ISOCHORIC THERMODYNAMICS AND BINARY MIXTURE P-X AND T-X DIAGRAMS[1]

Ian Bell[1,*], Ulrich Deiters[2]

[1]Applied Chemistry and Materials Division, National Institute of Standards and Technology, Boulder, CO, USA
[2]Institute of Physical Chemistry, University of Cologne, Köln, Germany
*ian.bell@nist.gov

ABSTRACT

A phase envelope of a binary mixture of two compounds expresses the phase equilibrium between a liquid and vapor phase in a three-dimensional representation - temperature, pressure, and composition. Figure 2 shows a phase envelope for the mixture of CO_2 + ethane. In nearly all cases (and here in Figures 3 and 4), cross-sections of a phase envelope are presented along lines of constant temperature, pressure or composition.

In this work, we have developed novel algorithms based on the use of isochoric thermodynamics as the fundamental thermodynamic potential. This allows for efficient methods of tracing lines of constant temperature or pressure from the integration of systems of differential equations *along* the phase envelope. This methodology is based on the work of Deiters [1] and Quiñones-Cisneros and Deiters [2]. Fundamentally, this methodology is based upon the expression of the mixture model in terms of the Helmholtz energy density $\Psi = A/V$. In the isochoric thermodynamics formalism, rather than temperature, pressure, and mole fractions (or alternatively amounts of substance) as independent variables, the independent variables become temperature and the *molar concentrations* of each component in the mixture.

The equation of state of the mixture must be cast into the functional form $\Psi = f(T, \rho_1, \rho_2, ...)$ where ϕ_i is the molar concentration of component i in the mixture. Cubic equations of state such as the Peng-Robinson or Soave-Redlich-Kwong equations (or at least their residual contribution) can be converted to the Helmholtz energy density via the methods in Bell and Jäger [3], and the high-accuracy multi-fluid mixture model of GERG/EOS-CG can also be converted into the Helmholtz energy density formalism with temperature and molar concentration as independent variables after some mathematical manipulations outlined in an upcoming publication.

The formulation of the differential equations are based upon the definition of phase equilibrium of a binary mixture:

$p' = p''$ (Pressure of liquid $'$ and vapor $''$ phases are the same)
$\mu_i' = \mu_i''$ (The chemical potential for each component in the mixture must be equal in liquid and vapor phases)

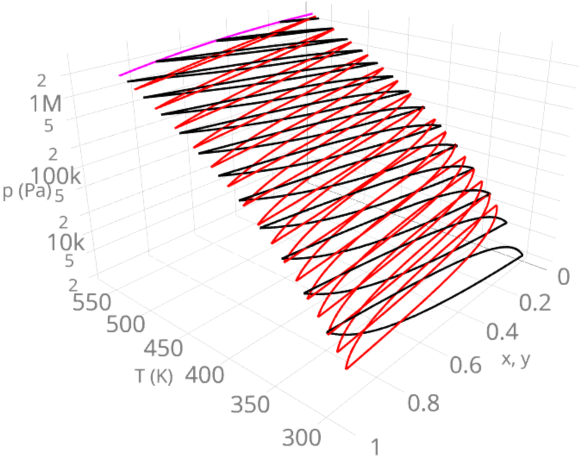

Figure 1: Screenshot of the three-dimensional phase envelope for a mixture of n-hexane + n-octane generated by the routines in this paper. Several isotherms (in black) and isobars (in red) are plotted, as well as the critical line (in magenta) calculated by the methods of Bell and Jäger [4].

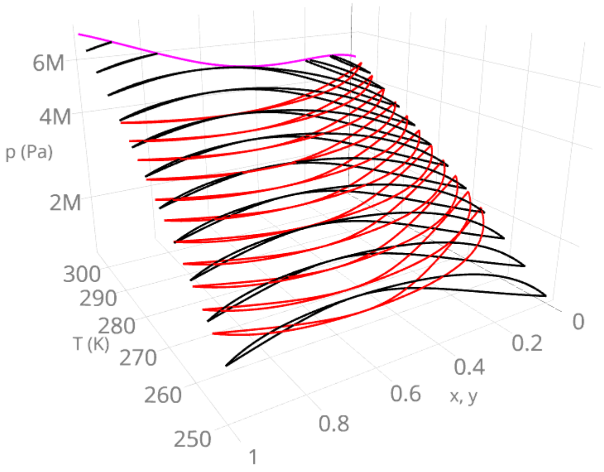

Figure 2: Screenshot of the three-dimensional phase envelope for a mixture of CO_2 + ethane generated by the routines in this paper. Several isotherms (in black) and isobars (in red) are plotted, as well as the critical line (in magenta) calculated by the methods of Bell and Jäger [4].

