Fluid data consistency testing incorporation into the ThermoDataEngine

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Thermophysical Property Data

- Present in most separation models
- Quality of great concern
- Literature:
  - Andrew R. Nelson, Jon E. Olson, Stanley I. Sandler, 1983. "Sensitivity of Distillatlon Process Design and Operation to VLE Data", Ind. Eng. Chem. Process Des. Dev., 22(3), 548.
  - Wallace B. Whiting, 1996. "Effects of Uncertainties in Thermodynamic Data and Models on Process Calculations", J. Chem. Eng. Data, 41, 935-941.
  - Paul M. Mathias, 2014. "Sensitivity of Process Design to Phase Equilibrium - A New Perturbation Method Based Upon the Margules Equation", J. Chem. Eng. Data 2014, 59, 1006−1015.
- Enhanced rate(s) of publication creates new challenges

Thermophysical Property Data

- Amount doubles each decade
- ~30% papers contain errors in values, metadata, & uncertainties
- Errors propagate & cause damage in analyses & models
- Data validation essential in critical evaluation to:
  - Identify questionable data
  - Prevent erroneous use
  - Increase “value” of
    - Information about accuracy & reliability
    - Knowledge to enforce consistency among properties
    - Wisdom to reliably support applications
- NIST ThermoData Engine (TDE) implements methods

Liquid Volumetric Data

- No rigorous consistency test (*e.g.*, Gibbs-Duhem Equation used for partial molar properties)
- Validation currently involves finding:
  - Outliers via
    - Examining trends (e.g., density vs. pressure)
    - Comparing independent measurements
  - Systematic issues via models
    - Compressed liquids: e.g.,Tait model or multiparameter EOS
    - Unsatisfactory if no theoretical basis or too many parameters
- Present work describes successful use of 3-parameter Corresponding States Model for
    - Densities > 1.5 $\rho_{critical}$
    - Temperatures < $T_{critical}$

Correlation of Reduced Bulk Modulus

- Reduced Bulk Modulus, *B*, related to integral, *C*, of molecular direct correlation function, *c*, (DCFI)

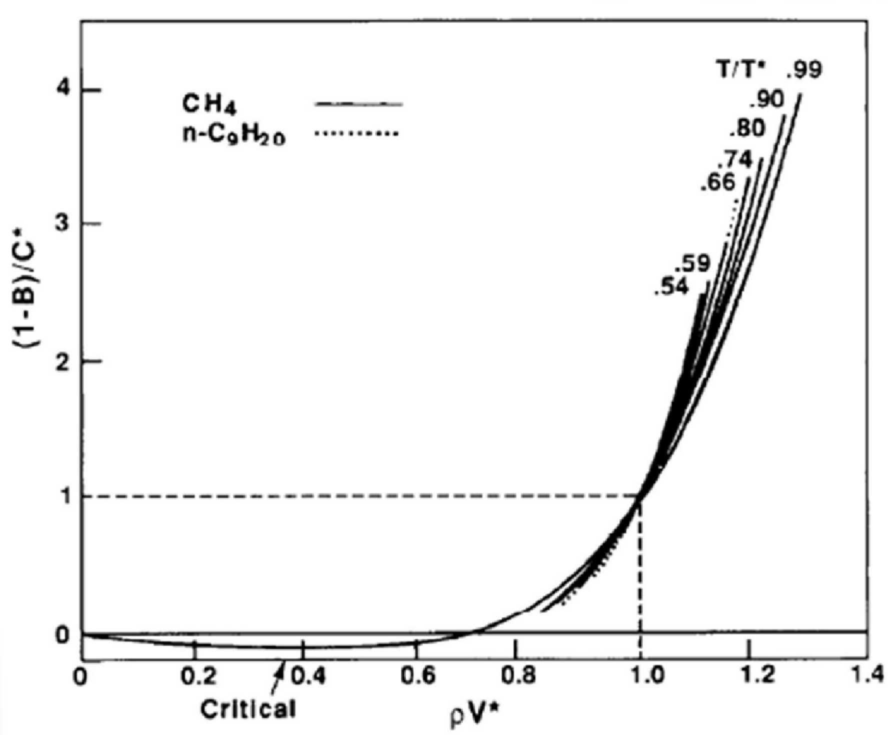
$$B \equiv \left.\frac{\partial P/RT}{\partial \rho}\right|_{T,\mathbf{x}} = \frac{1}{\rho \kappa_T RT} = 1 - \rho \int c(r;T,\rho)\, d\mathbf{r} \equiv 1 - C$$

- Corresponding States Correlation for *C* (Huang, 1987)

$$1 - \left.\frac{\delta(P/RT)}{\delta \rho}\right|_T = C(T,\rho)$$

$$= C^* \left\{ \sum_{i=0}^{3} \sum_{j=0}^{2} a_{ij} (\rho/\rho^*)^i (T/T^*)^j \right\}$$

