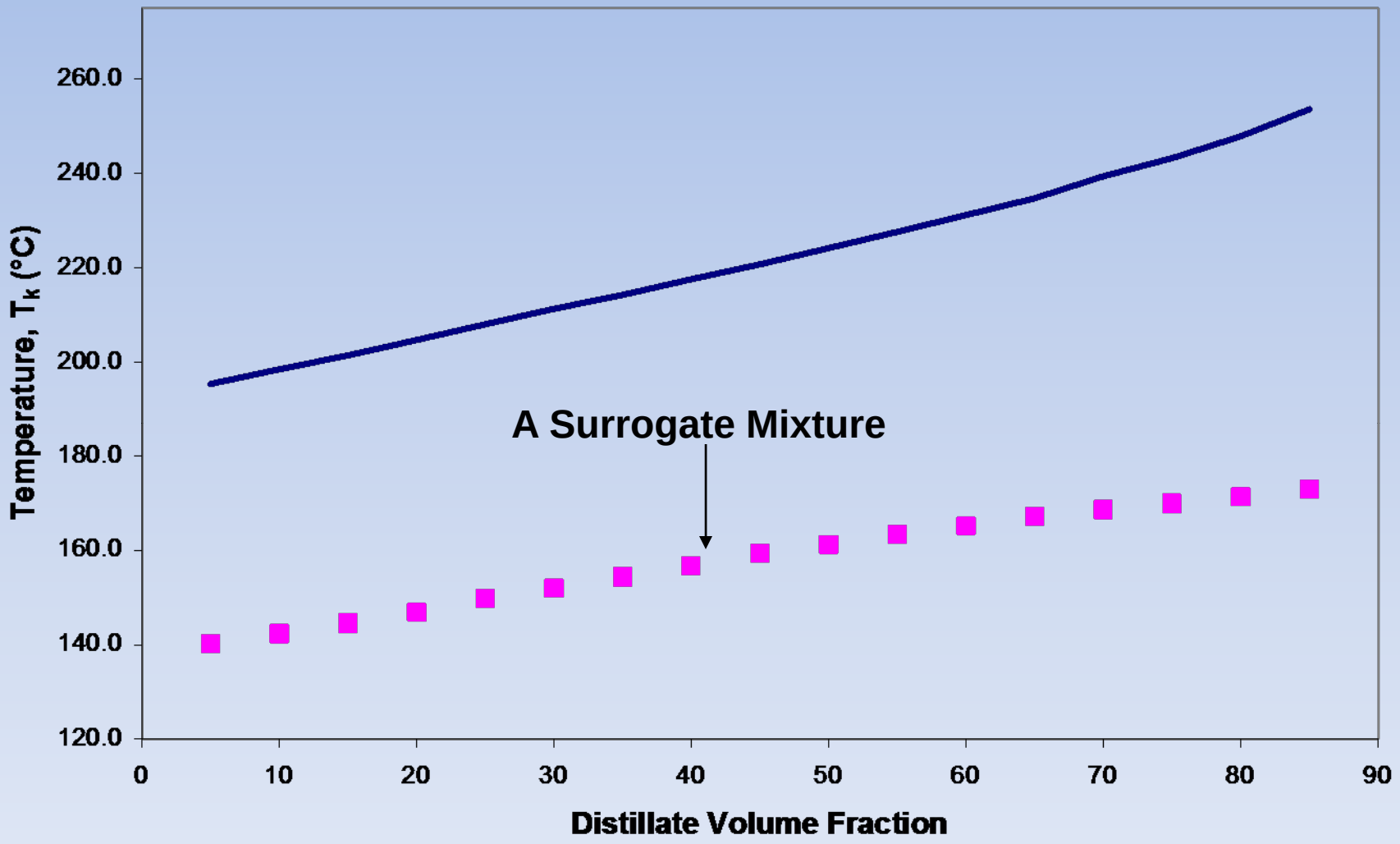


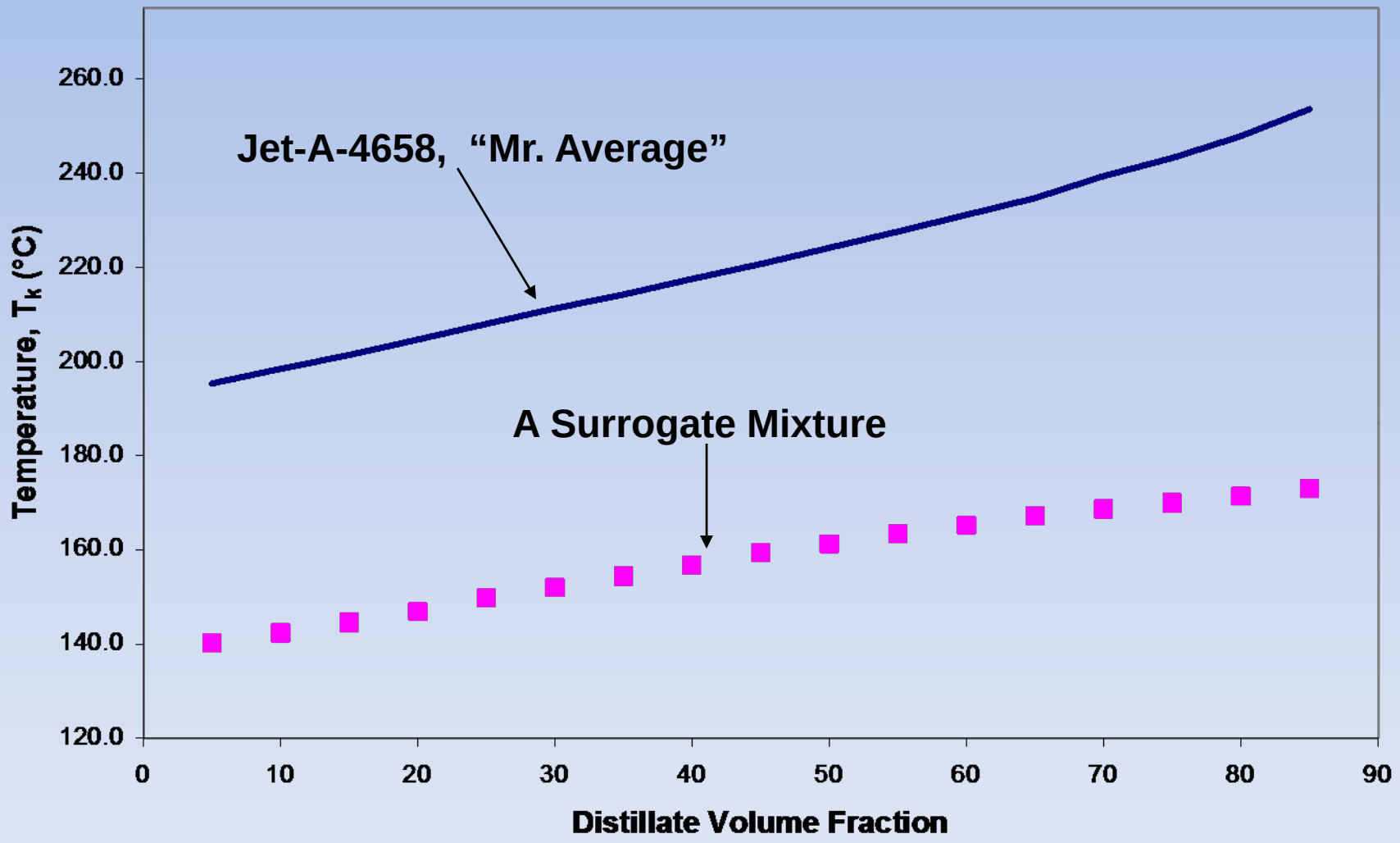
The Complex Surrogates:



Point by point evaluations:




A Surrogate Mixture
Temperature, T_k (°C)
260.0
240.0
220.0
200.0
180.0
160.0
140.0
120.0
0
10
20
30
40
50
60
70
80
90
Distillate Volume Fraction


Jet-A-4658, "Mr. Average"
A Surrogate Mixture
Temperature, T_k (°C)
260.0
240.0
220.0
200.0
180.0
160.0
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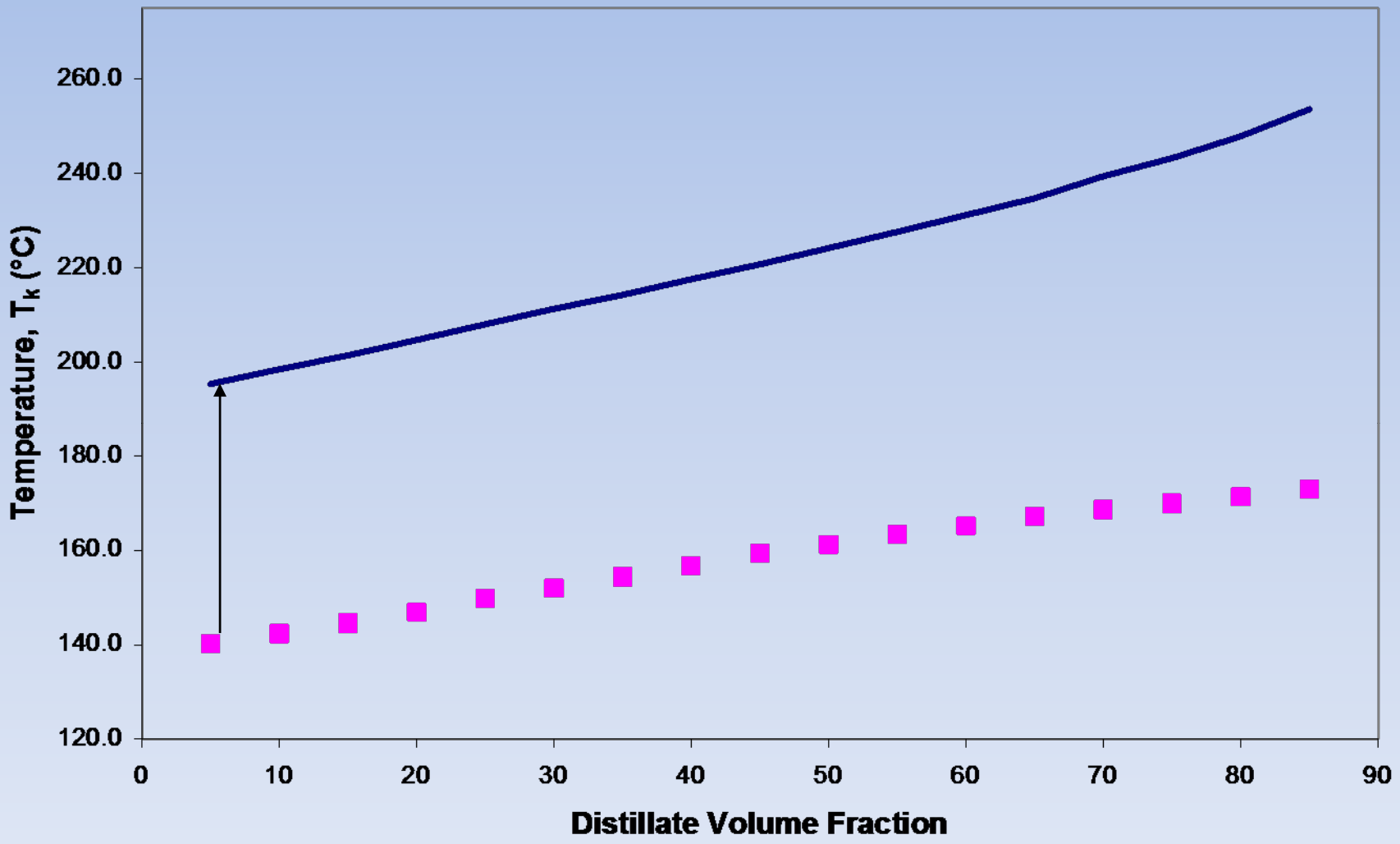
Distillate Volume Fraction


