

THERMODYNAMICS—OLD SCIENCE AND NEW CHALLENGES

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ABSTRACT

Thermodynamics is one of the oldest branches of physical chemistry; its foundations were laid in the late 19th Century. This leads to some peculiar problems. The first is that some good ideas and good data from “thermodynamic antiquity” became forgotten. This could happen if there was no practical application, but also if—before the advent of electronic computers—the mathematical treatment was too difficult or time-consuming. The second peculiarity is that some old concepts, developed solely as means of survival in the age of the logarithmic tables and slide rules, are still in use today. Now, in the 21st Century, there are new classes of chemical compounds to consider (e.g., ionic liquids) as well as old classes under unusual conditions (e.g., hydrocarbons at pressures exceeding 1 kbar), and there are new models based on statistical thermodynamics and quantum mechanics.

In this contribution we shall give examples for these peculiarities. In particular, it will be demonstrated that a “clean and lean” axiomatic approach can simplify and speed up computations. Furthermore, the problem of recognizing weaknesses of equations of state will be discussed, as well as molecular theory-based ways to improve them.

INTRODUCTION

In a recent textbook on physical chemistry¹, the chapter on freezing-point depression contains a derivation of the famous equation

$$\frac{1}{T} = \frac{1}{T_{\text{fus},1}} - \frac{R \ln x_1}{\Delta_{\text{fus}}H_{\text{m},1}}, \quad (1)$$

(component 1 being the solvent) which then leads to the final result

$$\Delta T = -\frac{RM_1 T_{\text{fus},1}^2}{\Delta_{\text{fus}}H_{\text{m},1}} c_2 \quad (2)$$

after making the simplifications

$$\ln x_1 = \ln(1 - x_2) \approx -x_2 \approx c_2 M_1 \quad (3)$$

and

$$\frac{1}{T} - \frac{1}{T_{\text{fus},1}} \approx -\frac{\Delta T}{T_{\text{fus},1}^2}, \quad (4)$$

which are allowed in the case of diluted solutions.

All this correct—but why do we have to make these simplifications? They were certainly useful 50 years ago, before the advent of pocket calculators, when calculations had to be made with a slide rule or logarithmic tables. But do we really have to burden our students with such equations anymore in the 21st Century?

The beginning of thermodynamics as an exact science can be placed in the first half of the 19th Century. We can therefore look back on a success story of about 200 years. But these 200 years were not merely a period of data accumulation; they were a period of quantitative and qualitative development, and of the evolution of concepts. It has happened—and may then happen again—that some concepts reach limits of applicability and then are superseded by new developments. So it may be necessary to replace an equation of state, that was good and sufficient in 1950, by a more powerful one in 2013. One can certainly chop wood with a stone axe, and one can make it really sharp—but in the long run, one should switch to steel!

This article will discuss some cases where models or procedures have arguably been kept too long.

OLD LAWS

Chemical reaction equilibria

One of the cornerstones of chemical thermodynamics is the mass action law, which states that for a chemical reaction

$$|v_1|X_1 + |v_2|X_2 + \dots \rightleftharpoons |v_k|X_k + |v_{k+1}|X_{k+1} + \dots$$

between chemical species X_i (stoichiometric factors v_i assumed to be negative for educts $i < k$ and positive for products $i \geq k$) the partial pressures p_i of the species must obey the equation

$$\prod_{i=1}^N \left(\frac{p_i}{p^\ominus} \right)^{v_i} = K, \quad (5)$$

where the equilibrium constant K is related to the Gibbs energy of the reaction,

$$K = \exp \left(-\frac{\Delta_r G_m^\ominus}{RT} \right). \quad (6)$$

¹reference purposely omitted

p^\ominus denotes the thermodynamic reference pressure (usually 0.1 MPa). Eq. (5) is correct for ideal gas mixtures only; for real systems, we have to use fugacities,

$$\prod_{i=1}^N \left(\frac{f_i}{p^\ominus} \right)^{v_i} = K, \quad (7)$$

with

$$f_i \equiv \exp \left(\frac{\mu_i - \mu_i^\ominus}{RT} \right); \quad (8)$$

here the μ_i and μ_i^\ominus denote the chemical potentials of the reacting species, which evidently are functions of temperature, pressure, and composition; the μ_i^\ominus are reference values. Moreover, there is an impressive number of variants of the mass action law expressed in terms of mole fractions, concentrations, or activities, most of these involving equilibrium constants that are no longer dimensionless.