- a_{ij} universal, insensitive T/T^* isotherm crossover at C^*
- fitted C^*, ρ^*, T^* to over 300
  - substances & mixtures

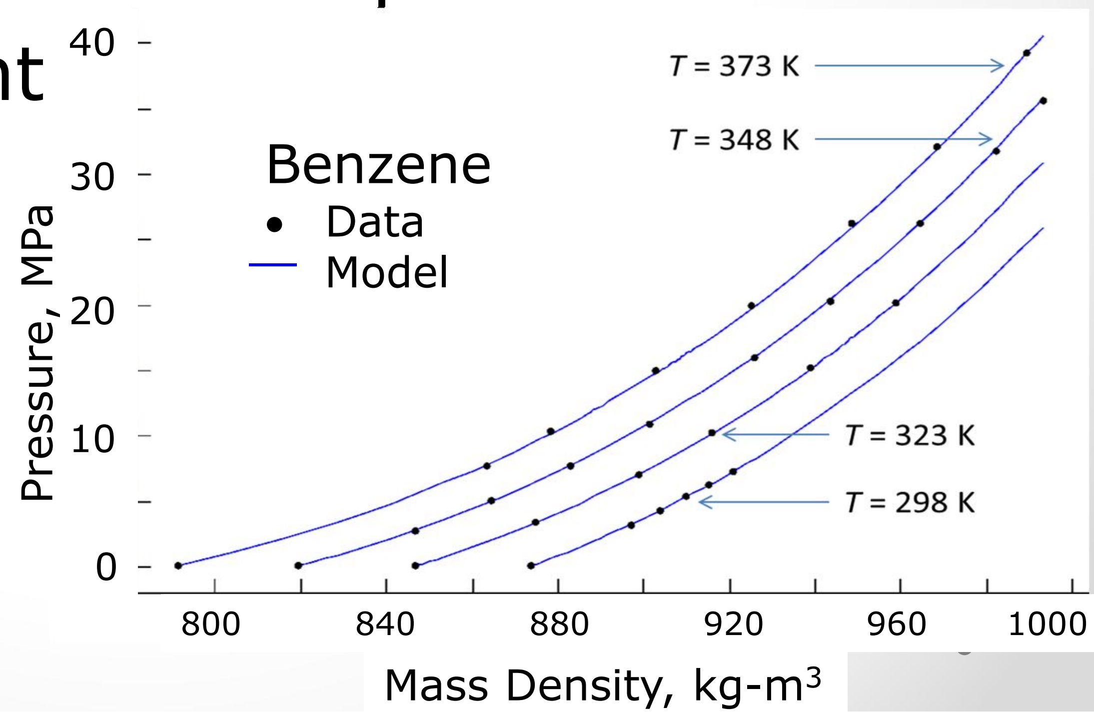


Pressure-Density Model

- Pressure-density relation from integrating *B*

$$\frac{P-P_0}{RT}=\int_{\rho_0}^{\rho}\sum_i\sum_j x_i x_j\left[1-C_{ij}\left(T,\rho,\{x\}\right)\right]d\rho$$

- Given *T*, *P*, **x**, find ρ from standard state of P^0, ρ^0 for pure or mixed liquid at low P^0
- Most reliable current model



Background. Xe with REFPROP†

†Lemmon E.W., Jacobson R.T., 2005. J. Phys. Chem. Ref. Data, Vol. 34(1)

Xe data:

- Streett W. et al. (J. Chem. Thermodynamics, 1973): Greatest deviations from REFPROP predictions
- Similar deviation from REFPROP EOS for high-pressure supercritical data (Michels et al., Physica (Amsterdam), 1954, 20: 99)

