THERMOPHYSICAL PROPERTY NEEDS INTO THE 21ST CENTURY:

PETROLEUM REFINING AND PETROCHEMICAL INDUSTRY VIEW

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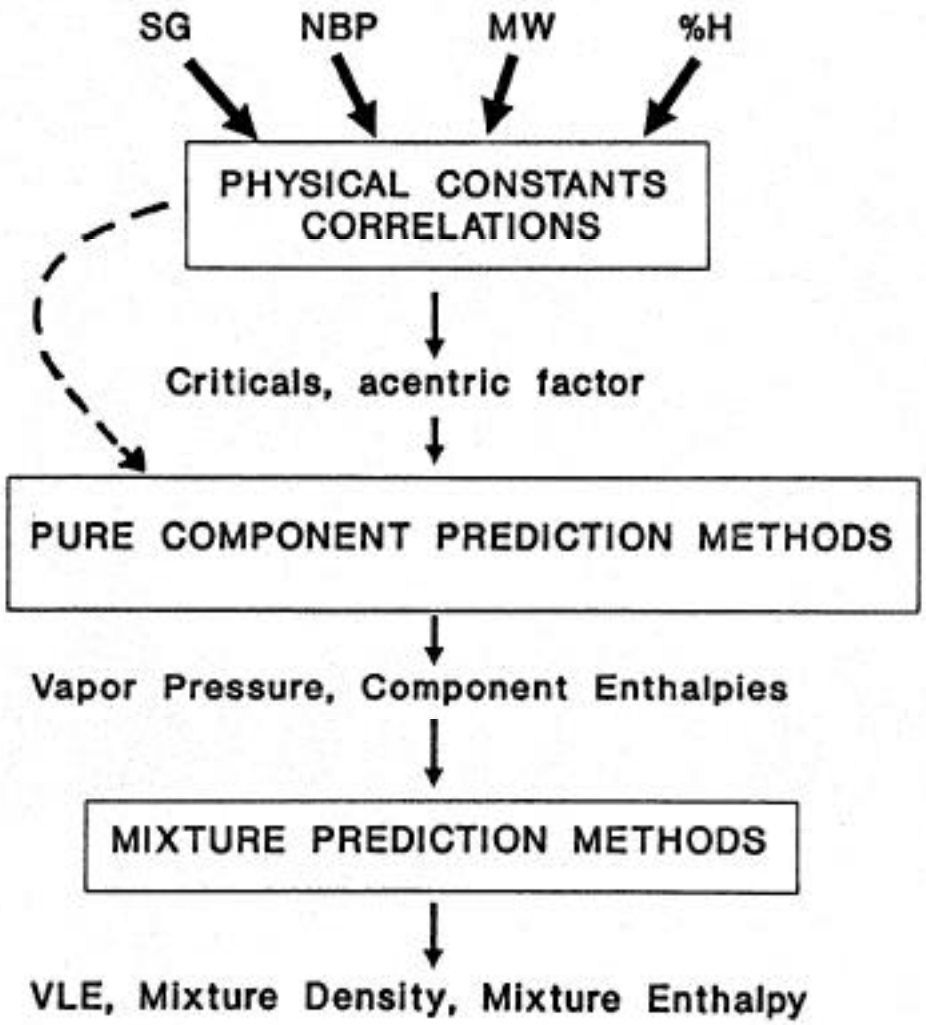
MAJOR NEEDS

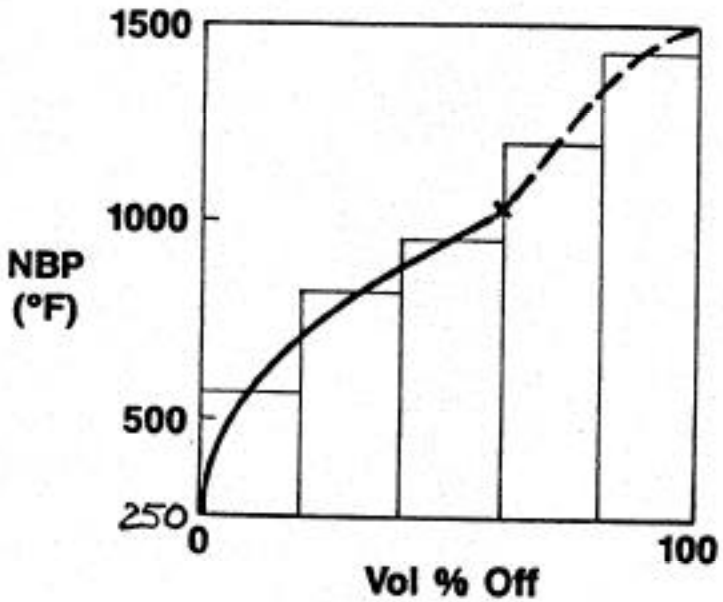
- Petroleum Refining
  - + $H_2 \rightarrow$ 1500 °F NBP
  - + mostly hydrocarbons with 1-2 wt% S; 0.1 - 0.2 wt% N; < 0.1 wt% 0
  - + major need: heavy hydrocarbons, NBP > 800 °F (700 K)
- Petrochemicals
  - + nonpolar (e.g., olefins)
  - + polar (e.g., water, alcohols, polyalcohols, ether alcohols)
  - + major need:
    - complex polyfunctional polars
    - polymers
- Characterization... Properties... Modes of data generation

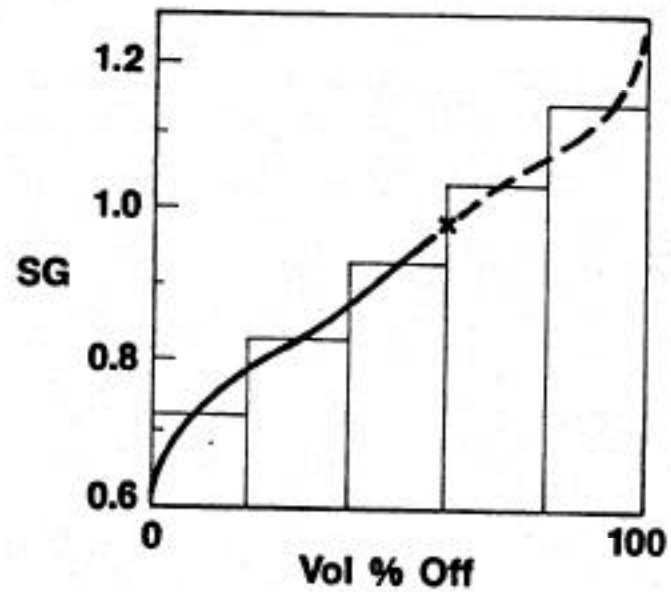
CHARACTERIZATION IS THE SELECTION OF MEASURABLE PROPERTIES USED TO PREDICT ALL OTHER PROPERTIES



CURRENT METHODS OF PROPERTY PREDICTION

- Pseudocomponet Breakdown by NBP (Lab Still)