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[1] Commercial equipment, instruments, or materials are identified only in order to adequately specify certain procedures. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the products identified are necessarily the best available for the purpose.

From this definition of the phase equilibrium, we can then derive the derivatives of the vector of molar concentrations $\vec{\rho}$ *along the phase envelope* at constant temperature or pressure:

$$\left(\frac{\partial\vec{\rho}}{\partial T}\right)'_{p,\sigma},\quad \left(\frac{\partial\vec{\rho}}{\partial T}\right)''_{p,\sigma},\quad \left(\frac{\partial\vec{\rho}}{\partial p}\right)'_{T,\sigma},\text{ and }\left(\frac{\partial\vec{\rho}}{\partial p}\right)''_{T,\sigma} \tag{1}$$

Each of these derivatives can be expressed in terms of *analytic derivatives* of Ψ with respect to the molar concentration vector $\vec{\rho}$. Furthermore, the independent variables of the isochoric thermodynamics formalism can be directly converted to the independent variables of the equation of state (temperature and molar density), and therefore evaluation of the derivatives in Eq. (1) does not require iteration. Iteration when temperature and pressure are inputs to obtain the temperature and molar density is often required in other methods, and is fraught with many computational dangers for more complex mixture models.

In order to trace an isoline of constant pressure or temperature cutting through the phase envelope, it is first necessary to find a good starting point on the phase envelope and then integrate the system of differential equations in Eq. (1) along the phase envelope. In many cases, a good starting point is a composition very near the pure fluid composition. The true pure-fluid endpoint (at a mole fraction of exactly 0 or 1) is not accessible (due to the divergence of the ideal-gas contribution to the Helmholtz energy density for the pure fluid), but a composition *very* near the pure fluid can be readily used to initialize the isoline.

Once an initial point on the isoline has been identified, the system of equations is integrated by an adaptive-step-sizing system of differential equations integrator. The use of an adaptive-step-size integrator results in a very robust and effcient integration, as small steps are taken when necessary, and large steps are taken when possible. The reliability and efficiency of this method for the construction of phase envelopes is exceptional. Tracing a low-pressure isotherm for a mixture that uses the multi-fluid mixture model implemented in CoolProp [5] takes on the order of 30 milliseconds in the C++ implementation.

There are a number of implementation details that have been glossed over here, and should be described in some more detail:

1. When tracing an isoline that would cross the critical line for a binary mixture, when approaching the critical line, the set of differential equations becomes impossible to integrate. As a result, the adaptive step sizing algorithm drives the step size to the minimal value, and the algorithm is forced to terminate. It is impossible to reach the critical line, but it can be closely approached by the integrator.
2. Some isotherms (e.g., high temperature isotherms for CO2 + ethane in Fig. 4) are discontinuous, and each part is connected to the pure fluid endpoint. These isolines are constructed in two parts; one integration starts at the pure fluid for ethane and integrates forwards until the critical line is reached, and the other integration starts at the pure CO2 endpoint and integrates backwards until the critical line is again intersected.
3. Selection of the marching variable for the integration could be temperature, pressure, or the concentration of one of the components in the mixture. For subcritical isolines or isotherms, it is most useful to force the integration to march in the molar concentration of one component, while at higher temperatures or pressures (e.g., high temperatures for mixtures like *n*-hexane + *n*-octane, see Fig. 3), it is necessary to march in pressure. Furthermore, there are cases where the marching variable must be changed during the integration to traverse minima or maxima of the curves, and that subject is the topic of continuing research.

In this work, the derivative formulation has been written in C++, and a thin wrapper for the python language was constructed. In this way, the convenience of high-level languages like python can be combined with the computational efficiency of C++. The C++ ⟷ python interface was constructed with the `pybind11` package. In all cases, the python wrapper is used to carry out the calculations. The complete codebase is available upon request to the authors.