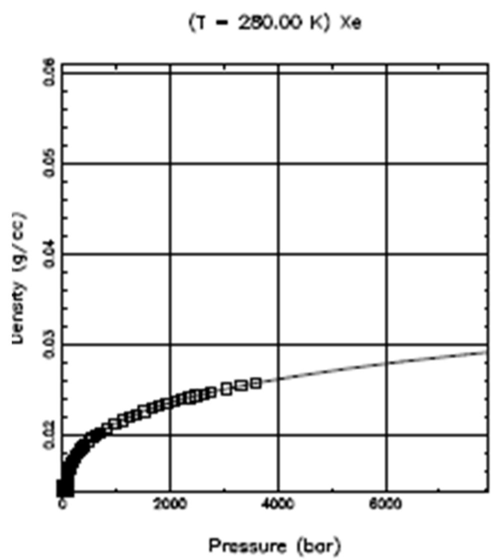
:з one or the other is erroneous

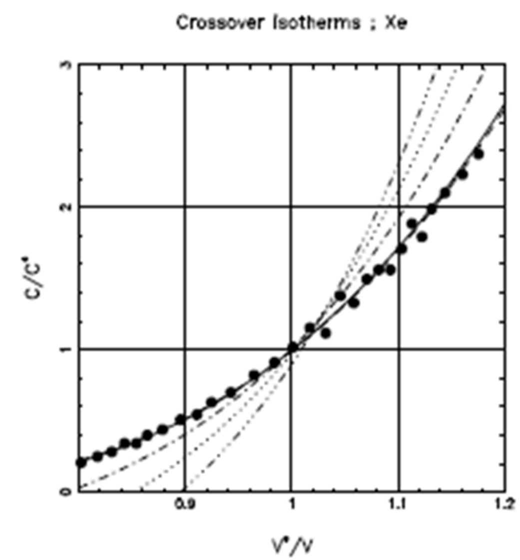
Streett W. et al. : Impeccable
Michels : World standard.

EOS (Huang/O'Connell, 1987):
- Streett et al. > REFPROP

Sending reliable data, but wanting to see if we picked up that REFPROP is not so good, though smooth

REFPROP is easier to over-train!