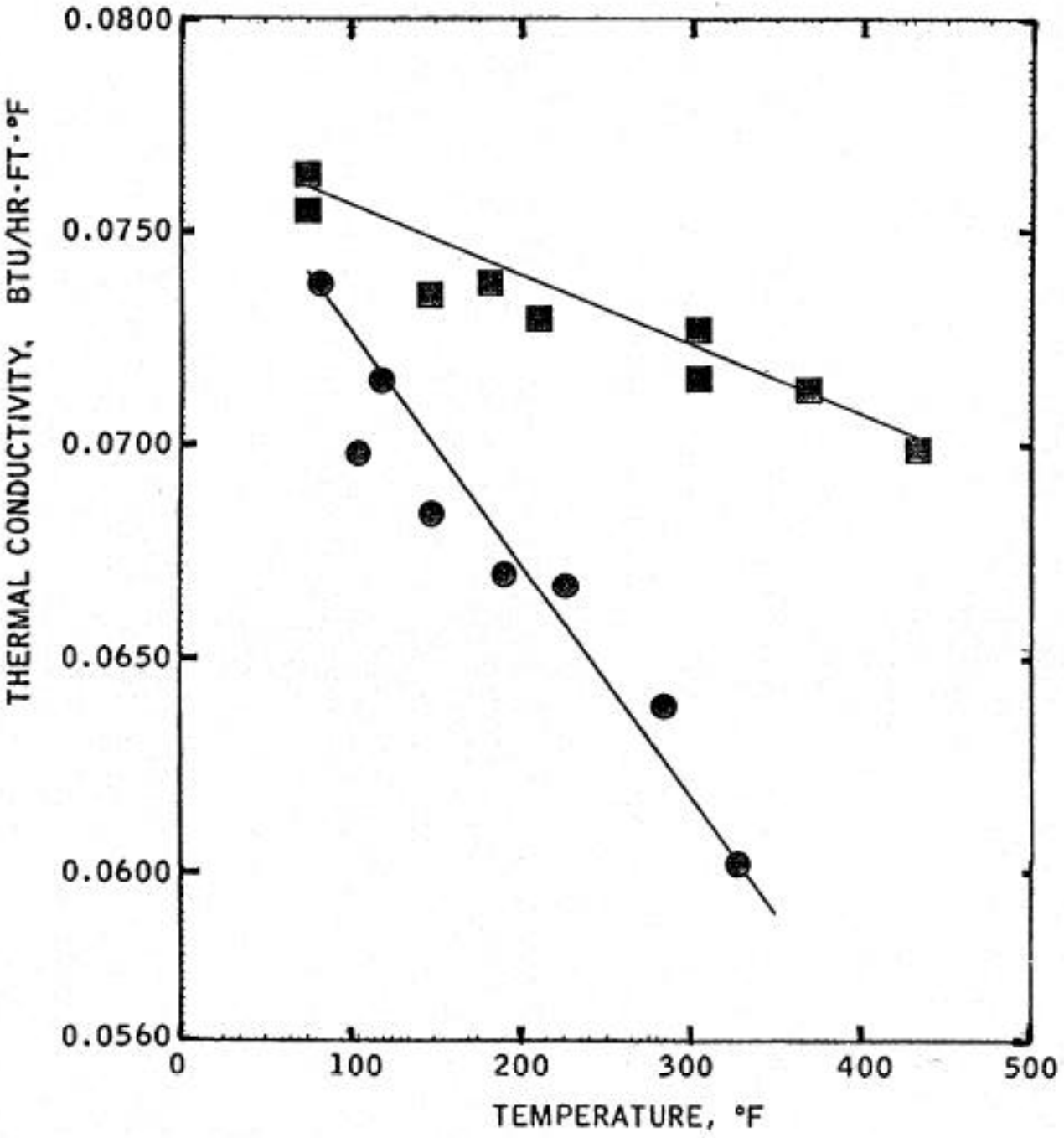




- NBP, SG Characterize Narrow Fractions
- Wide Boiling Range Cuts Treated as Mixtures
- Property = function (NBP, SG)
- Problems for Residua, Highly Aromatic Synfuel or Converted Fractions

THERMAL CONDUCTIVITY OF TWO SIMILAR PETROLEUM FRACTIONS

	NBP, °F	°API	Kw
■	805	22.1	11.75
●	817	22.4	11.80



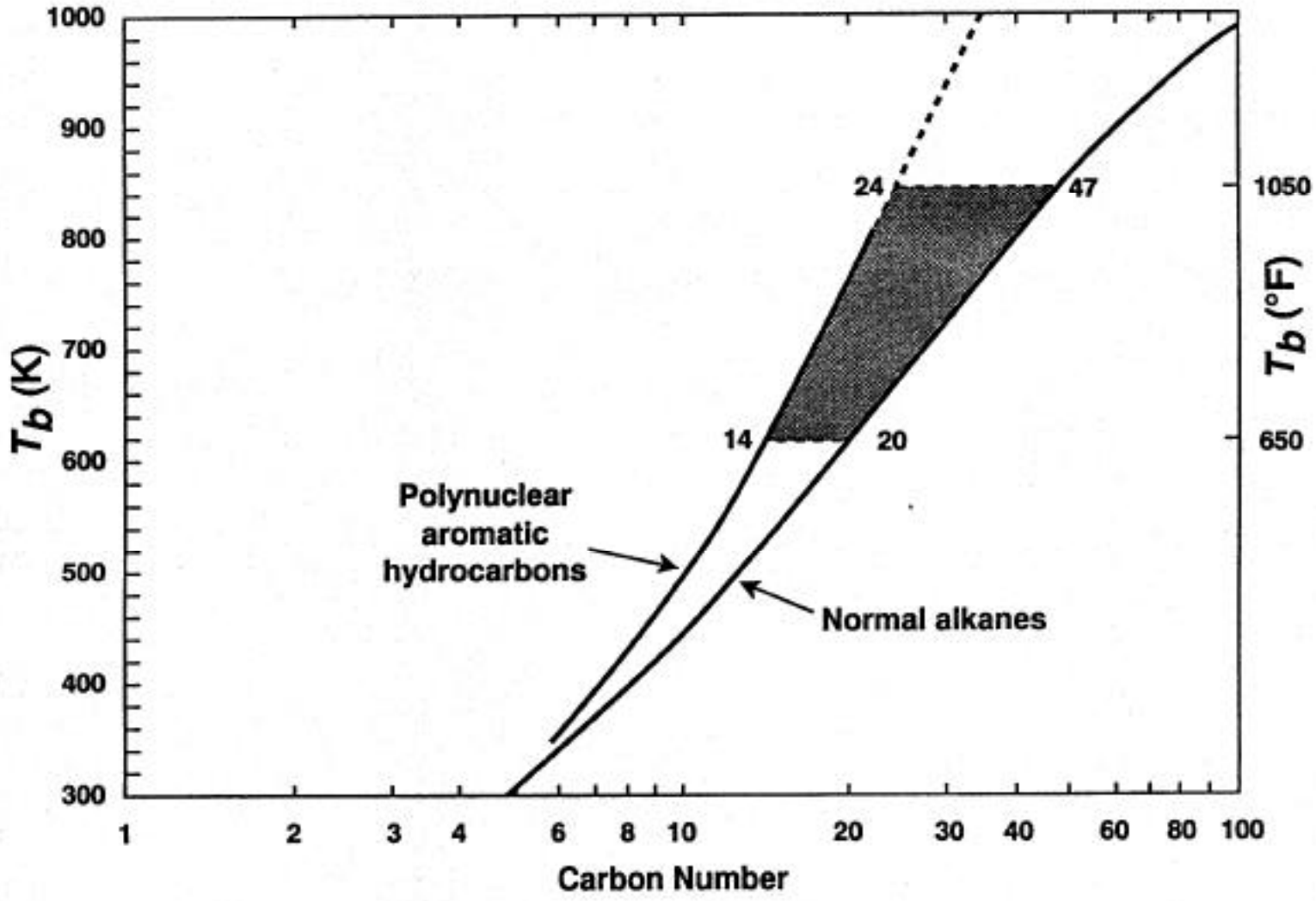
PETROLEUM HYDROCARBON CHARACTERIZATION--WHERE IS IT GOING?

- Current framework limited to NBP (MW?) and SG
  - more info readily available via new analytics (e.g., GC-MS)

- Typically front-end components identified through C_5
  - C_5^+ characterized by NBP/SG via distillation up to 1050 °F

- Analytics extending front-end to C_{10} and beyond -- <u>many</u> isomers!
  - Need experimental data, reliable predictions -- for component properties first, then mixtures
  - May be a practical limit in number of components