Temperature, T_k (°C)
260.0
240.0
220.0
200.0
180.0
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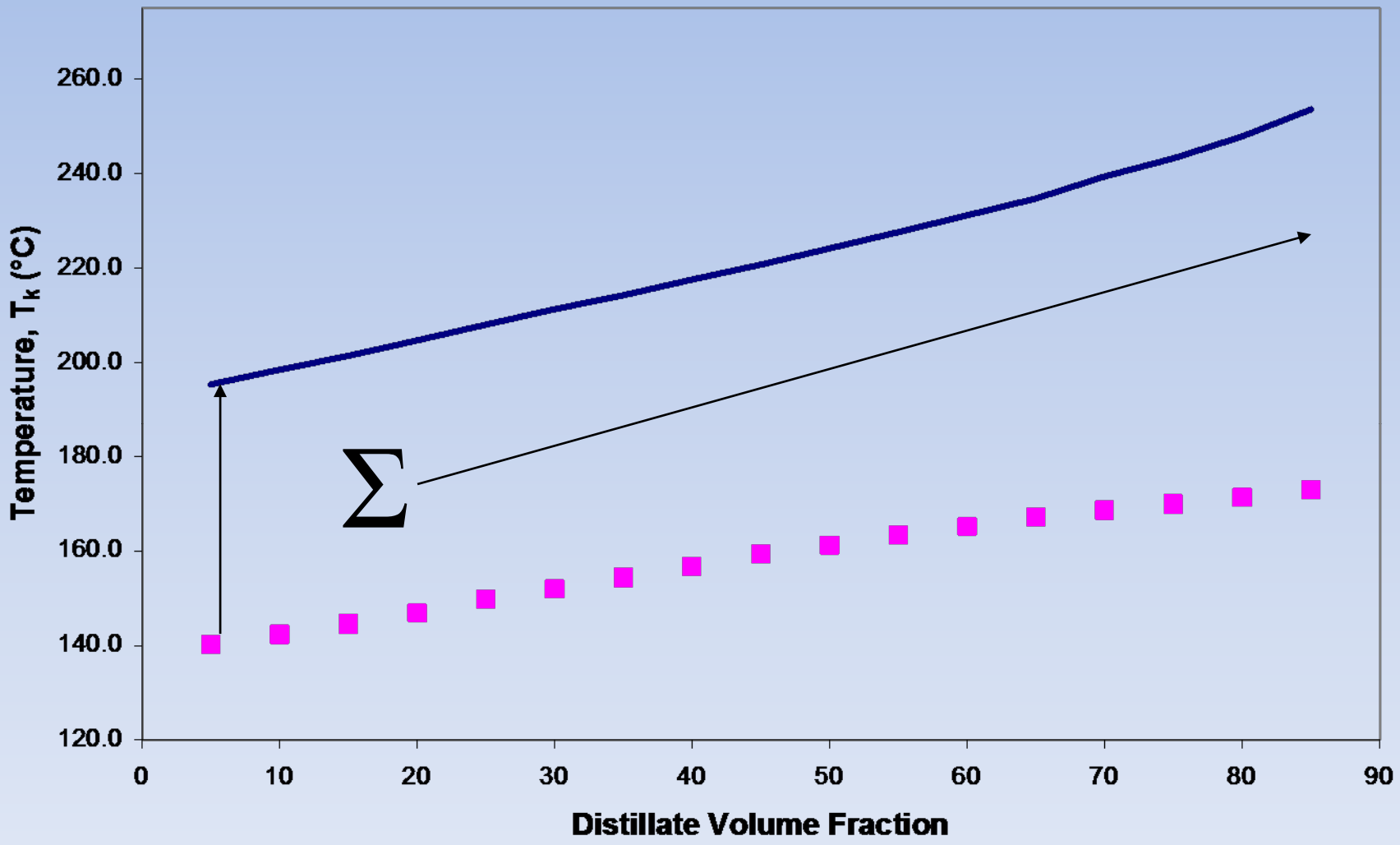
Distillate Volume Fraction


260.0
240.0
220.0
200.0
180.0
160.0
140.0
120.0
Temperature, T_k (°C)
0
10
20
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40
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60
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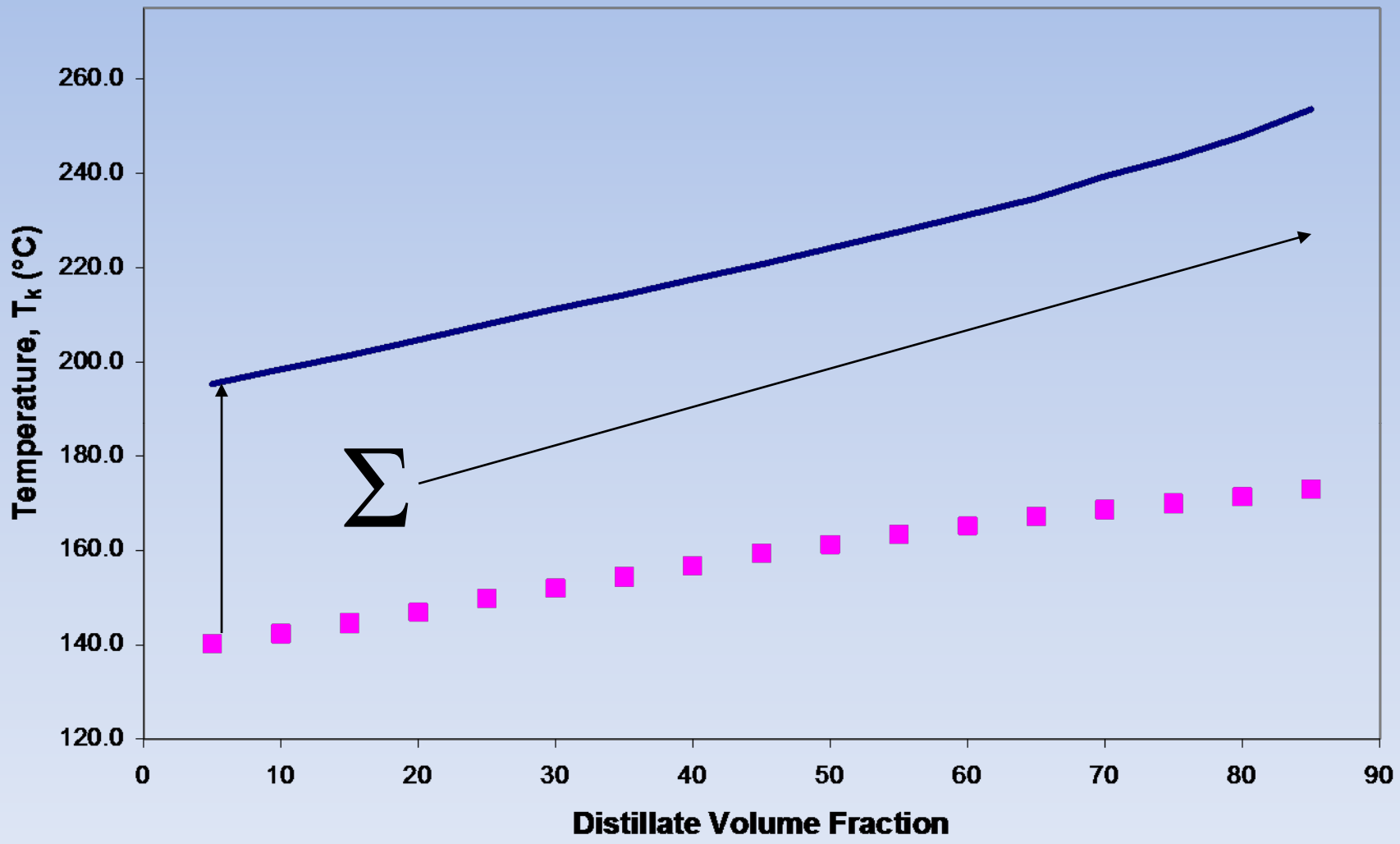
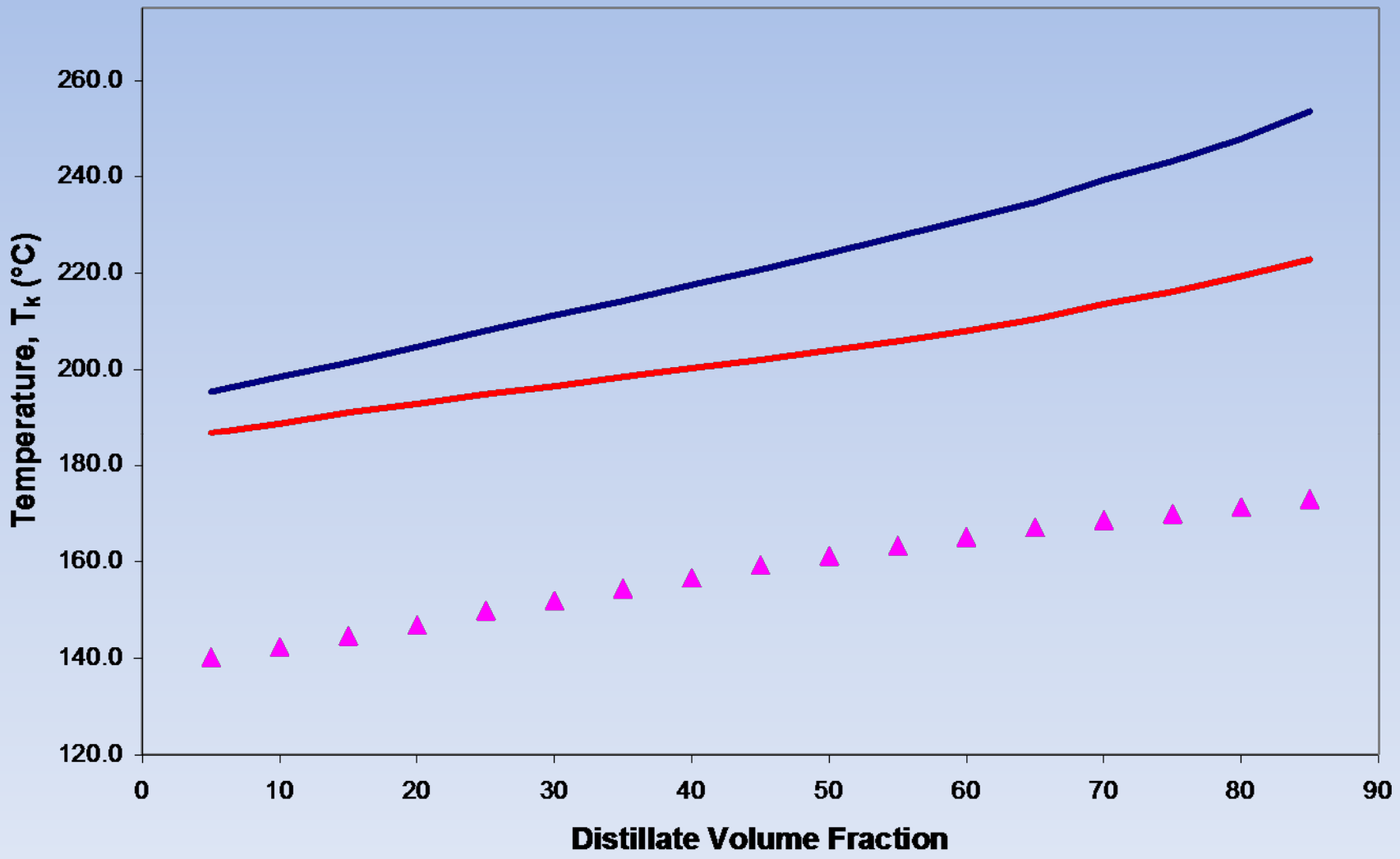
80
90
Distillate Volume Fraction
Σ