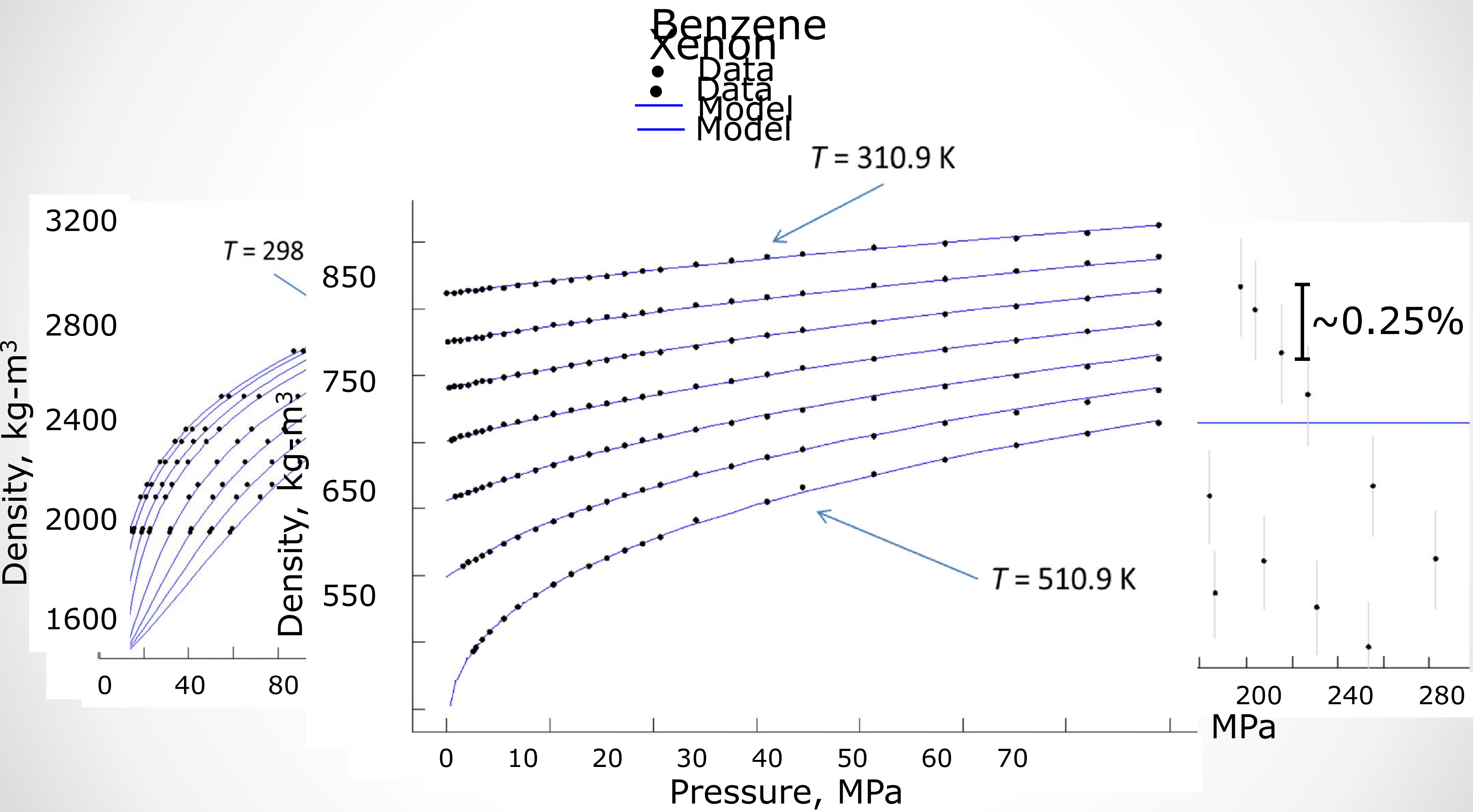




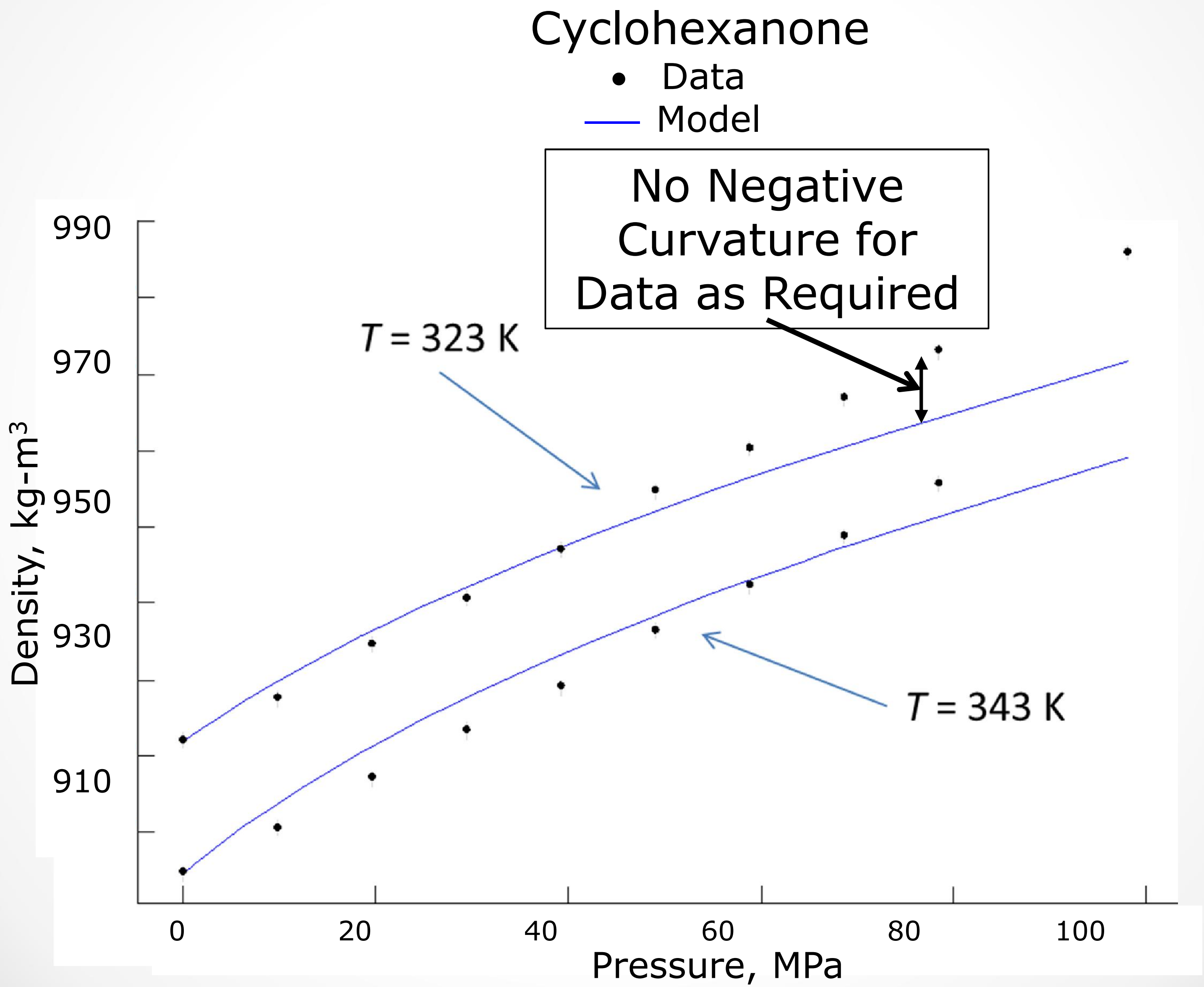
Equation	%-deviation (Street, 1973)	%-deviation (Refprop)
CS	1.7	10.2

Discrepancy showed up as we might hope!