Figure 3 shows some isolines for the mixture of *n*-hexane + *n*-octane. This mixture is relatively straightforward to understand and exhibits classical mixture behavior. There is a continuous critical line connecting the pure fluids. The isolines are each monotonic, and no azeotropy is found. The integration starts at the near-pure *n*-octane composition. At low pressure, the integration is done in the molar concentration of *n*-hexane until the near-pure *n*-hexane composition is reached. At higher temperatures (above the critical temperature of *n*-hexane), the integration is carried out with the pressure as the marching variable and the integration terminates when the critical line is reached.

Figure 4 shows some isolines for a mixture of CO_2 and ethane. This mixture is significantly more challenging from the standpoint of constructing its phase envelope isolines. This mixture, like many others, demonstrates azeotropy. That is, there is a composition at which the two phases are at the same composition, temperature, and pressure. Many methods for constructing phase envelope isolines would be challenged by the presence of the azeotrope. In this case, at low temperature we march in molar concentration, and therefore, due to the use of isochoric thermodynamics, the presence of the azeotrope poses no challenge; the integrator effortlessly traverses the azeotrope. At higher temperatures, the isolines become discontinuous, being divided by the critical line. As described above, we integrate in two parts, each starting at each pure fluid. In all cases, even at high temperature, we march in molar concentration.

Figures 1 and 2 show three-dimensional phase envelopes for *n*-hexane + *n*-octane and CO_2 + ethane mixtures. These phase envelopes are generated with the `plotly` library and can be manipulated (rotated, zoomed) in modern browsers. The HTML files are available upon request from the authors. They can also serve as useful pedagogical tools from the standpoint of educating the next generation of chemical engineers in the beauty of thermodynamics.

In this work we have limited our scope to isolines that can be completely traced out by integrating in one of temperature, pressure, or molar concentration. There are many phase envelope isolines for which more exotic algorithms must be employed in order to trace the isoline due to the presence of minima or maxima in the potential tracing variable. Work is ongoing to develop more generic algorithms that can handle complex phase envelope isolines with potentially multiple minima and maxima, and which allow for the integration variable to be changed on the fly.

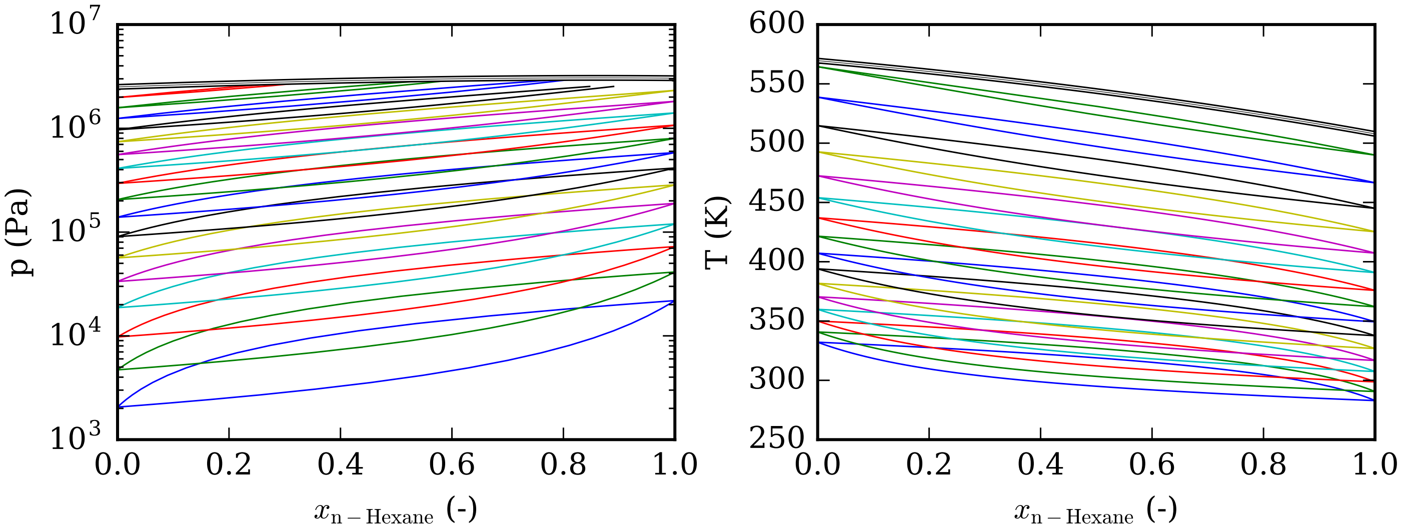

Figure 3: *p*-*x* and *T*-*x* diagrams for a mixture of *n*-hexane + *n*-octane.