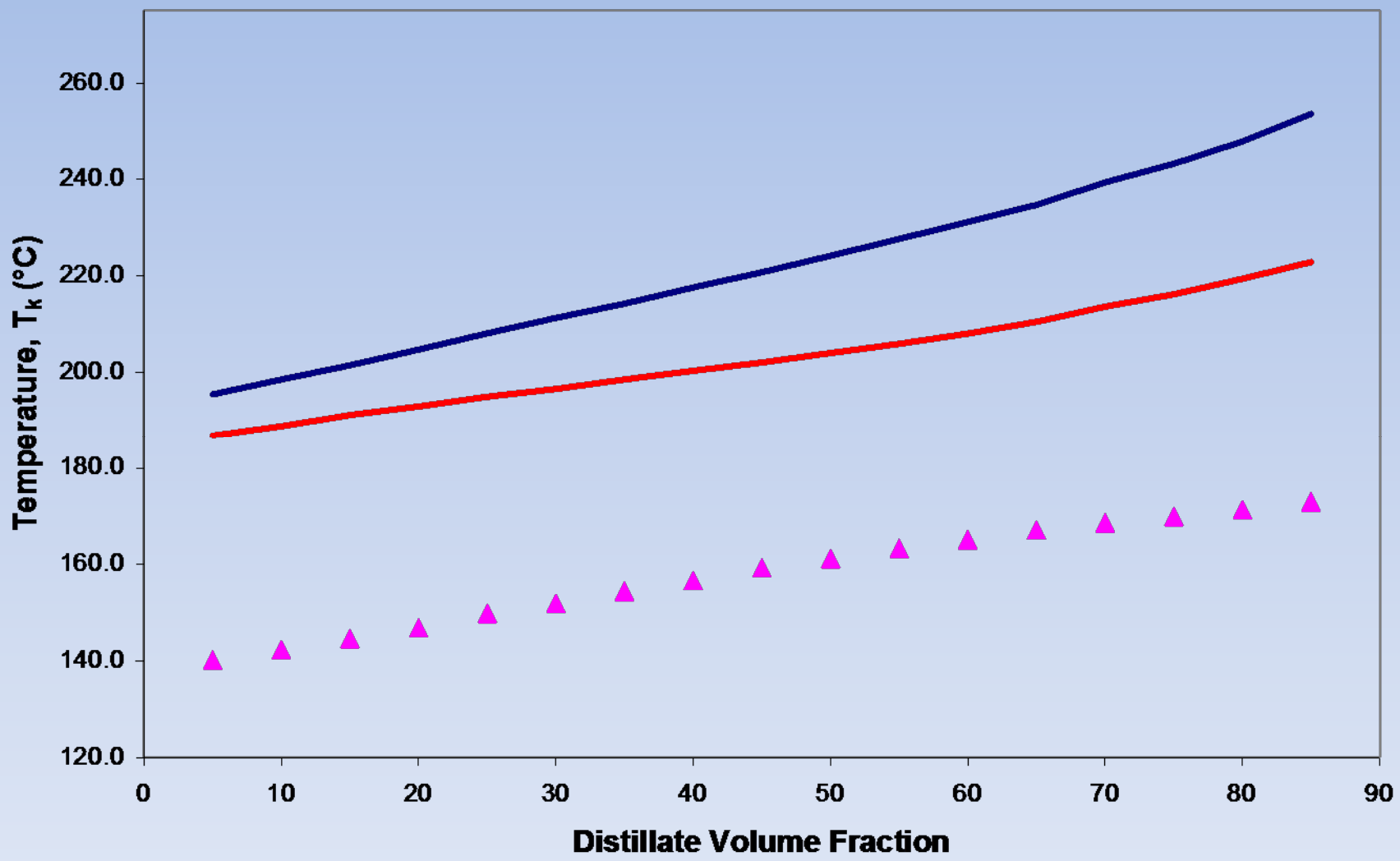
$$\text{Metric } 1 = \frac{1}{n}\sum_{i=1}^{n}\left| T^{i}_{\text{Jet-A-4658}} - T^{i}_{\text{surrogate}} \right|$$



$$\text{Metric 2} = \frac{1}{n}\sum_{i=1}^{n}\frac{\left|T^{i}_{\text{Jet-A-4658}} - T^{i}_{\text{surrogate}}\right|}{\left|T^{i}_{\text{Jet-A-4658}} - T^{i}_{\text{Jet-A-3638}}\right|}$$



$$\text{Metric 3} = \frac{1}{n}\sum_{i=1}^{n}\text{Min}\left(\left|T^{i}_{\text{Jet-A-4658}} - T^{i}_{\text{Surrogate}}\right|, \left|T^{i}_{\text{Jet-A-3638}} - T^{i}_{\text{Surrogate}}\right|\right)$$



Point by Point Evaluation Results:

Criterion	Surrogate A	Surrogate B	Surrogate C	Surrogate F	Surrogate G	Aachen	Modified Aachen
Metric 1	69.20	64.00	32.40	44.90	66.50	49.30	13.50
Metric 2	4.25	3.77	2.20	2.36	4.06	2.63	0.60
Metric 3	50.26	45.11	14.85	26.01	47.58	30.34	4.51

Criterion	Utah	Drexel 1	Drexel 2	Schulz	Surrogate 1	Surrogate 3	Violi
Metric 1	31.50	10.50	10.70	10.10	31.20	21.00	28.90
Metric 2	2.39	0.70	0.70	0.80	2.39	1.46	2.21
Metric 3	23.33	9.82	9.02	5.90	23.51	10.51	20.06

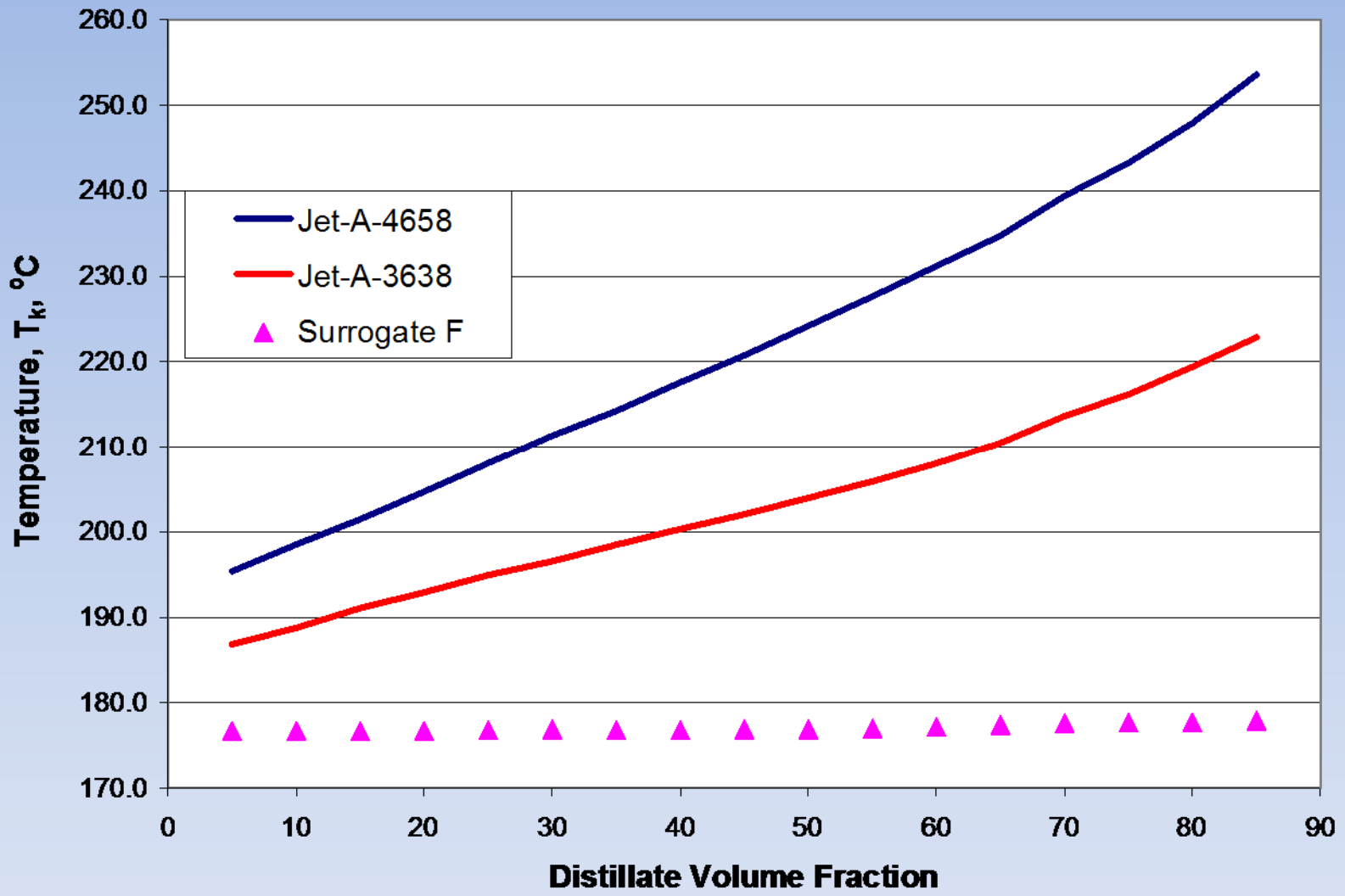
The winners are:

Criterion	Surrogate A	Surrogate B	Surrogate C	Surrogate F	Surrogate G	Aachen	Modified Aachen
Metric 1	69.20	64.00	32.40	44.90	66.50	49.30	13.50
Metric 2	4.25	3.77	2.20	2.36	4.06	2.63	0.60
Metric 3	50.26	45.11	14.85	26.01	47.58	30.34	4.51

Criterion	Utah	Drexel 1	Drexel 2	Schulz	Surrogate 1	Surrogate 3	Violi
Metric 1	31.50	10.50	10.70	10.10	31.20	21.00	28.90
Metric 2	2.39	0.70	0.70	0.80	2.39	1.46	2.21
Metric 3	23.33	9.82	9.02	5.90	23.51	10.51	20.06

Shape and Slope Evaluations:

- Go – No-Go test
  - Eliminate flat and bimodal curves


260.0
250.0
240.0
230.0
220.0
210.0
200.0
190.0
180.0
170.0
Temperature, T_k, °C
Jet-A-4658
Jet-A-3638
Surrogate F
0
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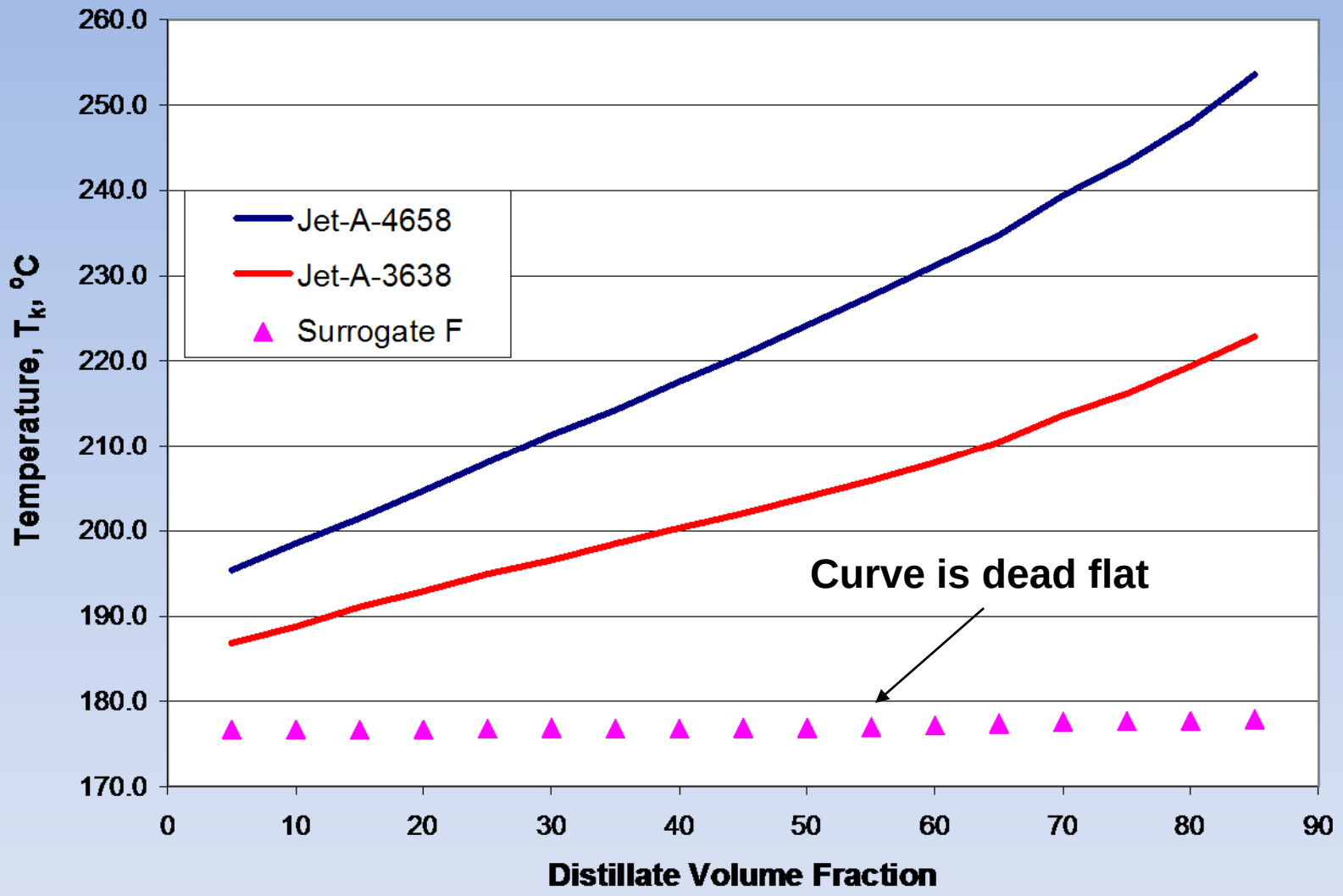
50
60
70
80
90
Distillate Volume Fraction


260.0
250.0
240.0
230.0
220.0
210.0
200.0
190.0
180.0
170.0
Temperature, T_k, °C
Jet-A-4658
Jet-A-3638
Surrogate F
Curve is dead flat
0
10
20
30
40
50
60
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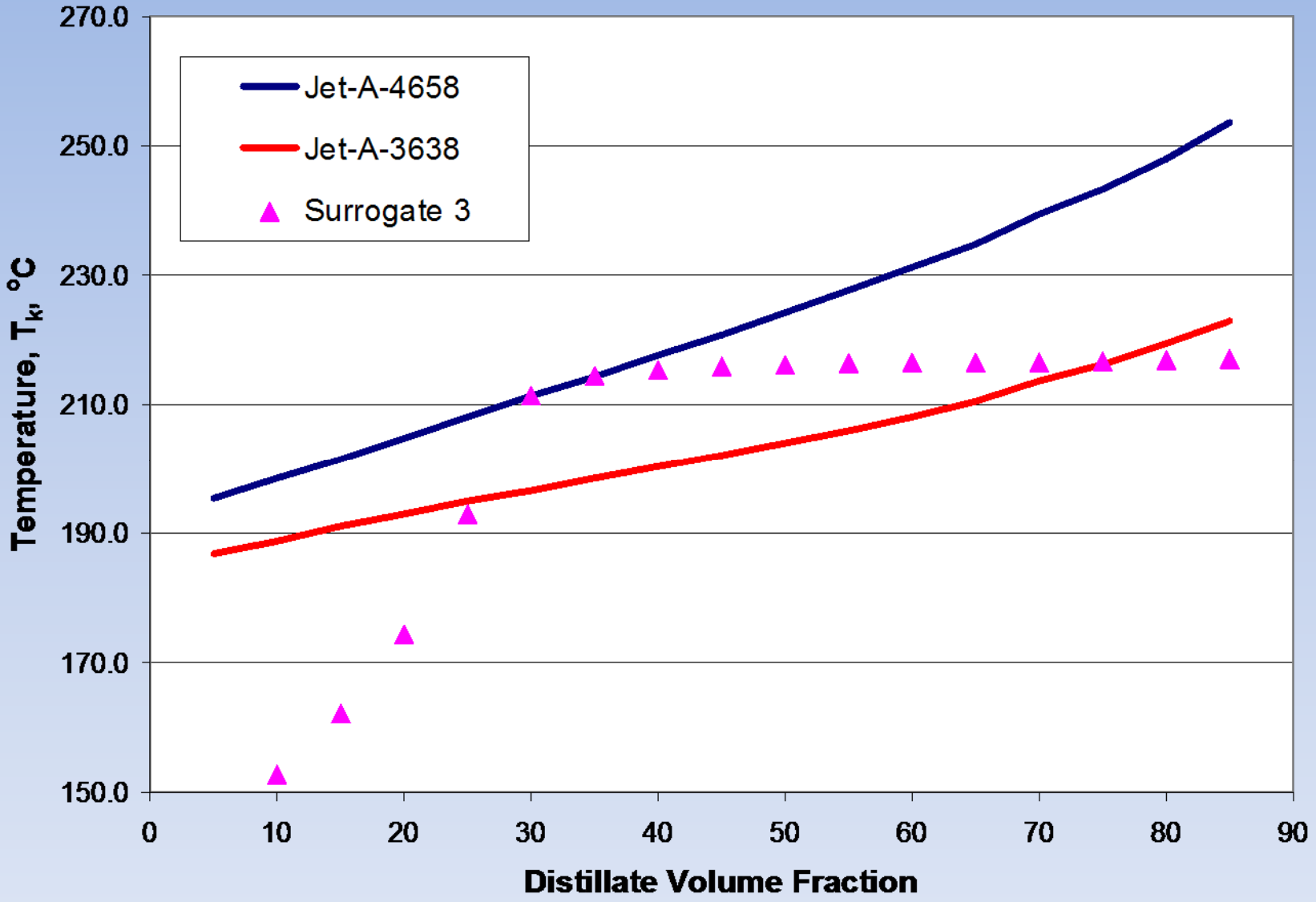
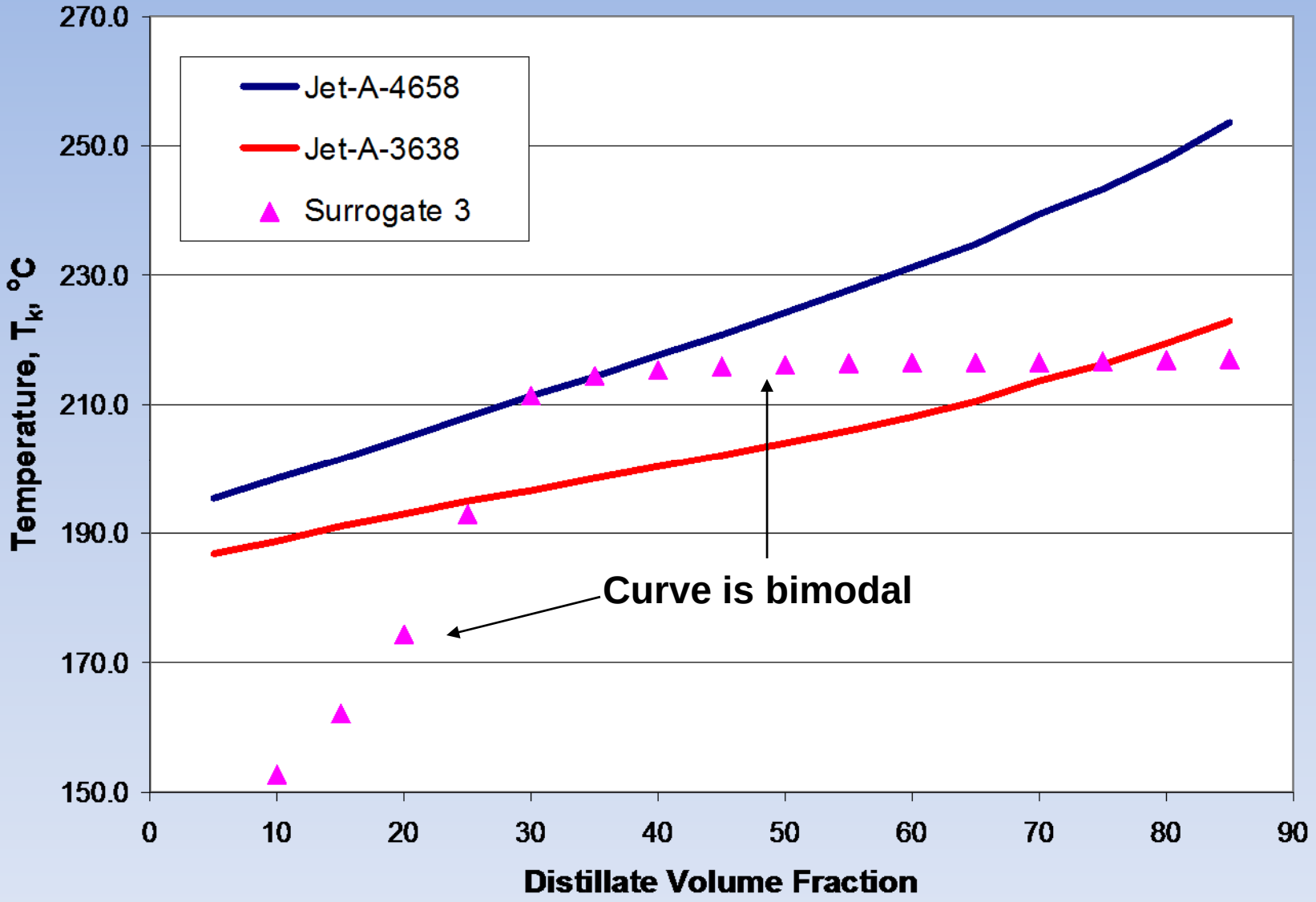
80
90
Distillate Volume Fraction