CARBON-NUMBER RANGE OF HYDROCARBONS IN PETROLEUM CRUDE



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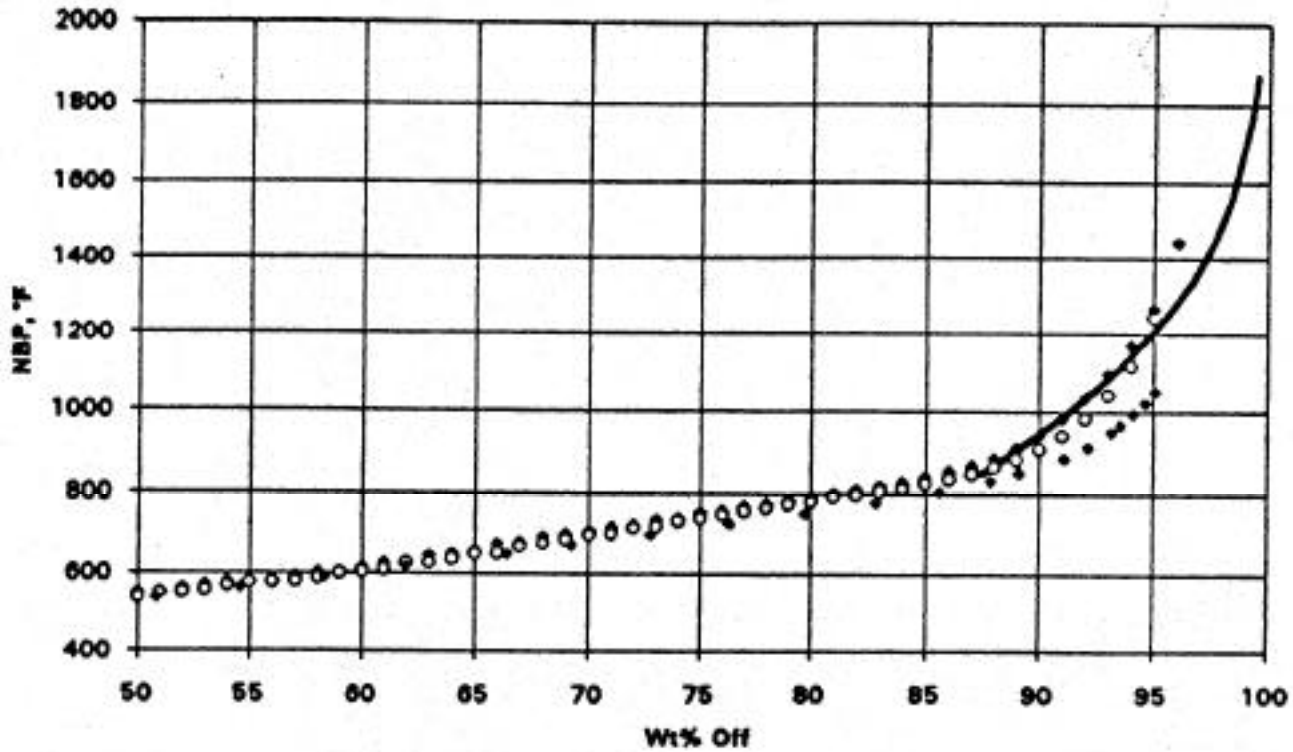
- New techniques extending back-end NBP's to 1300 °F (endpoint > 1500 °F)
  - Molecular complexity suggests that
    - full component characterization not feasible
    - but need more than NBP/SG to describe heavy hydrocarbons

A VARIABLE END POINT IN PLACE OF 1500 °F

- Even a light crude (< 10 wt% has NBP > 1050 °F) can have an EP > 1500 °F



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  - + Molecular complexity suggests that
    - full component characterization not feasible
    - but need more than NBP/SG to describe heavy hydrocarbons
  - ► + Data needed for heavy model components to define characterization basis
    - API 42 provides a good starting point

ANALYSIS OF API 42 DATA

- Volatility, melting point, and viscosity index
  - + Key properties of lubricants
  - + VI is inversely related to Temp. Dep. of kinematic viscosity
- Volatility is strongly related to molecular size
  - + Easiest property to correlate
- Melting point and VI are strongly related to molecular structure
  - + Dependence on structure differs for two properties
  - + MP depends on ability of molecule to fit into 3-D network
  - + VI is primarily affected by molecular flexibililty
- What structural parameters can quantify
  - + Ability of a molecule to fit into a 3-D network?
  - + Molecular flexibility?

CHARACTERIZATION OF POLARS

- Models still based on 3-parameter CS concepts with extensions

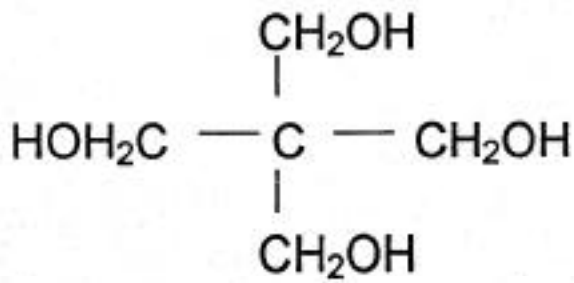
- Proposed extensions include
  - + Alternative and/or multiple reference fluids
  - + 4th CS parameter--dipole moment, polarizability

$$\mu' = \mu + \alpha \cdot f(\rho)$$

  - + Self-association contributions

- Not much progress made for typical engineering applications
  - + One exception is area of group-contribution-based models
    - ⇒ Mostly success for pure component properties (e.g., ideal gas properties, liquid density)
    - ⇒ Limited success for mixtures (e.g., activity coeff. via UNIFAC)
    - ⇒ Limited/no use for heavy HC's in current charact. framework

EXAMPLE: PENTAERYTHRITOL



- Can pure-component properties be predicted?

  + Benson's method probably adequate for ideal-gas properties
  + Correlations for most other properties too unreliable

- Can VLE/LLE/H^{ex} properties be predicted?

  + UNIFAC (or ASOG) not reliable for polyfunctional polar compounds
  + Limitations due to lack of experimental data and understanding of intramolecular effects

- Computational chemistry may lead to rigorous group-contribution models that account for intramolecular effects

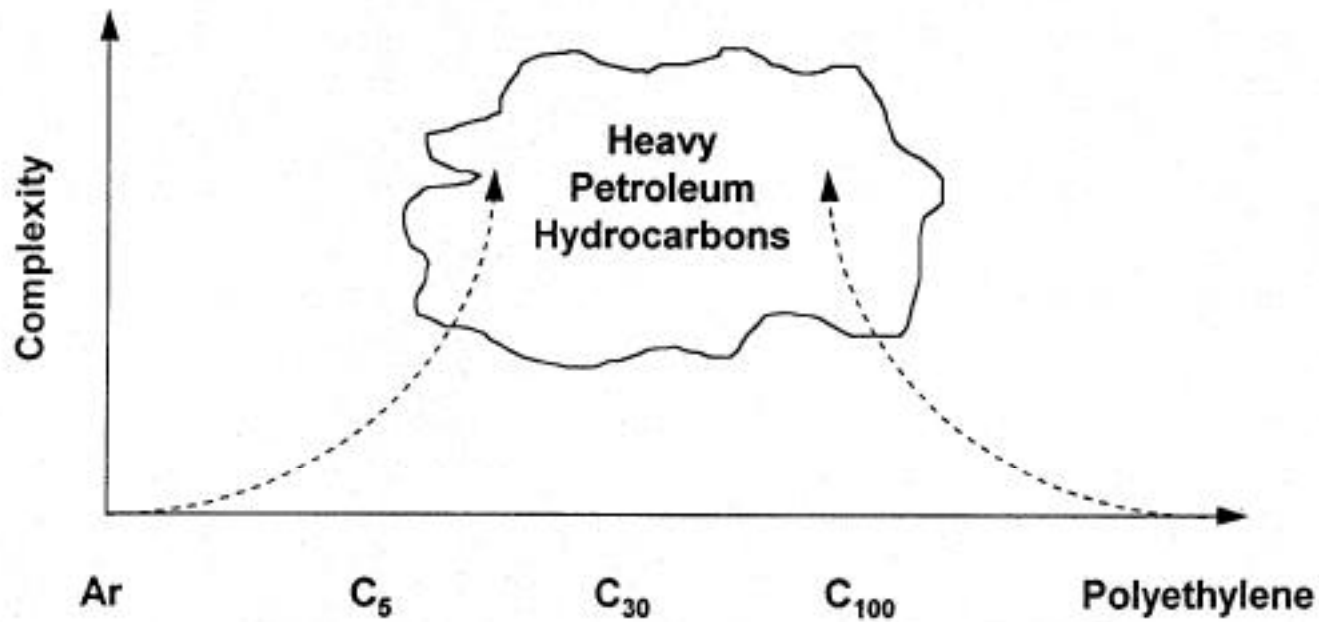
CHARACTERIZATION OF POLYMERS

- Different approach dictated by available data--and properties needed
  - + MW and liquid density may be available
  - + NBP or critical properties do not exist
- Characterization parameters typically are property - and model - specific
  - + E.g., P-V-T data $\Rightarrow P^*, V^*, T^*$ in 3-parameter CS (Prigogine, Flory)
  - + CS parameters are not "universal"
- Polar contributions may be included via model parameters
  - + Self- and cross-association terms in SAFT EOS

CAN POLYMER THEORY PROVIDE GUIDANCE IN HEAVY HC CHARACT.?