Examples I. Accurate Data



Examples II. Erroneous Data



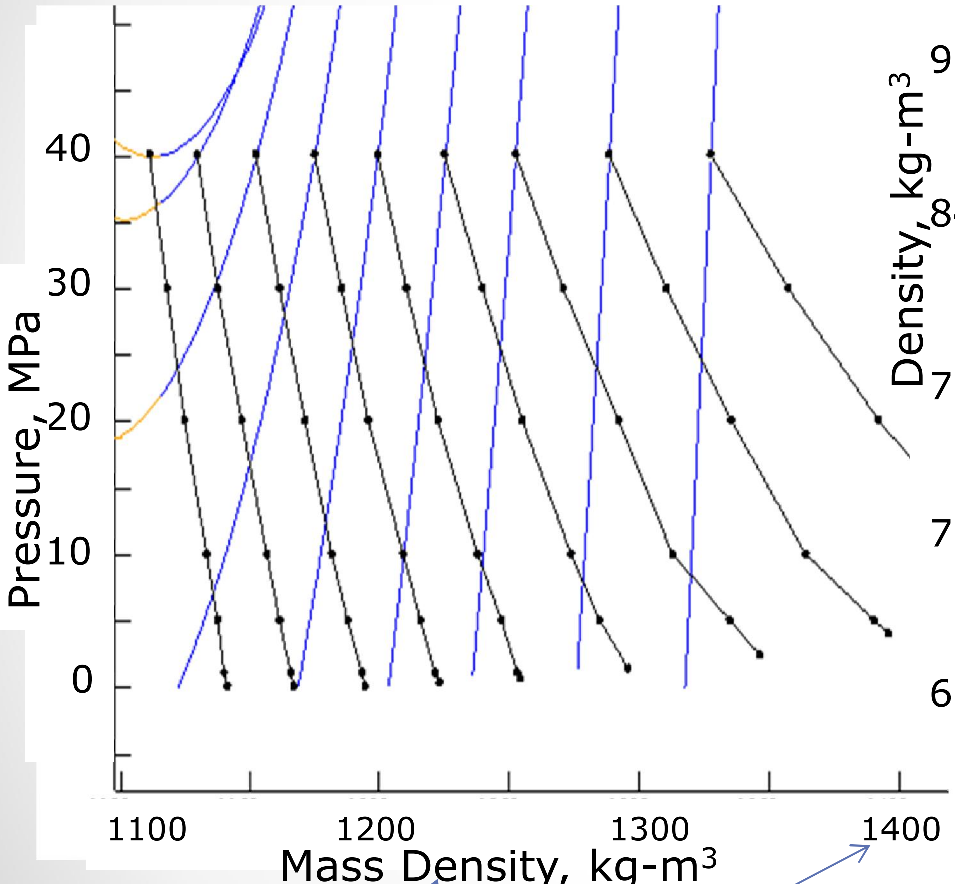
Examples IIIa. Publishing Typos

Methanol/LiCl

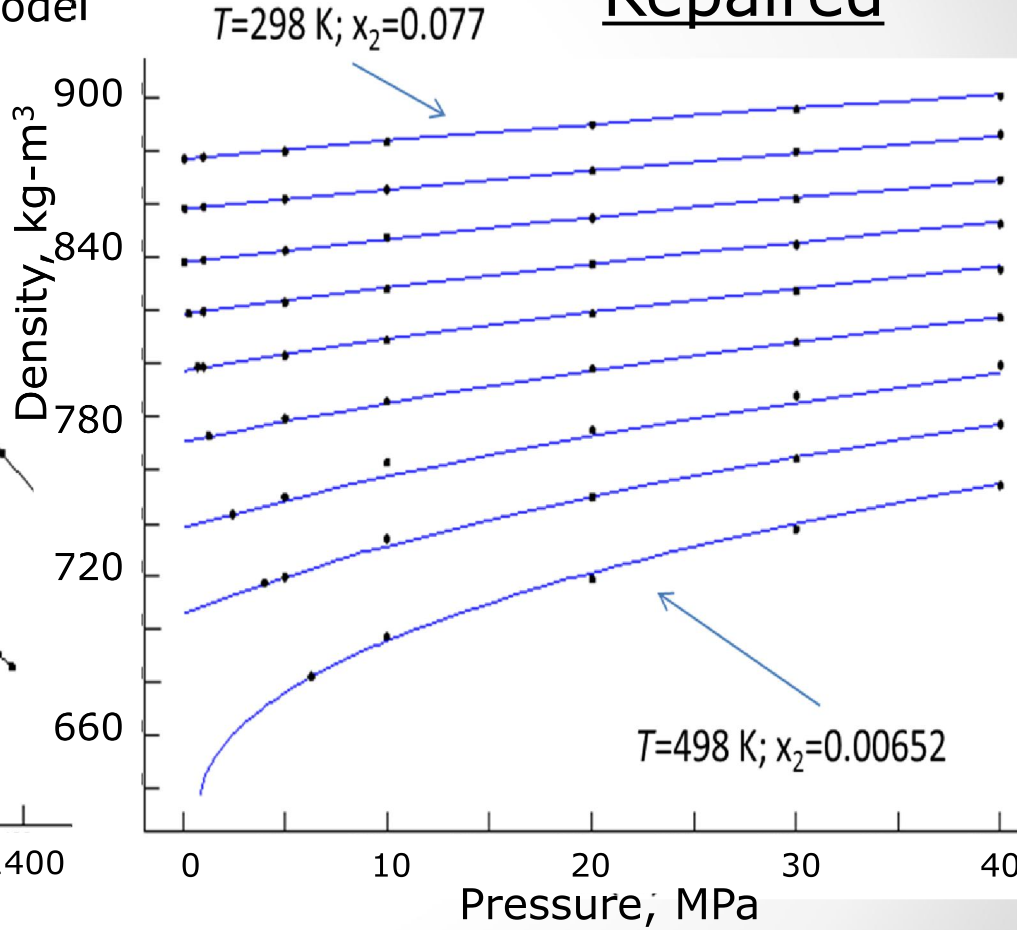
Data

Model

Published



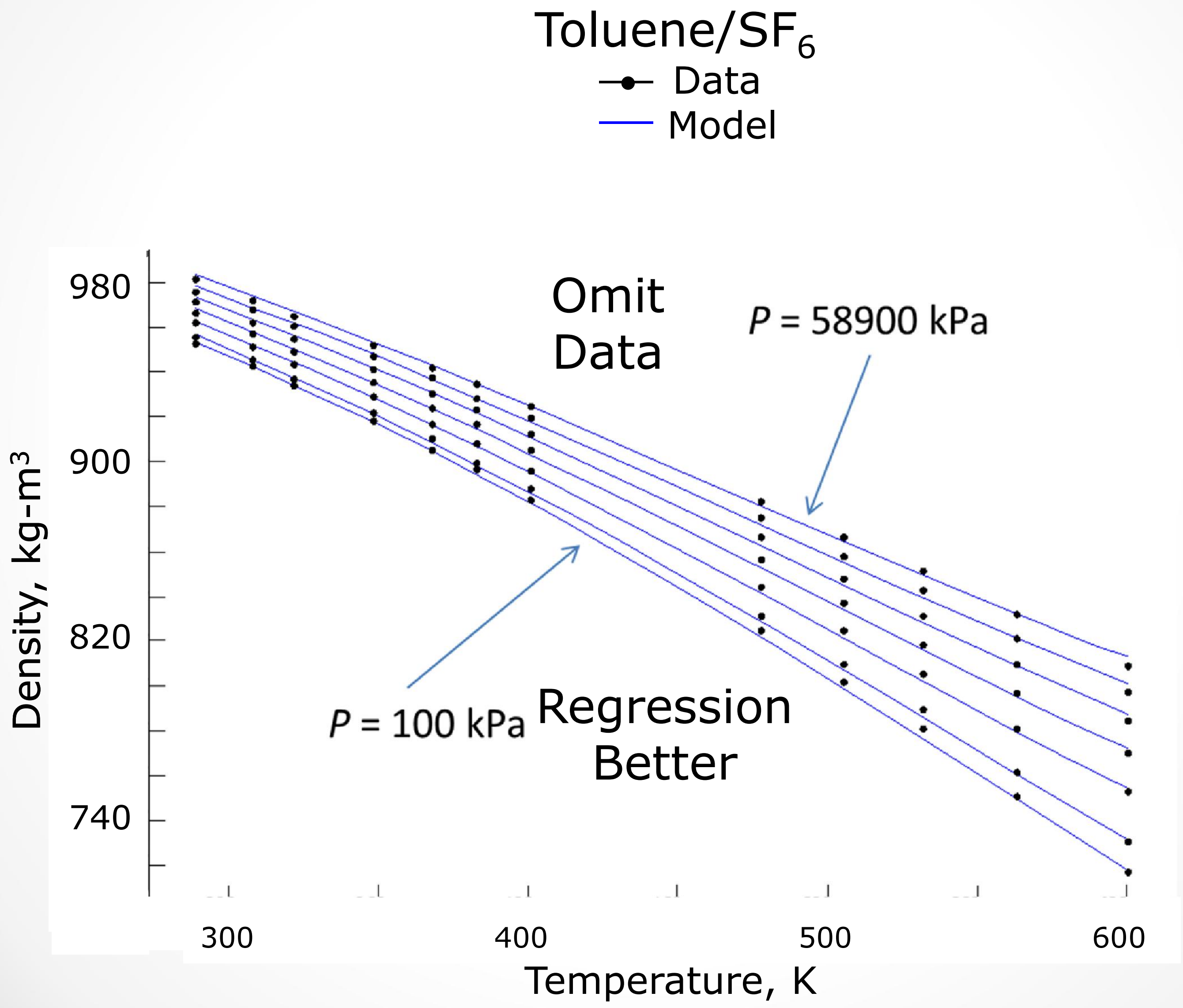
Repaired



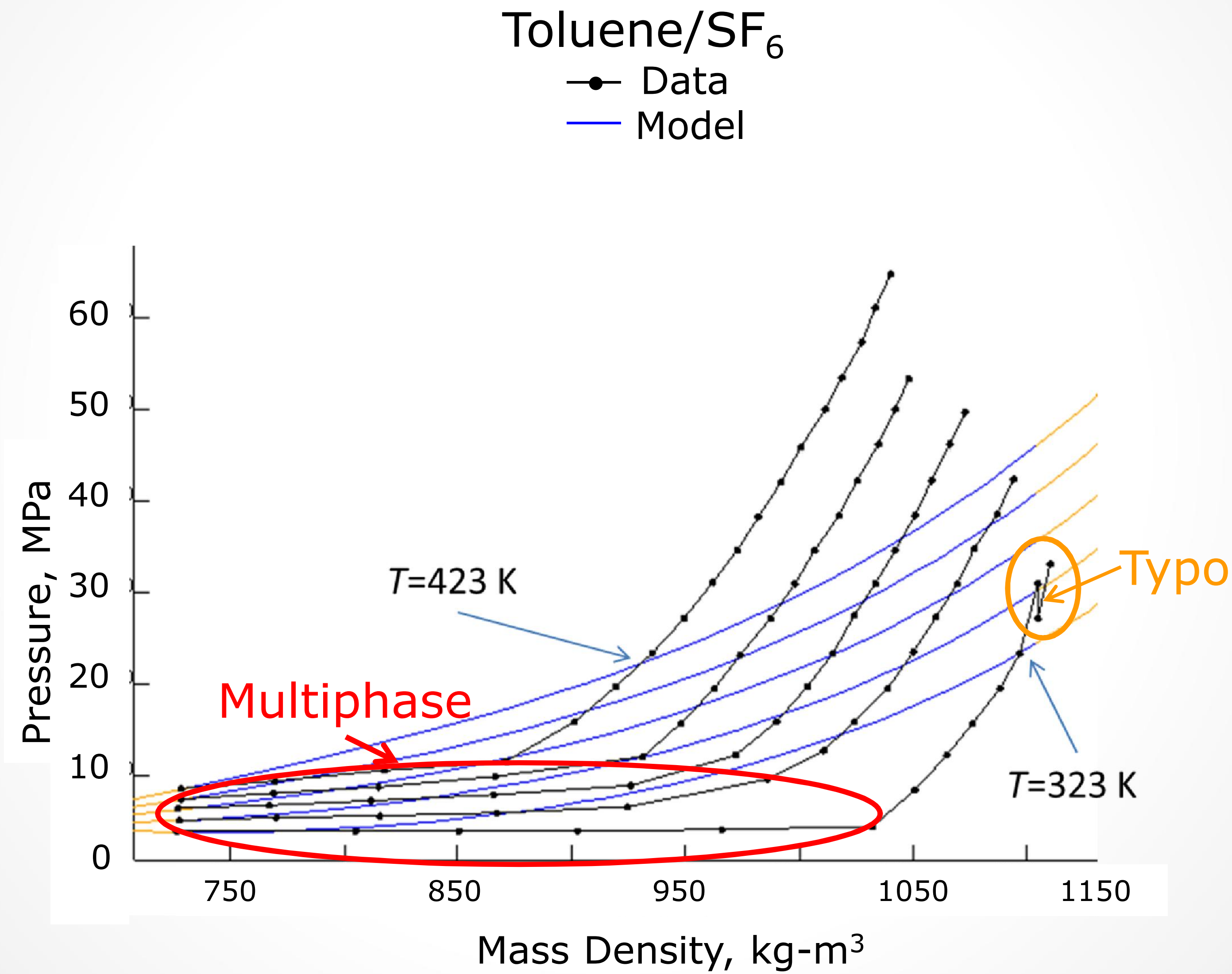
Title in density

Numbers in specific volume

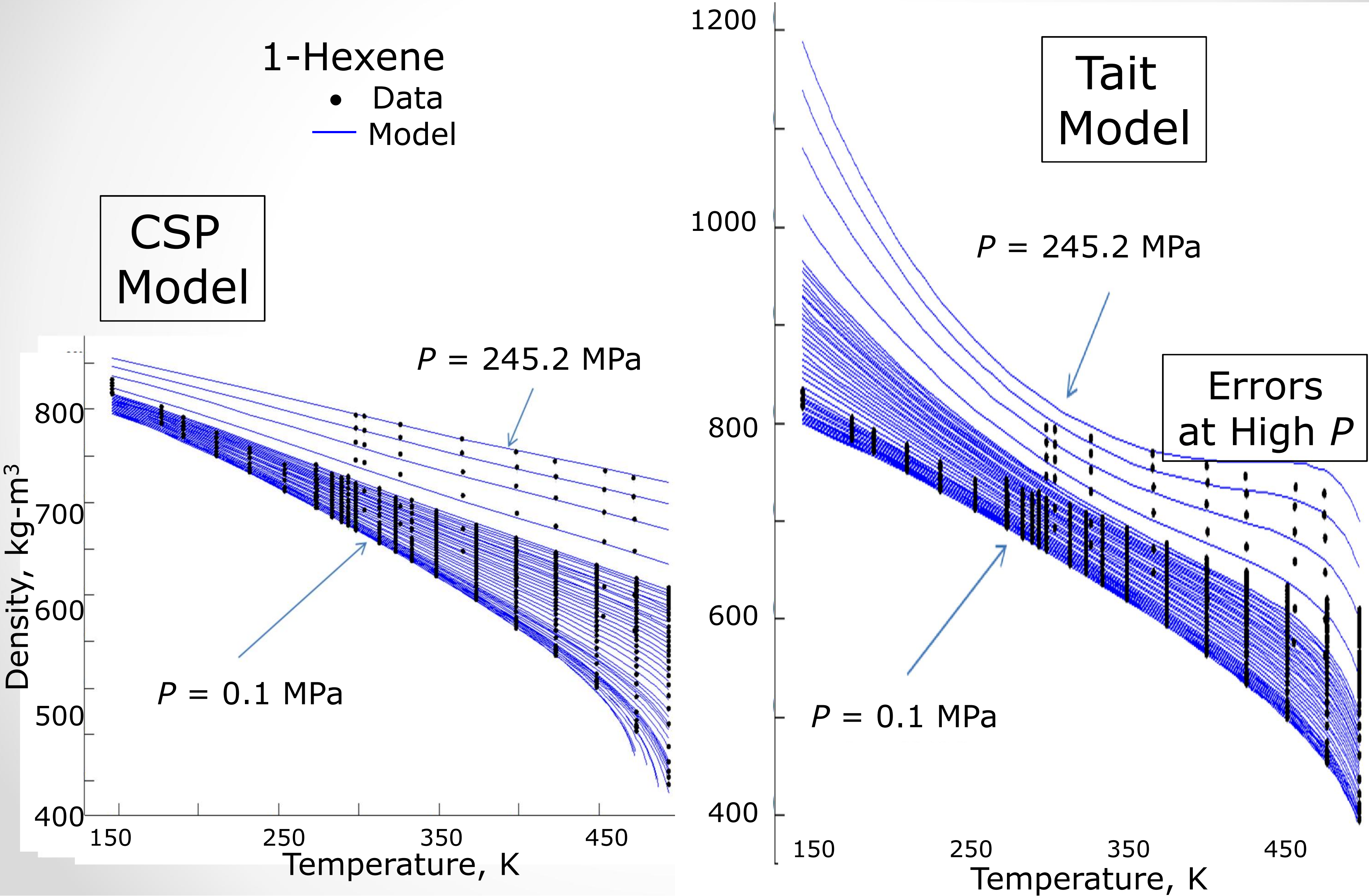