Jet-A-4658
Jet-A-3638
Surrogate 3
270.0
250.0
230.0
210.0
190.0
170.0
150.0
Temperature, T_k, °C
0
10
20
30
40
50
60
70
80
90
Distillate Volume Fraction


Jet-A-4658
Jet-A-3638
Surrogate 3
Curve is bimodal
Temperature, T_k, °C
Distillate Volume Fraction
270.0
250.0
230.0
210.0
190.0
170.0
150.0
0
10
20
30
40
50
60
70
80
90

Shape and Slope Evaluations:

- Go – No-Go test
  - Eliminate flat and bimodal curves
- Shape Rating (on simple linear model: $y = mx + b$)
  - Linear normal probability plot
  - Residual plot with 2 nodes
  - Residual magnitude less than 2 ^{o}C

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  - Eliminate flat and bimodal curves
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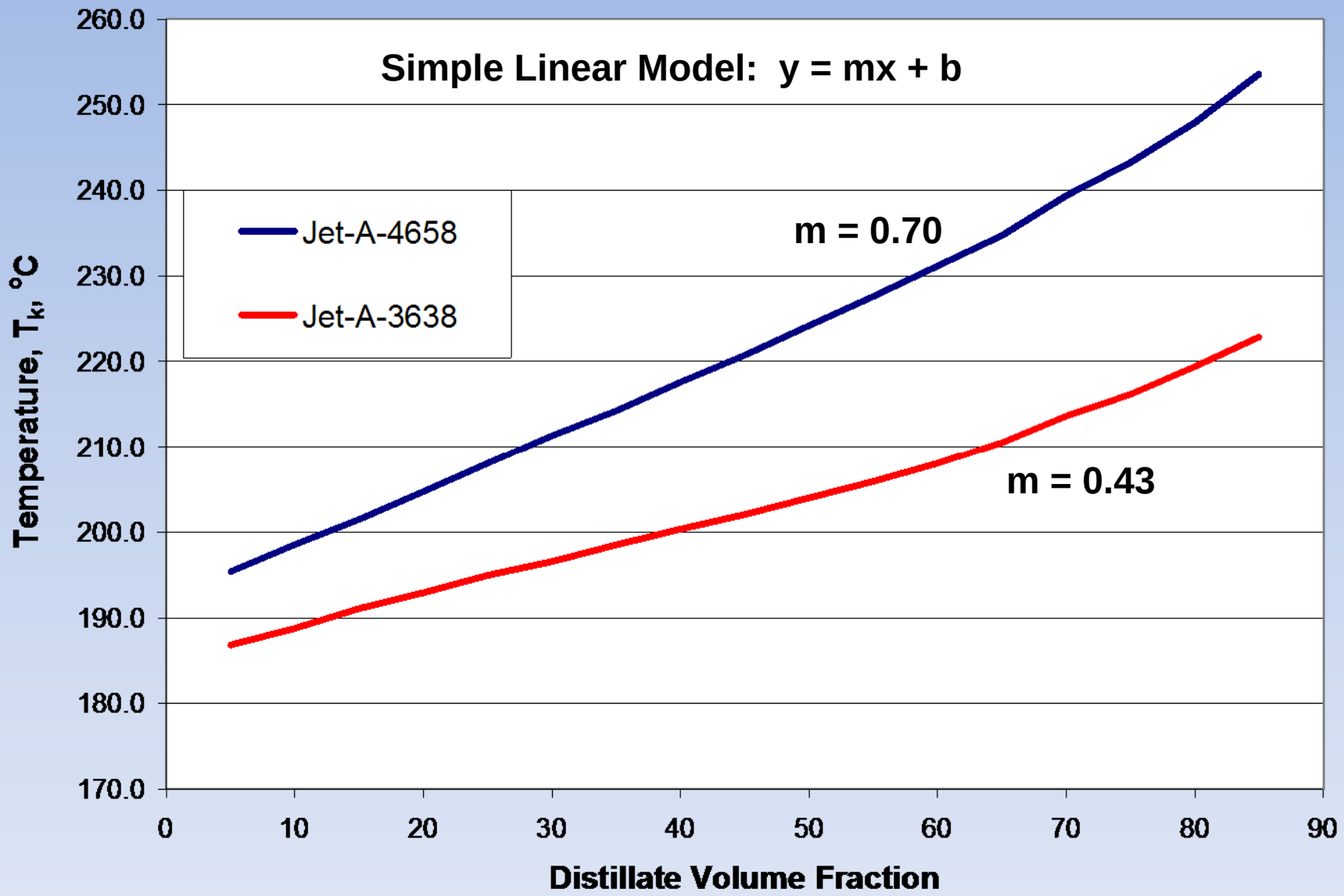
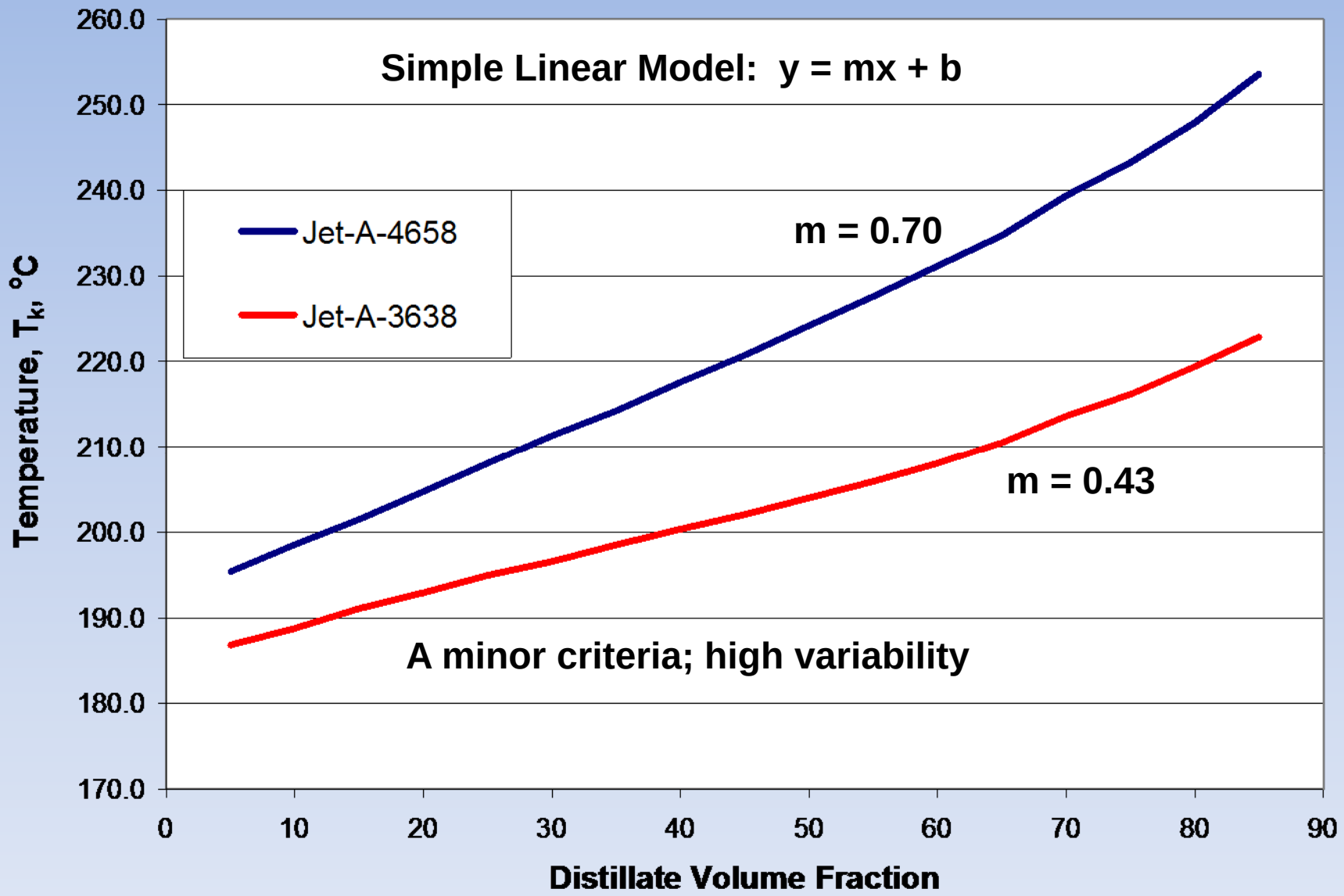
  - Linear normal probability plot
  - Residual plot with 2 nodes
  - Residual magnitude less than 2 ^{o}C

because this is how Jet-A, JP-8 behaves

Shape and Slope Evaluations:

- Go – No-Go test
  - Eliminate flat and bimodal curves
- Shape Rating (on simple linear model: $y = mx + b$)
  - Linear normal probability plot
  - Residual plot with 2 nodes
  - Residual magnitude less than 2 ^{o}C
- Slope Departure
  - Based on a simple linear model: $y = mx + b$


Simple Linear Model: y = mx + b
Jet-A-4658
Jet-A-3638
m = 0.70
m = 0.43
Temperature, T_k, °C
260.0
250.0
240.0
230.0
220.0
210.0
200.0
190.0
180.0
170.0
0
10
20
30
40
50
60
70
80
90
Distillate Volume Fraction


Simple Linear Model: y = mx + b
Jet-A-4658
Jet-A-3638
m = 0.70
m = 0.43
A minor criteria; high variability
Temperature, T_k, °C
Distillate Volume Fraction
260.0
250.0
240.0
230.0
220.0
210.0
200.0
190.0
180.0
170.0
0
10
20
30
40
50
60
70
80
90

Now, add shape and slope evaluation:

Criterion	Surrogate A	Surrogate B	Surrogate C	Surrogate F	Surrogate G	Aachen	Modified Aachen
Metric 1	69.20	64.00	32.40	44.90	66.50	49.30	13.50
Metric 2	4.25	3.77	2.20	2.36	4.06	2.63	0.60
Metric 3	50.26	45.11	14.85	26.01	47.58	30.34	4.51
Slope Validity	poor	good	poor	invalid	poor	invalid	good
Slope	0.70	0.42	0.99	NA	0.66	NA	0.25

Criterion	Utah	Drexel 1	Drexel 2	Schulz	Surrogate 1	Surrogate 3	Violi
Metric 1	31.50	10.50	10.70	10.10	31.20	21.00	28.90
Metric 2	2.39	0.70	0.70	0.80	2.39	1.46	2.21
Metric 3	23.33	9.82	9.02	5.90	23.51	10.51	20.06
Slope Validity	poor	invalid	invalid	fair	good	invalid	fair
Slope	0.97	NA	NA	0.97	0.99	NA	0.99

Overall Ratings:

- **Modified Aachen Surrogate:**
  - 80% n-dodecane + 20% 1,2,4-trimethylbenzene

- **Schulz Surrogate:**
  - 21% n-dodecane + 16.2% n-decane + 15.6% n-tetradecane + 10.2% n-hexadecane + 5.7% isooctane + 5.1% methylcyclohexane + 4.7% cyclooctane + 4.6% butylbenzene + 4.5% m-xylene + 4.4% 1,2,4,5-tetramethylbenzene + 4.1% tetralin + 3.9 % 1-methylnaphthalene

Can we use our modeling approach in reverse, to design a surrogate?