- Polymers are structurally well-defined but high MW (up to 10^6)
  - + Typical properties are MW, liquid density, melting point (?)
  - + Cannot link to defined compounds (via T_c) or petroleum hydrocarbons (via NBP)

- Petroleum heavy ends are structurally complex (ill-defined) and lower MW (up to 10^4)
  - + Presence of heteroatoms/functional groups adds to complexity



- At present, only limited connections can be made
  - + e.g., extension of normal alkanes to polyethylene as CN gets large
  - + Other opportunities?

THERMOPHYSICAL PROPERTY NEEDS FOR DESIGN

- First and most important use of thermophysical properties is in heat and material balance calculations
  - Uncertainties in data/predictions directly affect results
  - Three essential properties:
    + Vapor-Liquid Equilibria
    + Enthalpy
    + Density (P-V-T)
- Emphasis on VLE (include vapor pressure) due to importance of distillation in separations
  - If separation by extraction, LLE become important
- Enthalpy includes heat capacity, heat of vaporization, heat of mixing, AND heat of reaction

VAPOR PRESSURE PREDICTIONS

- Key property in VLE calculations

- Corresponding - states models most common

  + Require critical properties, acentric factor (or Riedel alpha)
  + For fractions (NBP/SG), Maxwell-Bonnell (M-B) is "standard"
    - Predict VP directly
    - Alternatively, use M-B to initialize C-S model

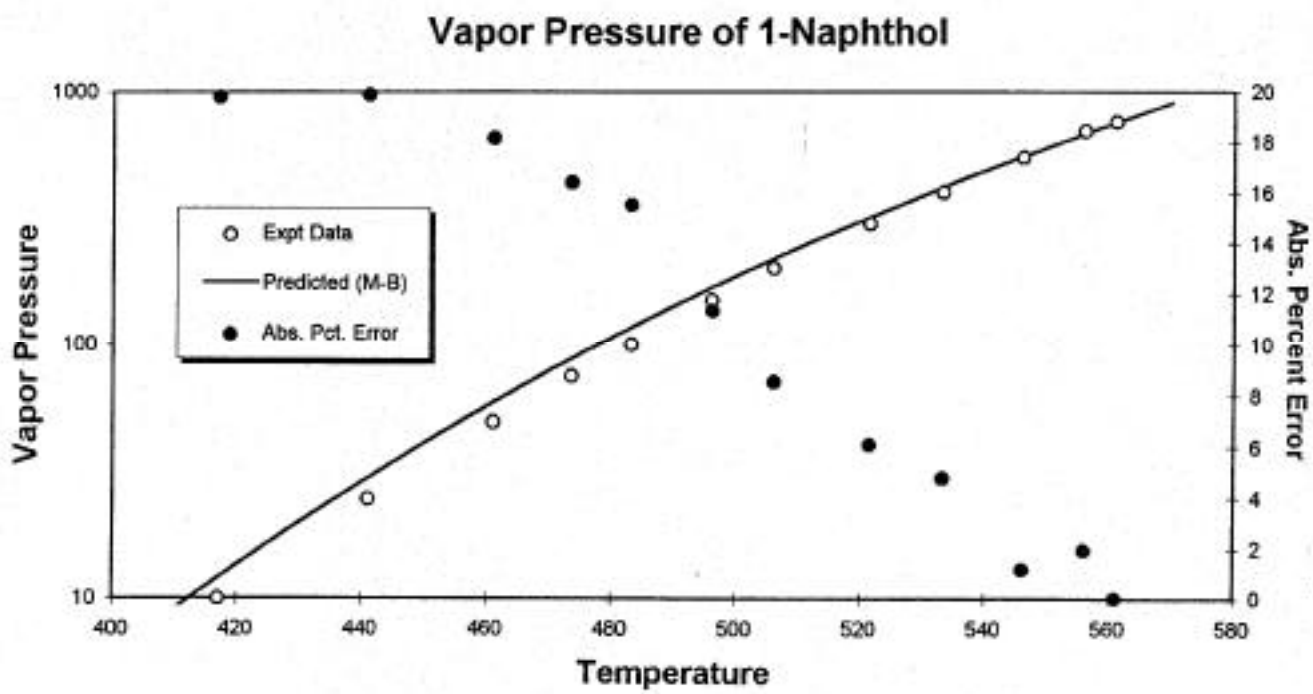
- Maxwell-Bonnell VP for petroleum fractions

  + one VP (NBP or some other P<1 atm) and average SG
  + Frequently extrapolated to high-boiling (1050 °F+) components
    - Limited VP data available to C_{43}
  + Large errors for polar fractions (e.g., phenolics in coal liquids)

WHAT ABOUT VP OF POLARS?

- C-S models proposed
  - + 4-parameter
  - + Alternative reference fluids

- Can VP of polars be superimposed on M-B for fractions?
  - + Correlate delta with,e.g., polarizability and/or dipole moment