Examples IIIb. Publishing Typos



Examples IV. Multiphase Data



Examples V. Model Inadequacy



Summary

- Criteria
  - Low adequacy function, $Q = N^{-1}\Sigma w_i(p_{calc}-p_{exp})_i^2$
  - $P(\rho)$ must be monotonically increasing
  - Abnormal parameter values ($T_i^* \approx T_{ci}$; $V_i^* \approx V_{ci}/3$; $C_i^* < 0$)
- Detections
  - High quality work compromised by errors in manuscript preparation
  - Single phase data mixed with multiphase data
  - Adequacy to represent data of sufficient quality

Conclusions

- Liquid density data validation established
  - Based on CSP formulation of reduced bulk modulus
  - Allows uncovering of variety of errors
    - Random & systematic measurement errors
    - Textural & typographical reporting errors
- Implemented in NIST TDE software (trc.nist.gov/tde.html)
- References:

  - Original CSP model – Huang & O'Connell *Fluid Phase Equil.* **1987**, 37, 75-84
  - Applied to ionic liquids - Abildskov, et al. *Fluid Phase Equil.* **2010**, 295, 215-229
  - TDE implementation - Diky, et al. *J. Chem. Eng. Data* ASAP **2015**, DOI: 10.1021/acs.jced.5b00477