Helmholtz Free Energy EOS:

$$a = a^{\text{idsol}} + a^{\text{excess}},$$

$$a^{\text{idsol}} = \sum_{j=1}^{m} x_i \left[a_i^0(\rho, T) + a_i^{\text{r}}(\delta, \tau) + RT \ln x_i \right],$$

$$a^{\text{excess}} = RT \sum_{i=1}^{m-1} \sum_{j=i+1}^{m} x_i x_j F_{ij} \sum_k N_k \delta^{d_k} \tau^{t_k} \exp(-\delta^{l_k}),$$

Complex mixtures are represented by surrogates

Surrogate components each have an EOS

We can predict the composition of the vapor and liquid phases as a function of T and P: VLE

Can we use our modeling approach in reverse, to design a surrogate?

- Limit ourselves to a simple surrogate mixture (2 - 3 components only)
- Limit ourselves to components on hand or easily obtained
- Properties to consider:
  - ADC, ρ, ss

Result: the Huber-Bruno Surrogate:

After 30 iterations:

Component	Mass Fraction
n-dodecane	0.31
n-tetradecane	0.38
1,2,4-trimethylbenzene	0.31

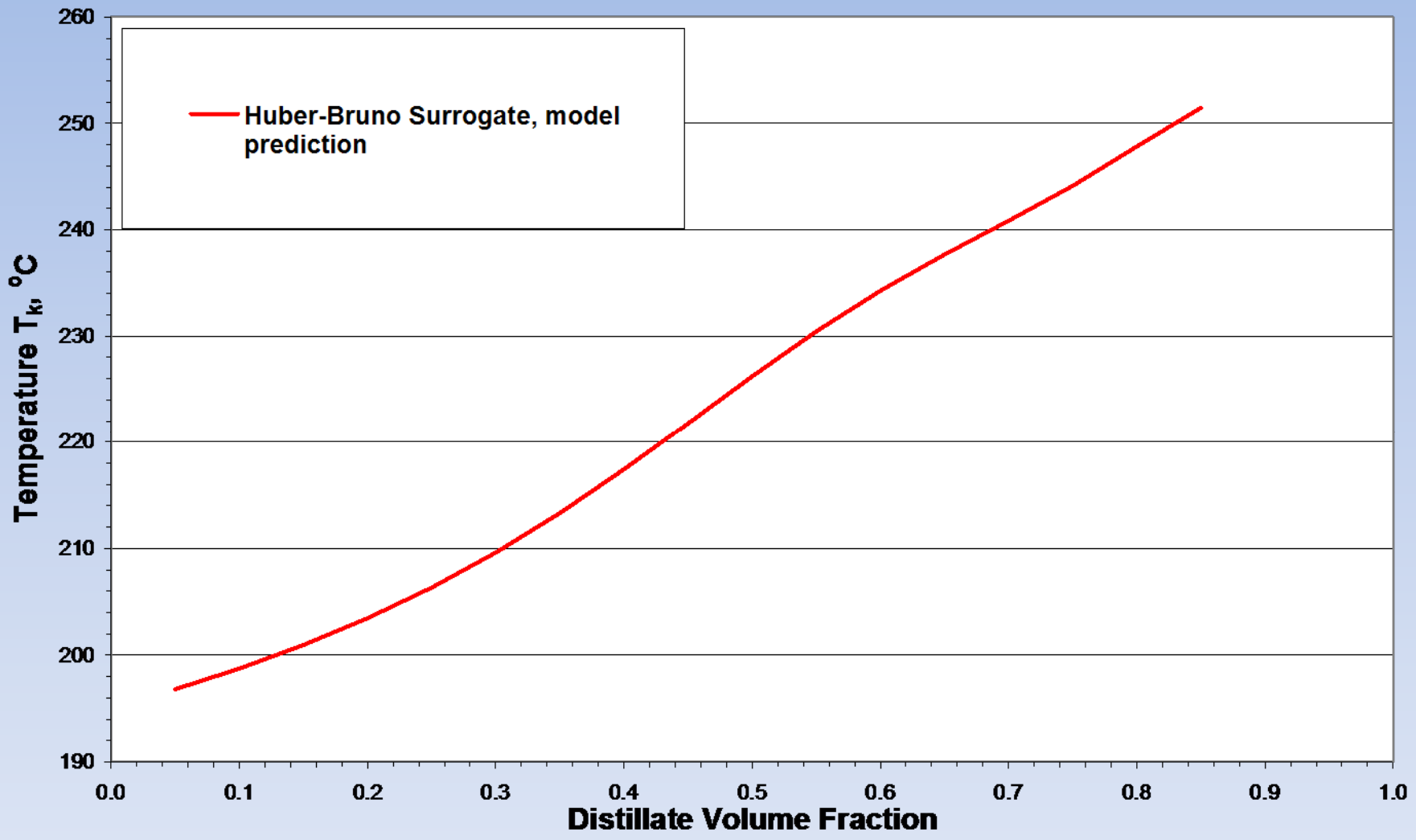
Result: the Huber-Bruno Surrogate:

After 30 iterations:

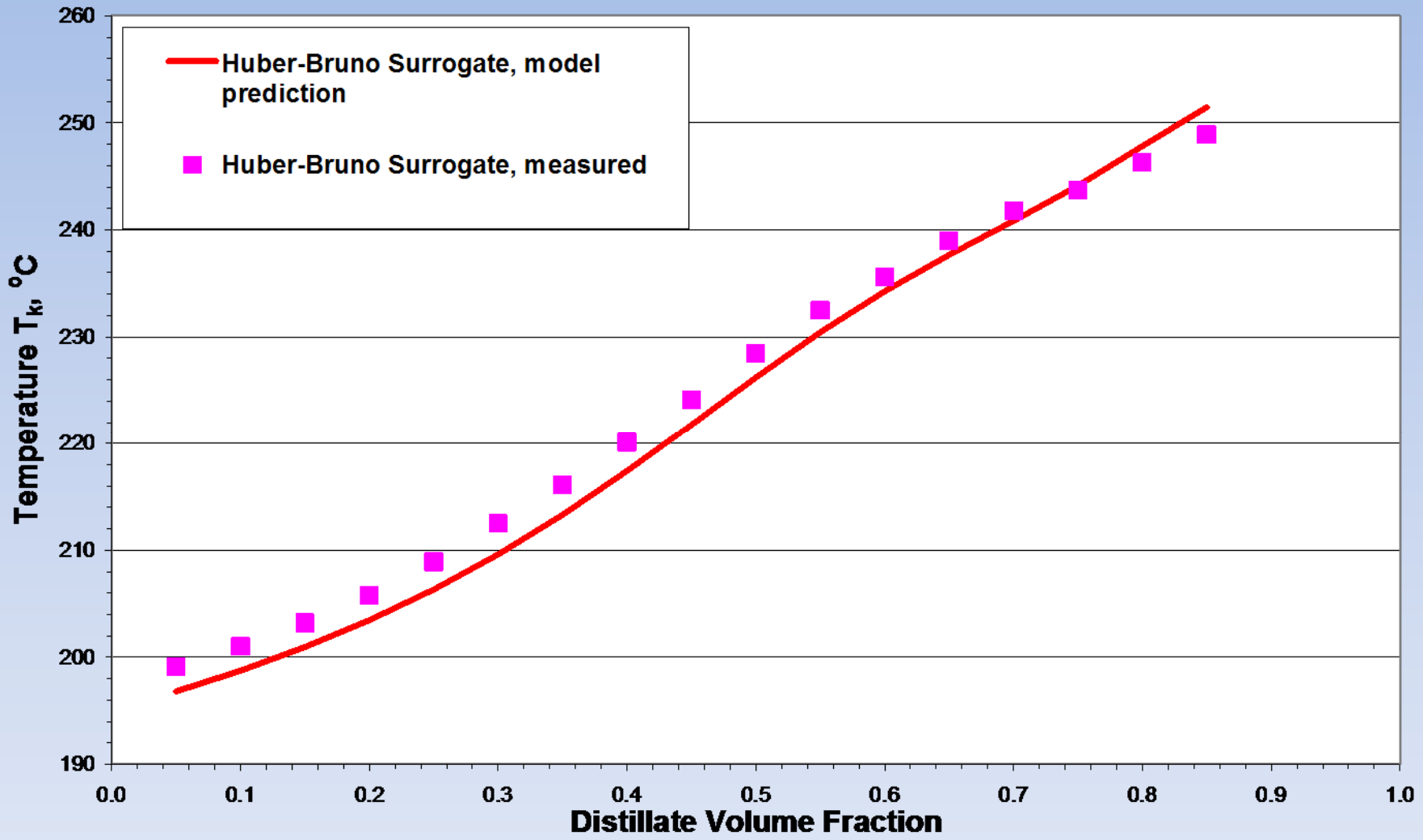
Component	Mass Fraction
n-dodecane	0.31
n-tetradecane	0.38
1,2,4-trimethylbenzene	0.31

Easy to mix and measure!

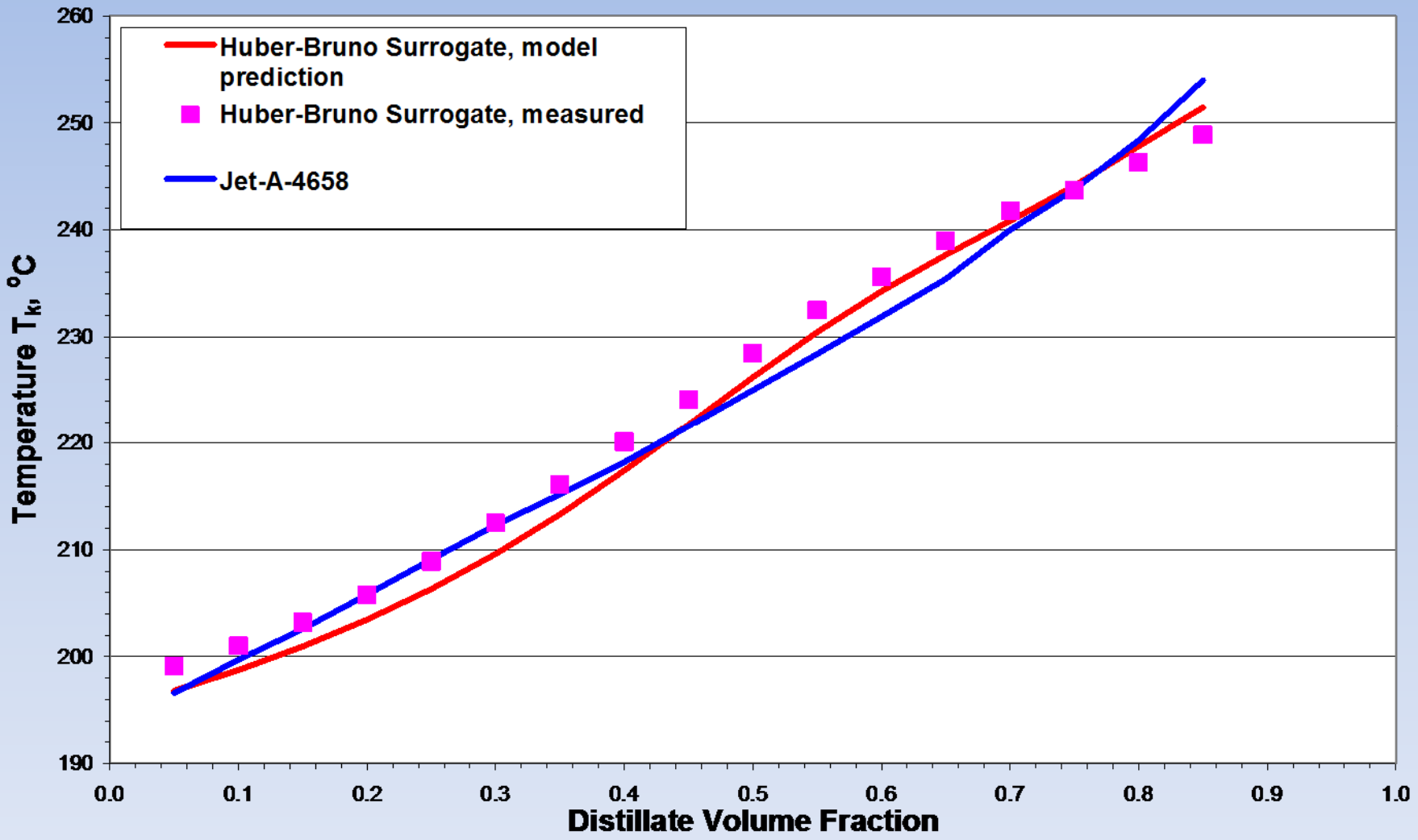
Predicted ADC:



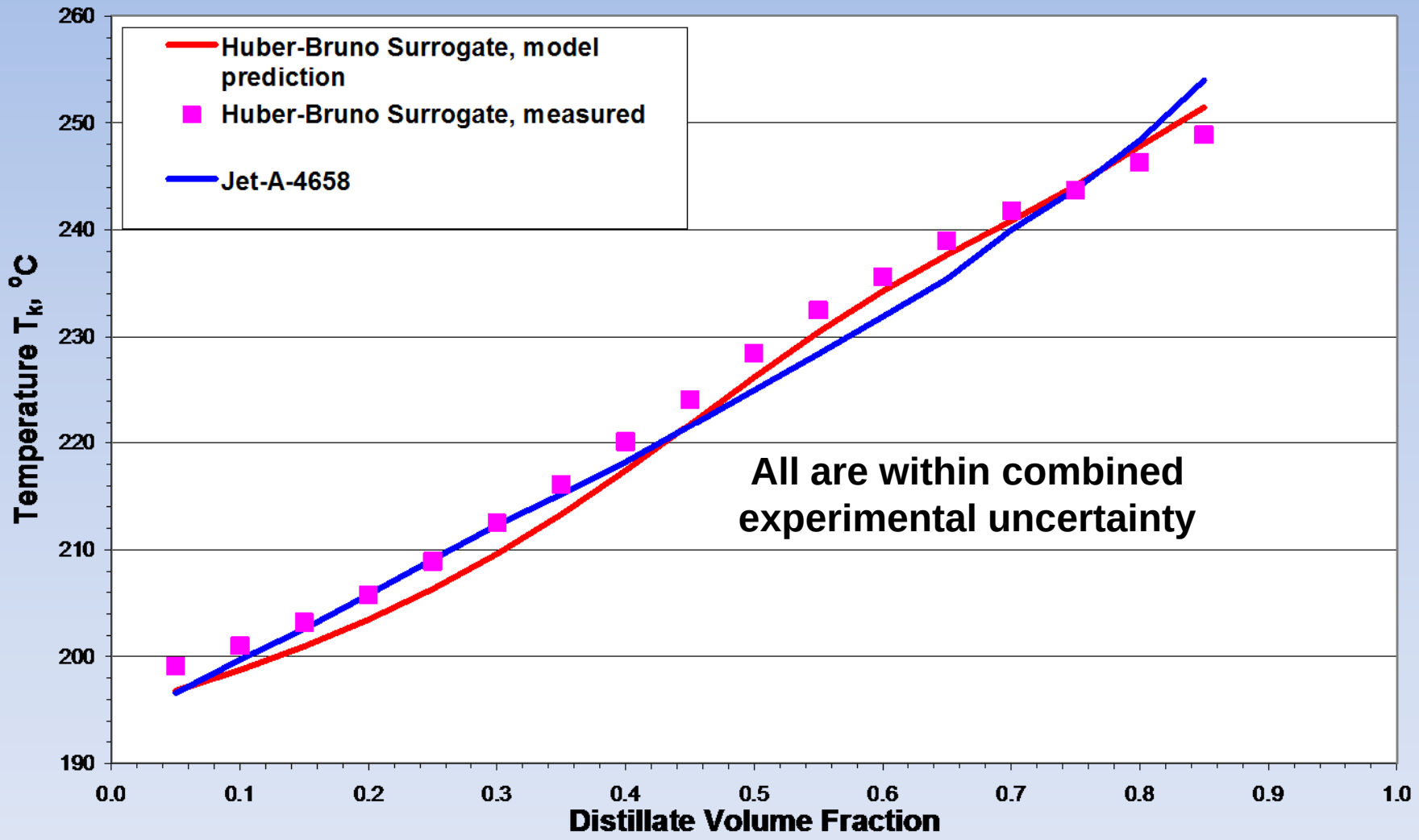
Now, mix it up amd measure it:

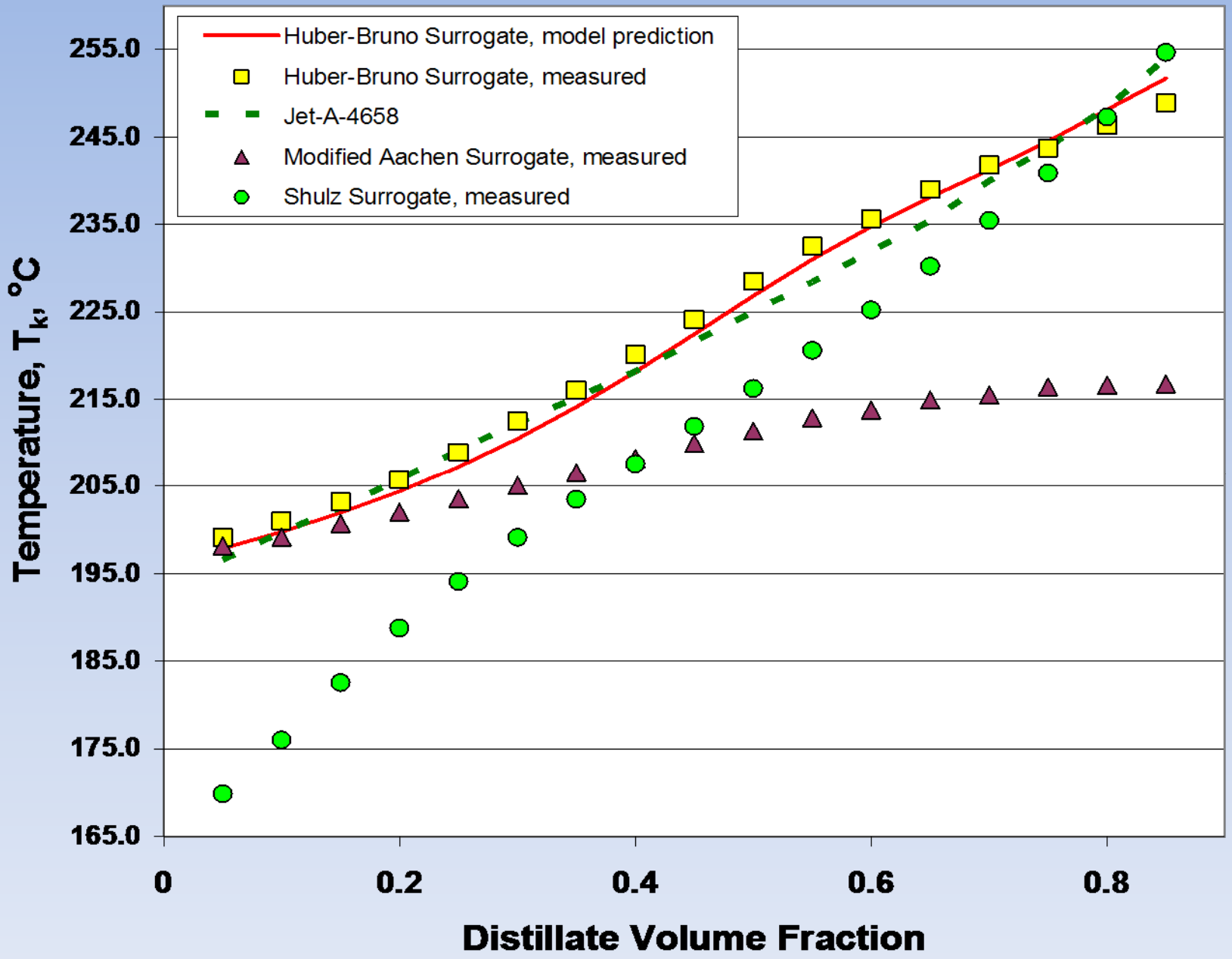


Now compare with Jet-A-4658:



Now compare with Jet-A-4658:



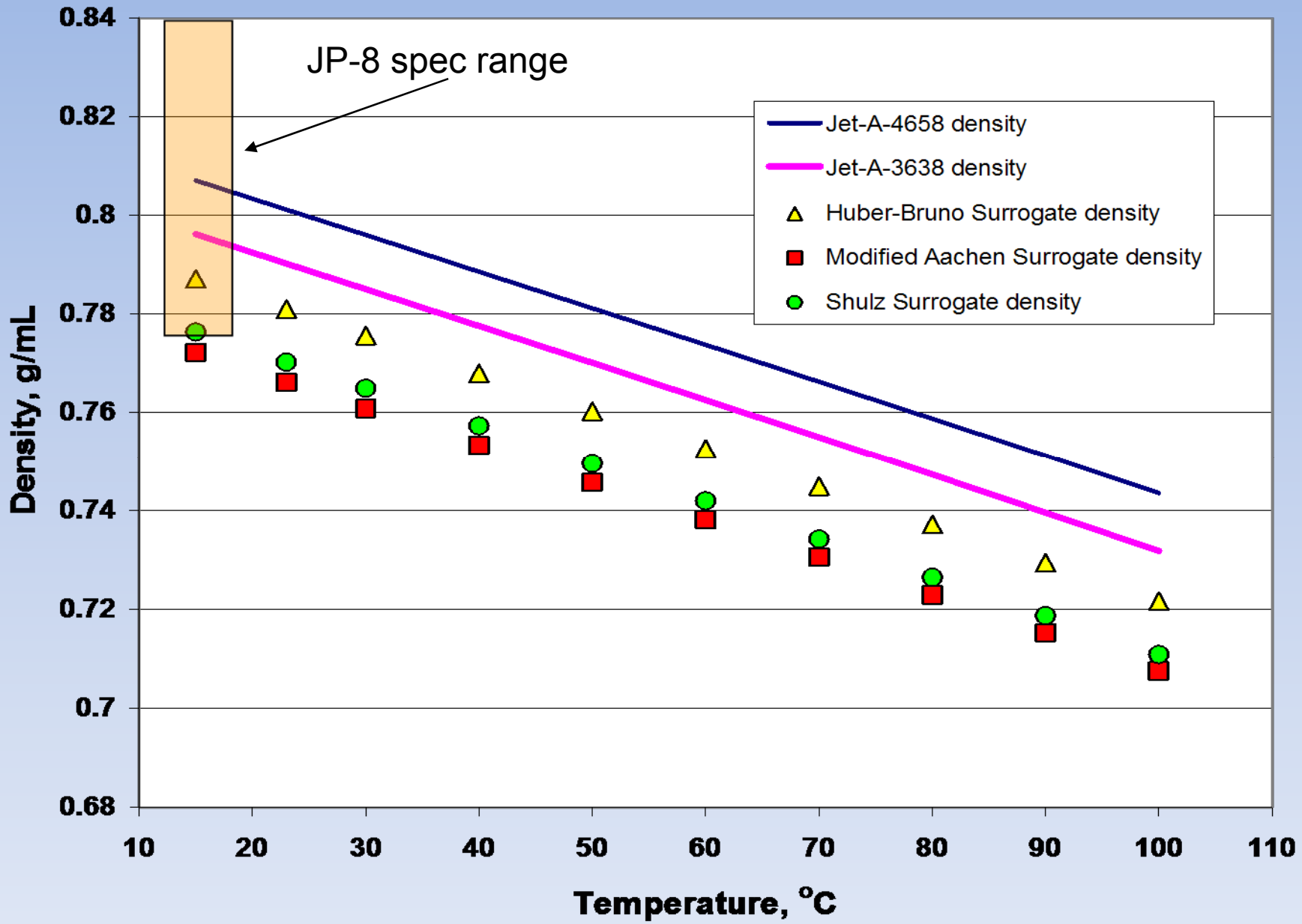

Huber-Bruno Surrogate, model prediction
Huber-Bruno Surrogate, measured
Jet-A-4658
Modified Aachen Surrogate, measured
Shulz Surrogate, measured
255.0
245.0
235.0
225.0
215.0
205.0
195.0
185.0
175.0
165.0
Temperature, T_k, °C
0
0.2
0.4
0.6
0.8
Distillate Volume Fraction