VLE METHODS

EQUATIONS OF STATE

CUBIC

SRK
PR

HIGHER ORDER

BWR
....
APACT
SAFT

EOS / G^{ex}

REQUIRE DATA

HURON-VIDAL
WONG-SANDLER

PREDICTIVE

MHV2
PSRK

HYBRID METHODS

VAPOR: EOS
LIQUID: G^{ex}

REQUIRE DATA

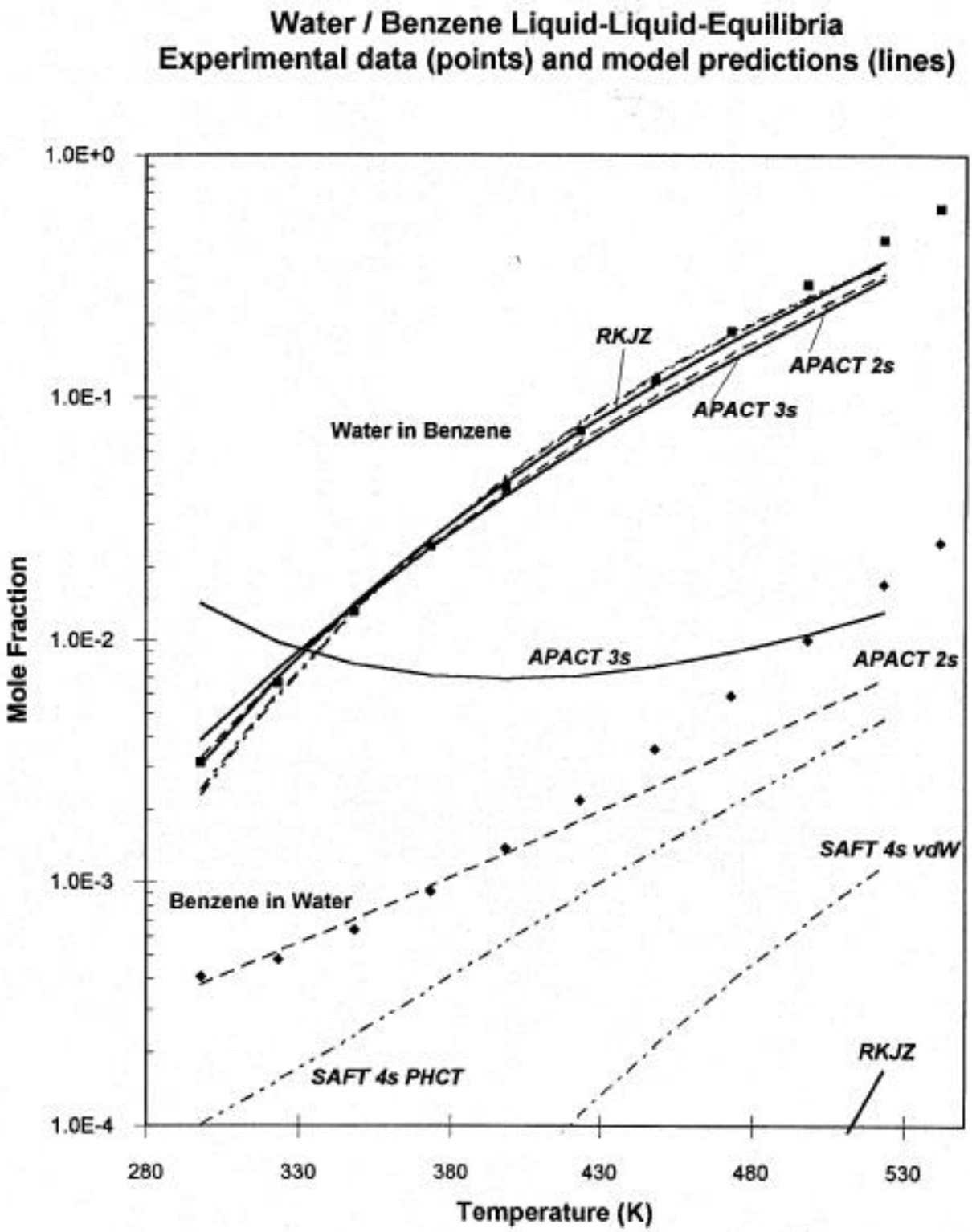
WILSON
NRTL
UNIQUAC

PREDICTIVE

ASOG
UNIFAC

VLE (VLLE) PREDICTIONS FOR HYDROCARBON SYSTEMS

- Equations of state - cubic
  - + Can go far with vdW mixing rule, one binary parameter
    - H_2/HC; water in HC
  - + However, significant limitations exist
    - HC in water; NBP's > 1050 °F (vdW mixing breakdown?)
    - Polars restricted to low-concentrations
- Equations of state - higher order
  - + Previous generation: BWR (limited to light ends)
  - + Current generation: PHCT, PACT, SAFT (light ends to polymers)
    - Include association contributions -- still not quantitative for HC/water


Water / Benzene Liquid-Liquid-Equilibria
Experimental data (points) and model predictions (lines)
1.0E+0
1.0E-1
1.0E-2
1.0E-3
1.0E-4
Mole Fraction
280
330
380
430
480
530
Temperature (K)
RKJZ
APACT 2s
APACT 3s
Water in Benzene
APACT 3s
APACT 2s
SAFT 4s vdW
Benzene in Water
RKJZ
SAFT 4s PHCT

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- Equations of state - higher order
  - + Previous generation: BWR (limited to light ends)
  - + Current generation: PHCT, PACT, SAFT (light ends to polymers)
    - Include association contributions -- still not quantitative for HC/water
    - ► SAFT extensively applied to polymer phase equilibria
    - Potentially better for heavy hydrocarbons (NBP > 1050 °F)
  - + Arguably, area of greatest recent advances -- but still in infancy

VLE (VLLE) PREDICTIONS FOR HYDROCARBON SYSTEMS (Cont)

- Hybrid Methods -- EoS (Vapor) + G^{ex} (Liquid)
  - + Handle polars at low pressure (away from critical region)
    - Data required for G^{ex} parameters
    - Group-contribution methods (ASOG, UNIFAC) for prediction
  - + Some methods (G^{ex}) applicable to polymer solutions
  - + Limitations for polyfunctional polars -- GC does not work
    - Opportunity for computational chemistry to build better models
- Equations of State with G^{ex} - Based Mixing Rules
  - + Cubic EoS + G^{ex} model (e.g., NRTL, UNIFAC)
  - + Data needed for parameters (e.g., H-V, W-S) or predictive (e.g., PSRK)
  - + For predictive models, new groups required for light gases
  - + Cannot be used for polymers -- EoS require criticals, VP

ENTHALPY AND DENSITY PREDICTIONS

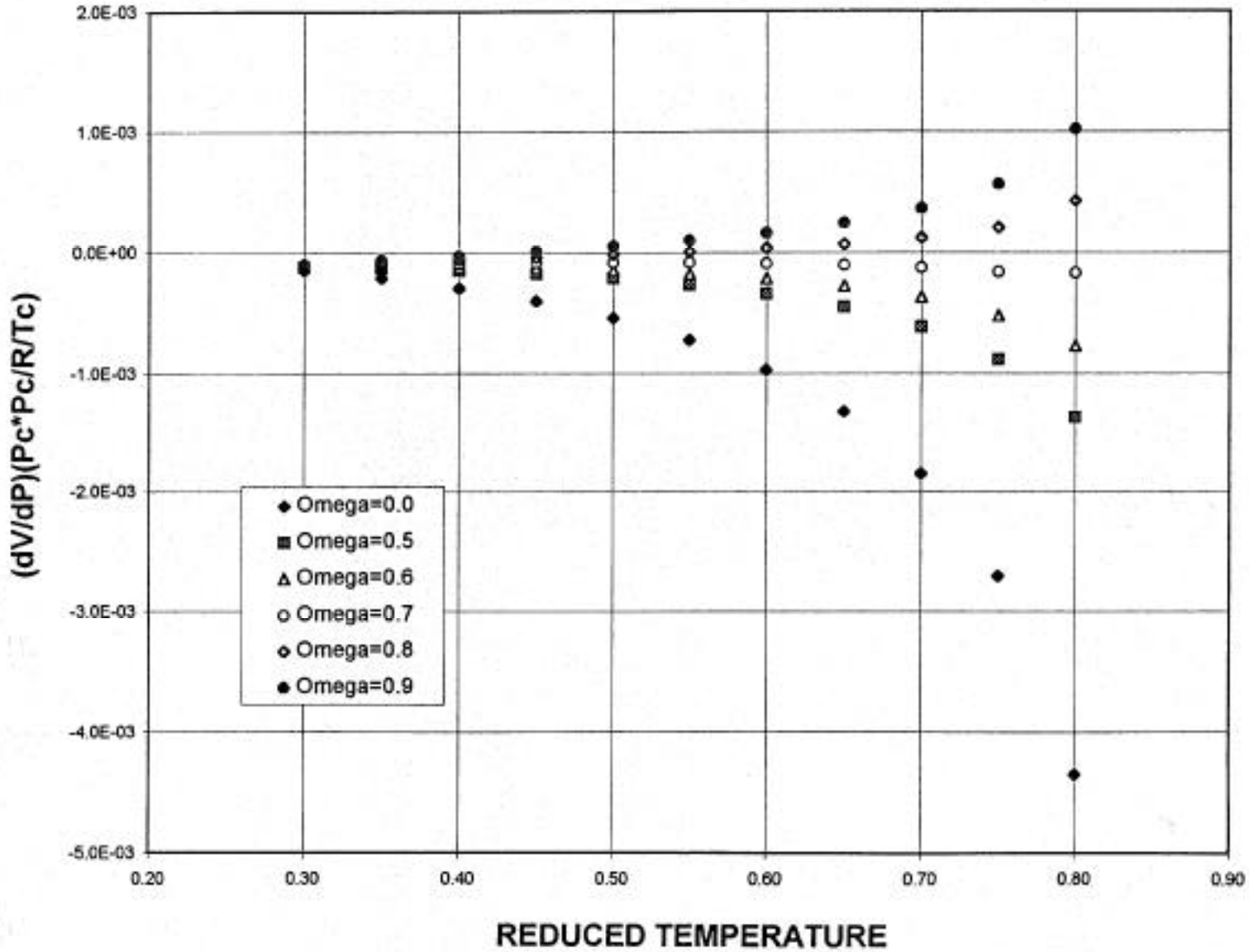
- Next to VLE, most important properties in H&MB calcs

- Corresponding-states models most common
  - + Again, based on criticals, acentric factor
  - + NBP/SG correlations still available for petroleum (e.g., API TDB)

- Lee-Kesler (1975) generally used for
  - + PVT and H (vapor phase), H (liquid); COSTALD for PVT (liquid)
  - + Heavy components (CN >> 10)
  - + Polars also (low concentrations ?)