Solving Eq. (5), together with the material balance equations, for the equilibrium compositions *analytically* is usually not feasible, except for very simple chemical reactions involving few components under ideal conditions. But if we have to resort to determine the equilibrium *numerically*, there is no need to invoke the mass action law at all. It is more straightforward to use the exact equation from which the mass action law is derived,

$$\sum_{i=1}^N v_i \mu_i = \vec{v} \cdot \vec{\mu} = 0, \quad (9)$$

where \vec{v} and $\vec{\mu}$ are vectors of stoichiometric coefficients and chemical potentials, respectively. This equation is applicable to all chemical reactions and to all states of aggregation. Furthermore, it can be easily extended to multiphase/multireaction systems by applying Eq. (9) to each phase and each chemical reaction, and observing the phase equilibrium condition of having the same μ_i in all phases, e.g., for a system consisting of two phases and having one chemical reaction,

$$\begin{aligned} \sum_{i=1}^N v_i \mu'_i &= \vec{v} \cdot \vec{\mu}' = 0 \\ \sum_{i=1}^N v_i \mu''_i &= \vec{v} \cdot \vec{\mu}'' = 0 \\ \vec{\mu}' &= \vec{\mu}''. \end{aligned} \quad (10)$$

This formulation is easy to teach and easy to program; it does not need activities or fugacities. This does not mean that, after formulating thermodynamic problems in terms of chemical potentials, all computational problems evaporate, but we have at least achieved a clean separation of the modeling (i.e., the way how we compute the $\mu_i(x_i, p, T)$) from the numerical problem of solving the above equations.

Phase equilibria

The phase equilibrium condition in Eq. (9) is applicable to all kinds of phase equilibria and not restricted to subcritical vapour–liquid equilibria like Raoult’s law, another left-over from the past.

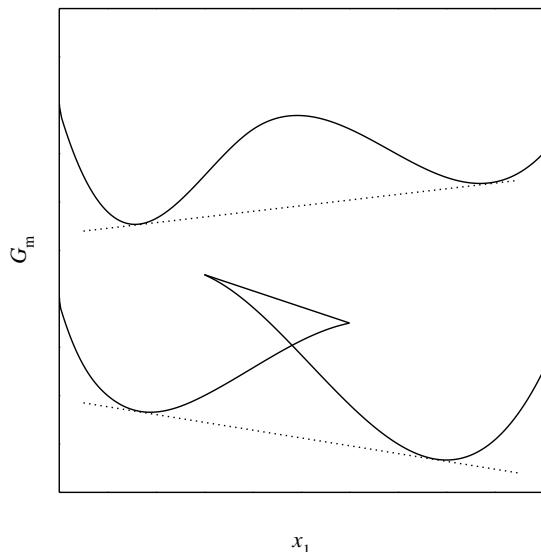


Figure 1. Schematic representation of the Gibbs energy “function” for a 2-phase equilibrium of a binary fluid mixture (continuous and discontinuous case). —: molar Gibbs energy,: double tangent indicating the equilibrium compositions.

It is possible, of course, to pull tricks that make Raoult’s law applicable at supercritical conditions, and the use other equations for liquid–liquid equilibria, and still others for solid–fluid equilibria. But why should me make thermodynamics more complicated than it is?

Principal energy functions

Another time-hallowed concept is the formulation of equilibrium and stability criteria with the help of the Gibbs energy. The Gibbs energy, $G_m(p, T, \vec{x})$ can be obtained from the internal energy, $U_m(V_m, S_m, \vec{x})$, by a series of Legendre transformations. These transformations replace “density variables” (i.e., variable that may have different values in coexisting phases) by “field variables” (i.e., variables that have the same value in coexisting phases). At a first glance, using the Gibbs energy function for phase equilibrium problems simplifies matters. But this simplification comes at a price: As there can be more than one density at a given pressure, the Gibbs energy is, in the strict sense, not a function. A diagram of the Gibbs energy vs. mole fraction for a two-phase equilibrium may exhibit the usual S-shape, but it may alternatively consist of three separate branches—a fact that is not mentioned in many textbooks (Fig. 1). Of course, the physically significant (= stable) value at each composition is always the one with lowest Gibbs energy. But the existence of three branches has consequences for the computation of phase equilibria: Algorithms relying on the local curvature may fail to find the phase equilibrium, as there is no locally concave region along the stable portion of the graph; algorithms not making use of the local curvature are less efficient.