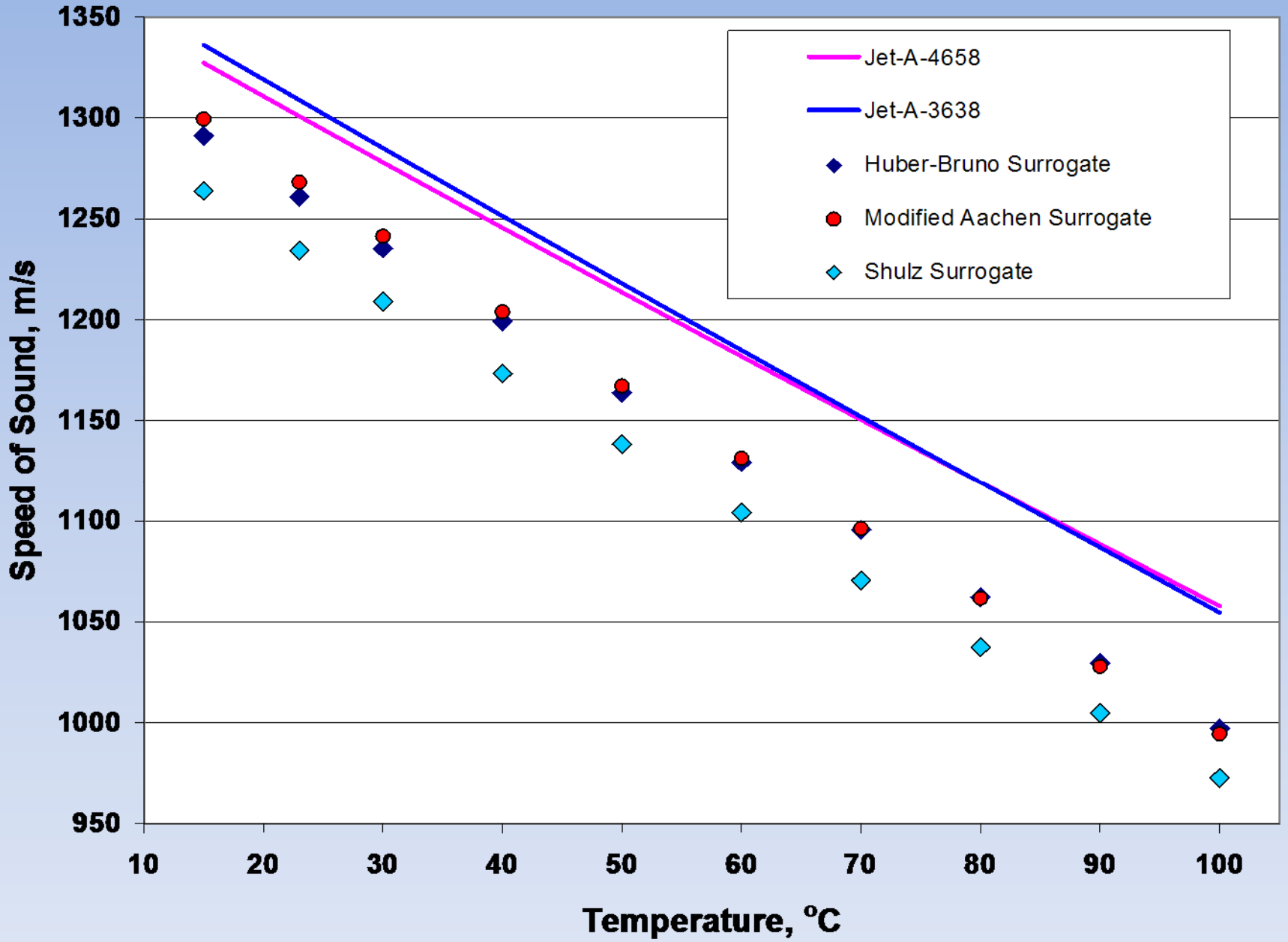
Evaluations, with H-B:

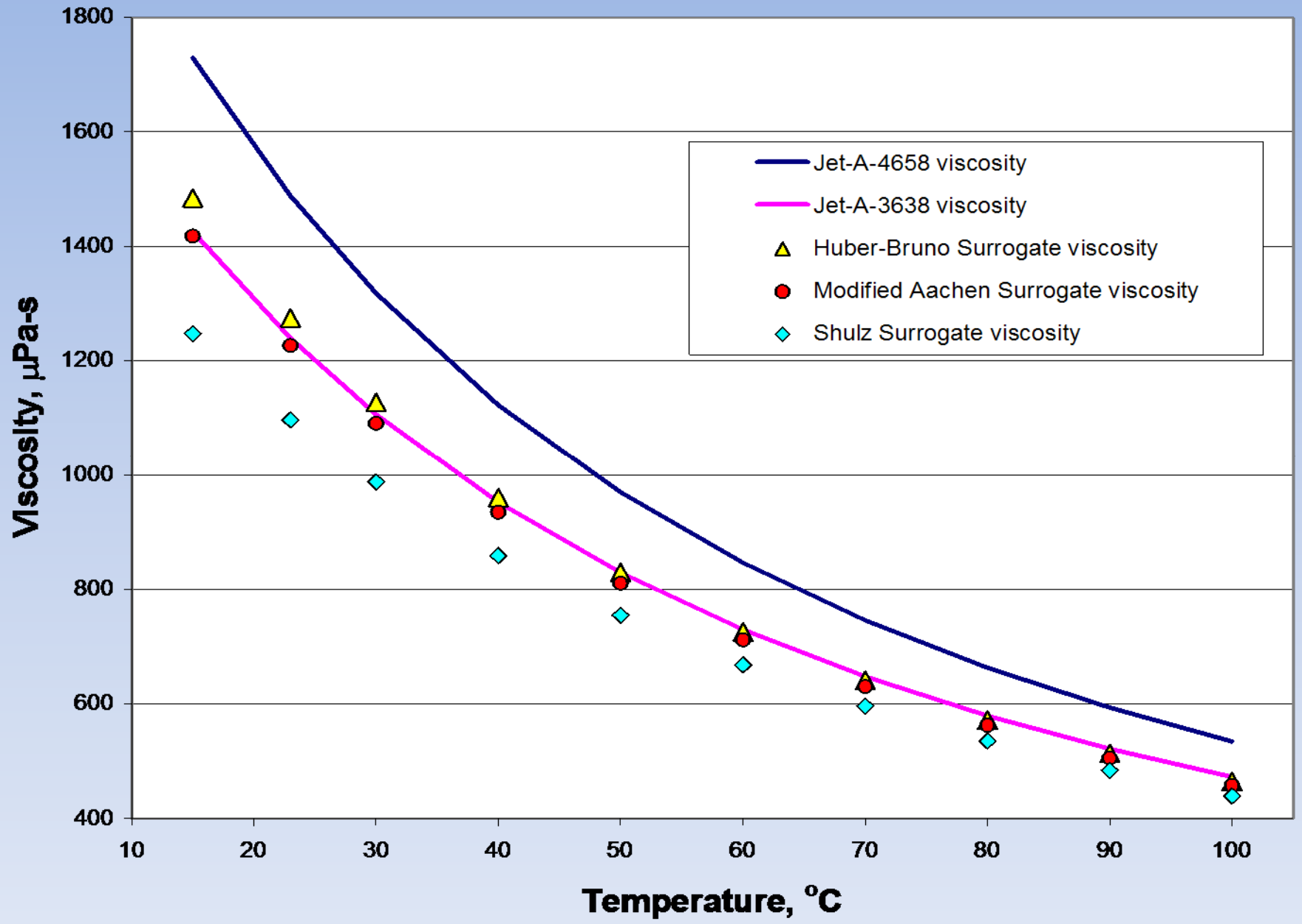
Criterion	Surrogate A	Surrogate B	Surrogate C	Surrogate F	Surrogate G	Aachen	Modified Aachen	Huber-Bruno
Metric 1	69.20	64.00	32.40	44.90	66.50	49.30	13.50	2.70
Metric 2	4.25	3.77	2.20	2.36	4.06	2.63	0.60	0.16
Metric 3	50.26	45.11	14.85	26.01	47.58	30.34	4.51	2.69
Slope Validity	poor	good	poor	invalid	poor	invalid	good	excellent
Slope	0.70	0.42	0.99	NA	0.66	NA	0.25	0.68

Going along for the ride:

Property	Jet-A-4658	H-B Surrogate
MW	156.9	158.4
H/C	1.87	1.89


JP-8 spec range
Jet-A-4658 density
Jet-A-3638 density
Huber-Bruno Surrogate density
Modified Aachen Surrogate density
Shulz Surrogate density
Density, g/mL
0.84
0.82
0.8
0.78
0.76
0.74
0.72
0.7
0.68
10
20
30
40
50
60
70
80
90
100
110
Temperature, °C


Jet-A-4658
Jet-A-3638
Huber-Bruno Surrogate
Modified Aachen Surrogate
Shulz Surrogate
Speed of Sound, m/s
1350
1300
1250
1200
1150
1100
1050
1000
950
10
20
30
40
50
60
70
80
90
100
Temperature, °C


1800
1600
1400
1200
1000
800
600
400
Viscosity, µPa-s
10
20
30
40
50
60
70
80
90
100
Temperature, °C
Jet-A-4658 viscosity
Jet-A-3638 viscosity
Huber-Bruno Surrogate viscosity
Modified Aachen Surrogate viscosity
Shulz Surrogate viscosity

Summary:

- **Evaluation strategy for surrogate mixture authenticity**
  - The technique is more important than the specific results
- **Used in reverse, the strategy can be used to design surrogate mixtures**
  - Can extend objective function to include operational properties
    - CN, TSI, etc., in addition to ADC, ρ, ss.
  - Again, the technique is more important than the specific result: the H-B surrogate mixture

Future Work

- Make the existing Jet-A/JP-8 model “tunable”
- Add additional properties
- Add the chemical in physicochemical
  - With the new toy

Acknowledgements:

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  - Julian Tishkoff
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- Tim Edwards