- L-K has significant limitations
  - + Poor density, C_P at low T_R
  - + $(\partial V/\partial P)_T$ is positive for CN > 15
    - - General problem for properties not linear in acentric factor

(dV/dP) AT SATURATION VIA LEE-KESLER EOS



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  - + $(\partial V/\partial P)_T$ is positive for CN > 15
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- Potential Enhancements?
  - + Improved ref. fluid EOS (must extrapolate below MP!)
  - + 2nd order effects (non-linear acentric factor dependence)
  - + Others?

THERMOPHYSICAL PROPERTY NEEDS FOR EQUIPMENT DESIGN

- Transport Properties (Especially Viscosity and Thermal Conductivity) and Surface Tension are Primarily Used in Design of Equipment

- Highly Accurate Data Might Not be Needed

  - Property May Have Little Influence on Equipment Size
    + Value may not vary much
    + Property is frequently raised to a fractional power

  - Model Based on Low-Quality Data May Not Benefit From High-Quality Data
    + Model for equipment design should be revised with high-Q data

  - Fouling of Equipment Diminishes Effect of Properties
    + Allowance must be made for fouling (which cannot be quantified)

SURFACE TENSION OF PURE COMPOUNDS

- Two Types of Models
  - Corresponding-States

$$\sigma = \sigma_o (1 - T_r)^b$$

σ_o, b are adjustable parameters

+ $\sigma_o = \sigma$ at O K; $\sigma_o = f(K_w)$ for petroleum fractions
+ b ≅ 11/9 for hydrocarbons; a function of temperature for polars

  - Parachor Method

$$\sigma = \left[\frac{[P]}{M} \left(\rho^L - \rho^V \right) \right]^4$$

where [P] = parachor of compound
+ a constant for hydrocarbons
+ a function of temperature for polars

SURFACE TENSION OF MIXTURES

- For mixtures of hydrocarbons: Weinaug-Katz equation

$$\sigma_m = \sum_i \left[[P]_i \left(\frac{x_i \rho^L}{M^L} - \frac{y_i \rho^V}{M^V} \right) \right]^4$$

  - VLE Flash Calculation Must Be Performed <u>First</u> to Obtain Equilibrium y and x

- For polar mixtures: Weinaug-Katz equation doesn't work

  - No general method for polar mixtures

- Rigorous treatment (e.g., Sprow and Prausnitz, 1966) requires bulk and surface activity coefficients, component surface areas

TRANSPORT PROPERTY PREDICTIONS (VISCOSITY)

- Available models relatively "primitive" -- benign neglect?
  - + Pure component properties with blending (liquid only)

KINEMATIC VISCOSITY OF PETROLEUM FRACTIONS

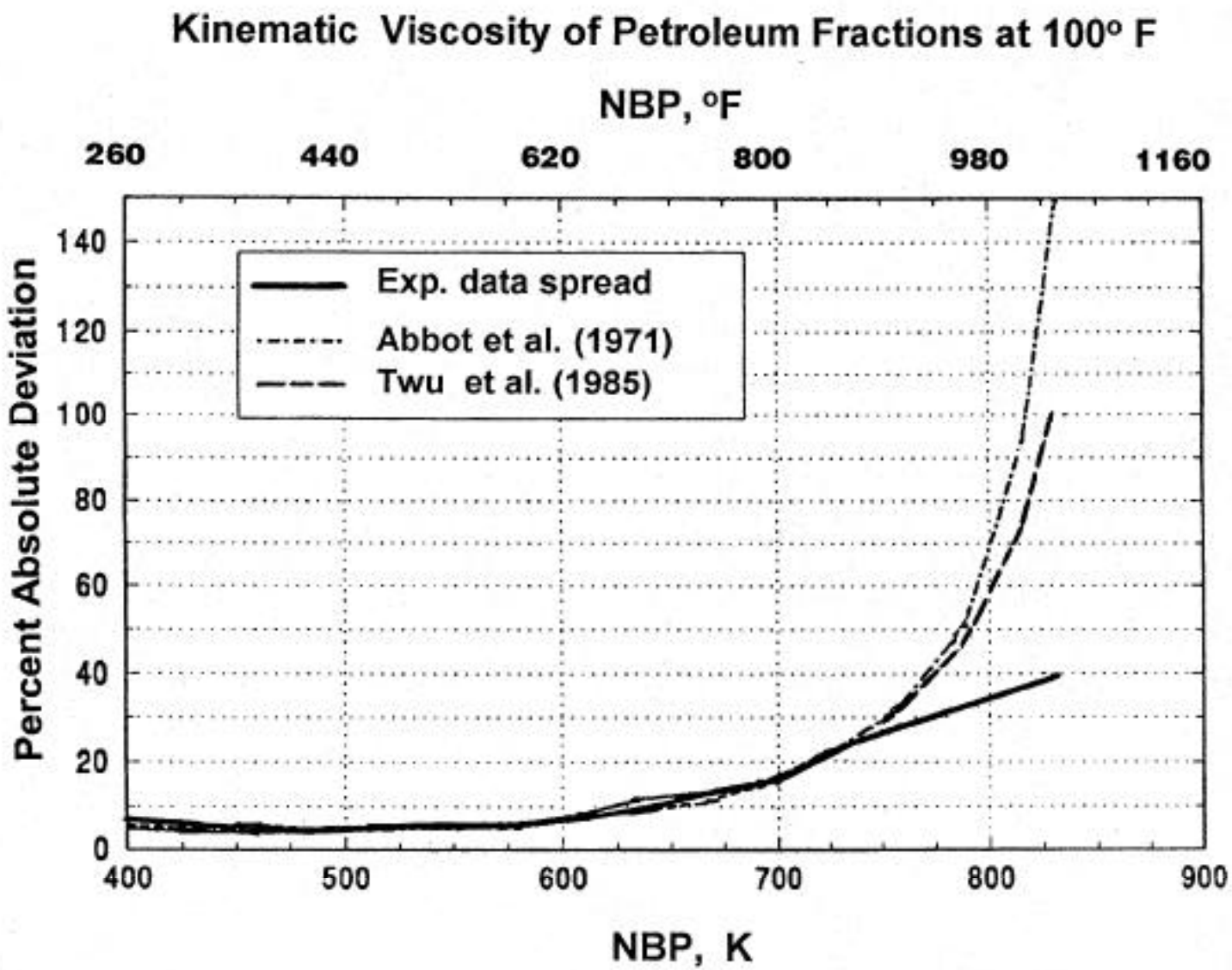
- Modified Walther equation is refining industry standard

$$\log_{10} \log_{10} (\nu + c) = a + b \log_{10} T$$

c = 0.7 for $\nu \geq 2$ cSt; f (ν) for $\nu < 2$ cSt
T is absolute temperature

- Measurement (or prediction) of KV at two temperatures is minimum required information

  + Various correlations for KV at 100, 210 °F: Abbott (1971), Twu (1985), etc.
  + For vacuum residua (NBP > 1050 °F [840 K]), best to measure KV at least at three temperatures


Kinematic Viscosity of Petroleum Fractions at 100° F
NBP, °F
260
440
620
800
980
1160
Percent Absolute Deviation
140
120
100
80
60
40
20
0
Exp. data spread
Abbot et al. (1971)
Twu et al. (1985)
400
500
600
700
800
900
NBP, K

TRANSPORT PROPERTY PREDICTIONS (VISCOSITY)

- Available models relatively "primitive" -- benign neglect?
  - + Pure component properties with blending (liquid only)
  - ► + Reduced density C-S (Vapor only)
  - + Other C-S models (L-K - like) not successful

- TRAPP model (1981) most widely used in refining and petrochemical industry
  - + Handles both liquid and vapor phases, mixtures of lights and "heavies"
  - + Extended to include petrochem fluids (Baltatu et al., 1982, 1996)
  - + Large errors for CN $\geq$ 10. What about CN >> 10?

- What about Polars?
  - + Group-contribution methods for (simple) polars (e.g. Van Velzen)
  - + Lacking generalized mixture models

- Polymers ??
  - + No predictive models
  - + Greater dependence on shear (which cannot be generalized)

TRANSPORT PROPERTY PREDICTIONS (THERMAL COND.)