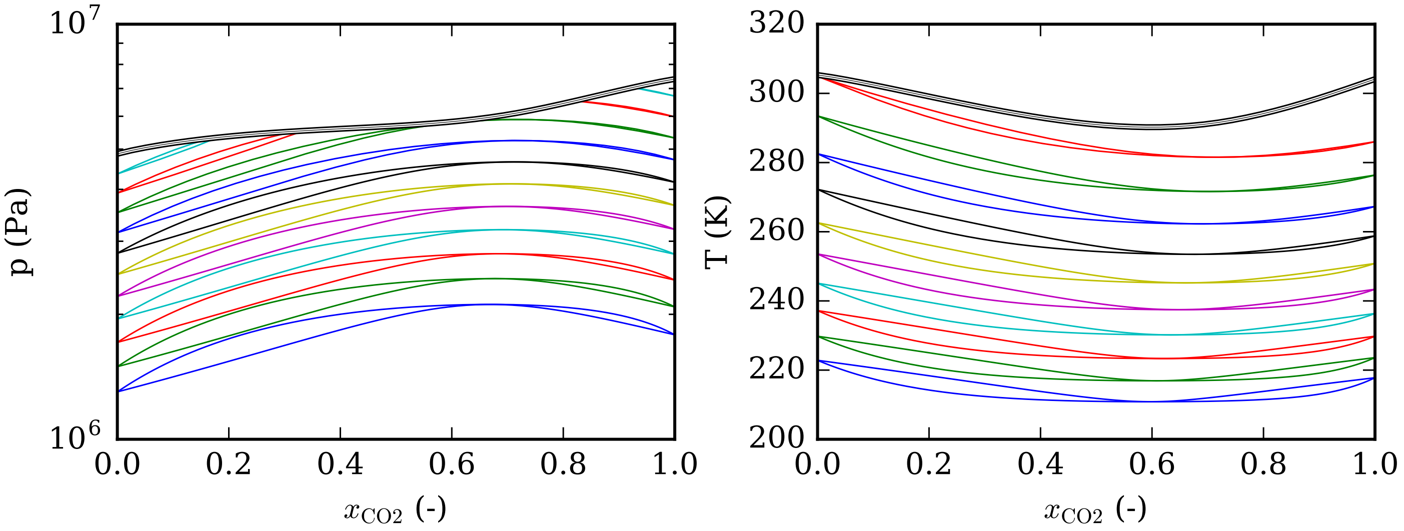

Figure 4: *p*-*x* and *T*-*x* diagrams for a mixture of CO_2 + ethane

REFERENCES

[1] U. K. Deiters. Differential equations for the calculation of fluid phase equilibria. *Fluid Phase Equilib.*, 428:164–173, 2016.

[2] S. E. Quiñones-Cisneros and U. K. Deiters. An efficient algorithm for the calculation of phase envelopes of fluid mixtures. *Fluid Phase Equilib.*, 329:22–31, 2012.

[3] Ian H. Bell and Andreas Jäger. Helmholtz energy transformations of common cubic equations of state for use with pure fluids and mixtures. *J. Res. NIST*, 2016.

[4] Ian H. Bell and Andreas Jäger. Calculation of critical points from helmholtz-energy-explicit mixture models. *Fluid Phase Equilib.*, 433:159 – 173, 2017.

[5] Ian H. Bell, Jorrit Wronski, Sylvain Quoilin, and Vincent Lemort. Pure and Pseudo-pure Fluid Thermophysical Property Evaluation and the Open-Source Thermophysical Property Library CoolProp. *Ind. Eng. Chem. Res.*, 53(6):2498–2508, 2014.