- Generally, less important than viscosity

- Available models very primitive
  - E.g., universal linear-temp model for petroleum (API TDB)
  - Other models similar to those for viscosity

- Again, TRAPP (1983) most widely used in refining / petrochemical industry
  - Large errors for CN $\geq$ 10... Data sparse for non-alkanes

- Polars
  - Methods available for (simple) pure components
  - Mixture models invoke simple blending... cannot handle dissolved gases

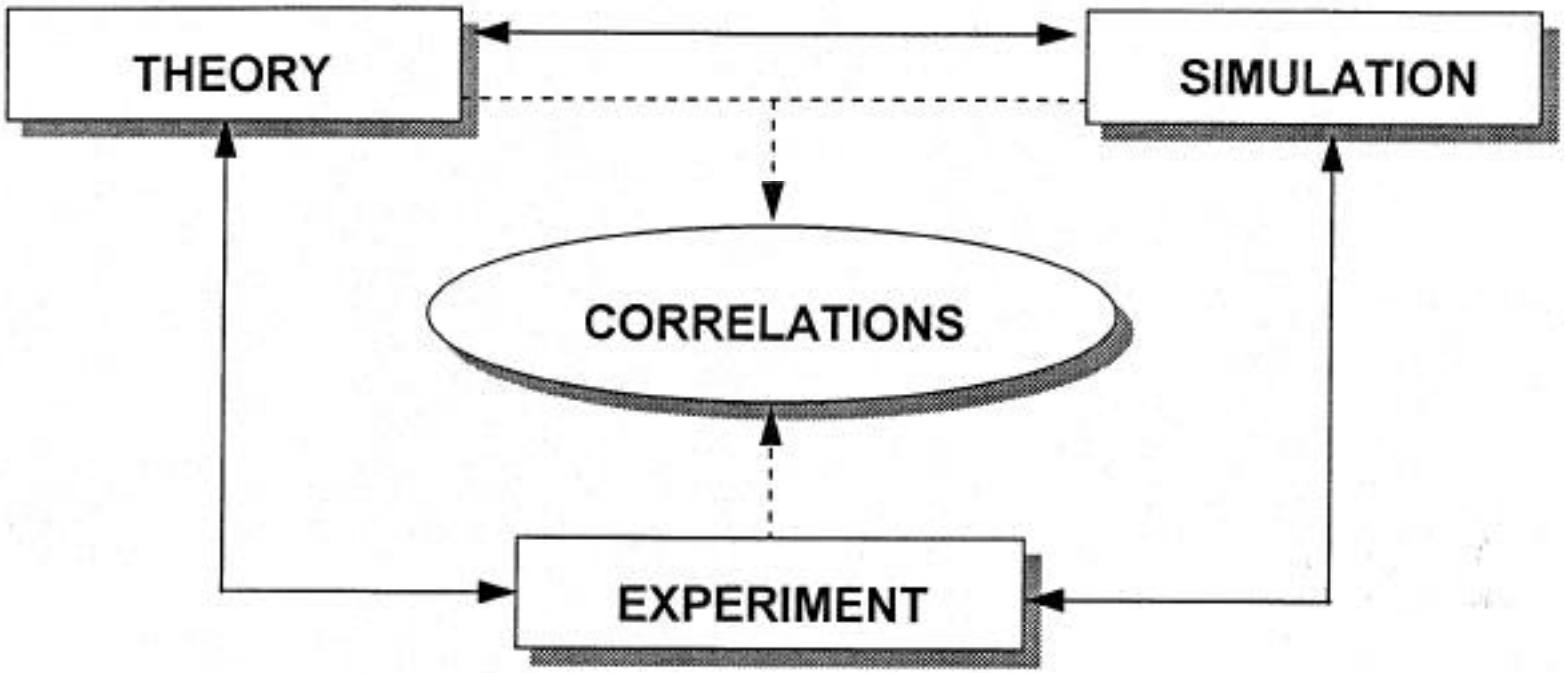
- Polymers
  - Little known--and even less is used in industry

INTEREST IN DIFFUSION COEFFICIENTS?

- Generally, the property that is least discussed in process design
  - 20% uncertainty is considered acceptable
  - More detailed process design of mass-transfer equipment may raise importance
- Recent focus on FT process has also raised interest in diffusion coefficients
  - $(D_{H2}\ H_{CO}) / (D_{CO}\ H_{H2})$ in paraffins is important process parameter; H_i is Henry's constant
- Density, viscosity, and diffusion coefficient: experiment vs. molecular simulation
  - Experimentally, density is easiest and diff. coeff. is most difficult to measure
  - In simulation, it's the other way around: diff. coeff. is easiest to model

INTO THE 21ST CENTURY - THEORY/MODELING/EXPERIMENT

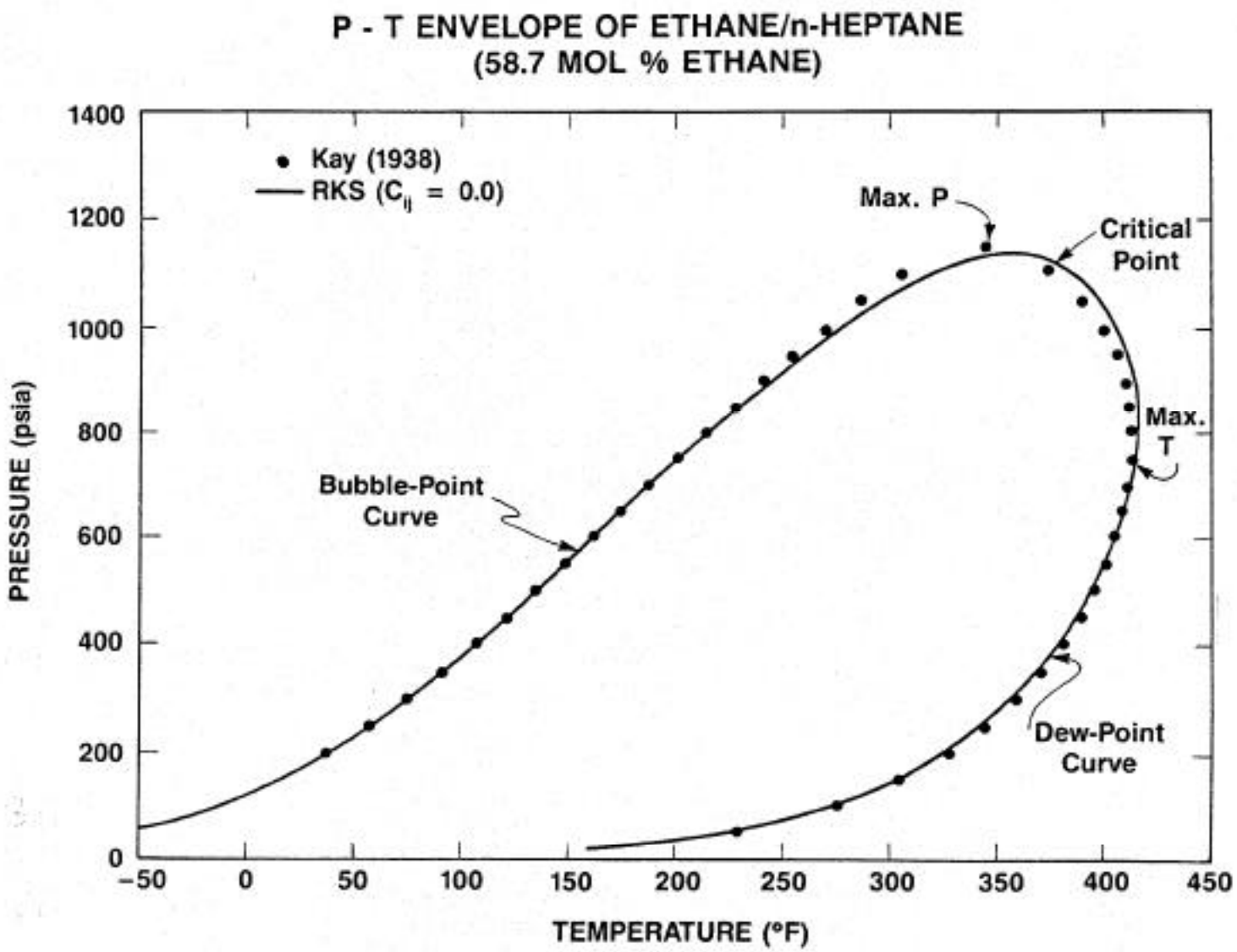
- From refining/petrochemical industry perspective



- Experiment provides necessary foundation (the "truth"!)
- Theory and simulation provide physically-based framework
  - Without this, we would be left only with empirical correlations

MOLECULAR SIMULATION... COMPUTATIONAL CHEMISTRY

- Significant advances...commercially available tools
- Molecular Simulation
  - + An important tool for the 21st century
    - Perhaps not for things we can do well today (Example: C_2/C_7 P-T envelope)?


P - T ENVELOPE OF ETHANE/n-HEPTANE
(58.7 MOL % ETHANE)
Kay (1938)
RKS (C_{ij} = 0.0)
Max. P
Critical Point
Max. T
Bubble-Point Curve
Dew-Point Curve
PRESSURE (psia)
TEMPERATURE (°F)
1400
1200
1000
800
600
400
200
0
−50
0
50
100
150
200
250
300
350
400
450

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  + An important tool for the 21st century
    - Perhaps not for things we can do well today (Example: C_2/C_7 P-T envelope)?
    - ► Very useful for "measuring" what we cannot do in the laboratory:
      ⇒ H_2O/HC phase behavior inside pores
    - Also useful for developing better models, EOS

- Computational (Quantum) Chemistry

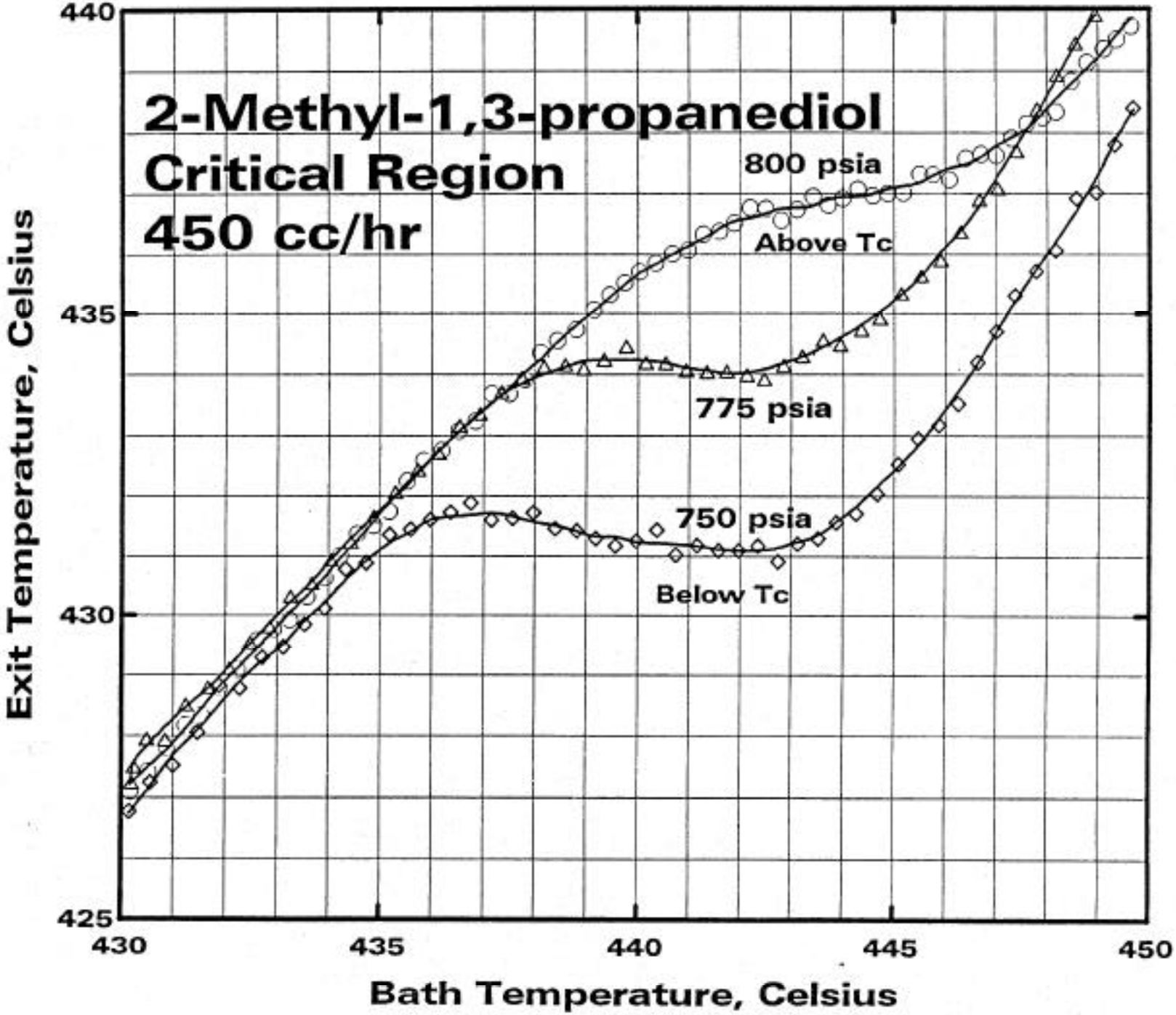
  + Already used in reaction chemistry
  + May provide a rigorous basis for identifying functional groups in group contribution methods (Sandler's group)

EXPERIMENTAL DATA WILL STILL BE NEEDED!

- "Good data are forever!"
- Data neded on systems and conditions <u>of interest</u>

VERY LOW RESIDENCE TIME METHODS

- Nikitin et al. (1993): 10^{-5} to 10^{-3} s
  - + Critical points of unstable substances with a pulse-heating method (temperature of attainable superheat approaches T_c)
  - + Critical points of normal alkanes up to C_{24}; polyethylene glycols
- Wilson (1997): 0.1 s from room to system T
  - + Critical points <u>and</u> vapor pressures with new flow method
  - + NBP up to ~C_{35}; CP up to ~C_{30}
  - + Method can possibly be used for other properties; e.g., heat capacity


2-Methyl-1,3-propanediol
Critical Region
450 cc/hr
800 psia
Above Tc
775 psia
750 psia
Below Tc
440
435
430
425
430
435
440
445
450
Exit Temperature, Celsius
Bath Temperature, Celsius

EXPERIMENTAL DATA WILL STILL BE NEEDED!

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► + Even for well-known processes
  - Tighter designs require data of ever higher quality
  - Technical challenges can still be found in common processes

PHASE EQUILIBRIA ISSUES IN THE ETHYLENE PROCESS

- Superfractionation ($\alpha \sim 1.1$)
  - + High accuracy needed in relative volatility (α) to reduce uncertainty in stages or reflux (α-1)
  - + 5% uncertainty in stages or reflux requires <0.5% uncertainty in α

- Cold Box (Low-Temperature Flash Separators)
  - + Temperatures down to 100 K, moderate pressures (30-40 bar)
  - + Distribution of contaminants (e.g., acetylene, NH_3, NO_x)

- Cold Box Safety Concerns -- Explosive Solids!
  - + Acetylene: VLE $\rightarrow$ SLE
  - + NO_x (+NH_3): VLE $\rightarrow$ SLE + chemical reaction $\rightarrow$ N_2O_3, NH_4NO_3
  - + Absolutely need experimental data!

EXPERIMENTAL DATA WILL STILL BE NEEDED!

- "Good data are forever!"
- Data neded on systems and conditions <u>of interest</u>
  - + Even for well-known processes
    - Tighter designs require data of ever higher quality
    - Technical challenges can still be found in common processes
  - ► + Predictions for complex polars and polymers not yet reliable for design, process optimization
- But data may not be needed for
  - + Ar (except for VLE in heavy hydrocarbons)
  - + VLE of ethanol/water (at 25 °C)
  - + Thermal conductivity of toluene

SEPARATION AND PURIFICATION
Critical Needs and Opportunities

(NRC, 1987)

- Separations research, development, and design are often hampered by a lack of reliable physicochemical data
  - + NIST is a logical focal point for coordinating the collection, evaluation, and dissemination of physicochemical data on separations
- Industrial support of separation research
  - + Industrial R&D projects are highly application-specific and often have proprietary elements
  - + Industrial research efforts cannot be expected to shoulder a significant portion of generic, more fundamental research
    - - Support of generic research should come from the government