It is advantageous to use the Helmholtz energy instead, $A_m(V_m, T, \vec{x})$, and for many years this has been the customary approach for work based on equations of state. It is better, however, to the Helmholtz energy density, $\Psi(\vec{p}, T)$, where \vec{p} is the vector of molar densities, $p_i = x_i/V_m$. Both functions do not have discontinuities for fluid phase equilibria. The local curva-

ture of the Helmholtz energy surface is described by its Hessian matrix,

$$\hat{A} = \begin{pmatrix} \frac{\partial^2 A_m}{\partial x_1^2} & \frac{\partial^2 A_m}{\partial x_1 \partial x_2} & \cdots & \frac{\partial^2 A_m}{\partial x_1 \partial x_{N-1}} & \frac{\partial^2 A_m}{\partial x_1 \partial V_m} \\ \frac{\partial^2 A_m}{\partial x_2 \partial x_1} & \frac{\partial^2 A_m}{\partial x_2^2} & \cdots & \frac{\partial^2 A_m}{\partial x_2 \partial x_{N-1}} & \frac{\partial^2 A_m}{\partial x_2 \partial V_m} \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ \frac{\partial^2 A_m}{\partial x_{N-1} \partial x_1} & \frac{\partial^2 A_m}{\partial x_{N-1} \partial x_2} & \cdots & \frac{\partial^2 A_m}{\partial x_{N-1} \partial x_{N-1}} & \frac{\partial^2 A_m}{\partial x_{N-1} \partial V_m} \\ \frac{\partial^2 A_m}{\partial V_m \partial x_1} & \frac{\partial^2 A_m}{\partial V_m \partial x_2} & \cdots & \frac{\partial^2 A_m}{\partial V_m \partial x_{N-1}} & \frac{\partial^2 A_m}{\partial V_m^2} \end{pmatrix}, \quad (11)$$

and that of the Helmholtz energy density by

$$\hat{\Psi} = \begin{pmatrix} \frac{\partial^2 \Psi}{\partial \rho_1^2} & \frac{\partial^2 \Psi}{\partial \rho_1 \partial \rho_2} & \cdots & \frac{\partial^2 \Psi}{\partial \rho_1 \partial \rho_N} \\ \frac{\partial^2 \Psi}{\partial \rho_2 \partial \rho_1} & \frac{\partial^2 \Psi}{\partial \rho_2^2} & \cdots & \frac{\partial^2 \Psi}{\partial \rho_2 \partial \rho_N} \\ \vdots & \vdots & \ddots & \vdots \\ \frac{\partial^2 \Psi}{\partial \rho_N \partial \rho_1} & \frac{\partial^2 \Psi}{\partial \rho_N \partial \rho_2} & \cdots & \frac{\partial^2 \Psi}{\partial \rho_N^2} \end{pmatrix}. \quad (12)$$

In principle, the two Hessians are equivalent. But the elements of \hat{A} have different dimensions, and this makes it impossible to calculate the trace or eigenvalues, which are very useful for stability analysis². It has been shown that initial values for phase equilibrium calculations can be found reliably and the calculation of the equilibrium performed more efficiently with algorithms based on an eigenvalue search on a $\Psi(\vec{\rho}, T)$ surface [1,2].

In particular, the well-known phase equilibrium conditions

$$\begin{aligned} p' &= p'' \\ \mu'_i &= \mu''_i, \quad i = 1 \dots N \end{aligned} \quad (13)$$

become vector equations,

$$\begin{aligned} \nabla \Psi' \cdot (\vec{\rho}'' - \vec{\rho}') &= \Psi'' - \Psi' \\ \nabla \Psi' &= \nabla \Psi''. \end{aligned} \quad (14)$$

Formulating thermodynamic equations this way is not merely an estheticism: modern computer languages and symbolic-algebra packages have built-in vector and matrix operations, and using these features makes programming easier the the program code better readable and maintainable.

The customary way to check for local (diffusion) stability is by calculating the determinant of \hat{A} ; $\det \hat{A} = 0$ is a necessary condition for spinodal and critical states. It can be shown, however, that the computation of eigenvalues λ_i of $\hat{\Psi}$ and setting $\lambda_{\min} = 0$ is a far more efficient method.

Another advantage is that, in a $\vec{\rho}$ -based system, azeotropy does not play a role and thus cannot disturb the convergence of the algorithms.

OLD CONCEPTS FOR EQUATIONS OF STATE

Many recently used equations of state are based on the concept of the hard-sphere fluid, and they are known to perform

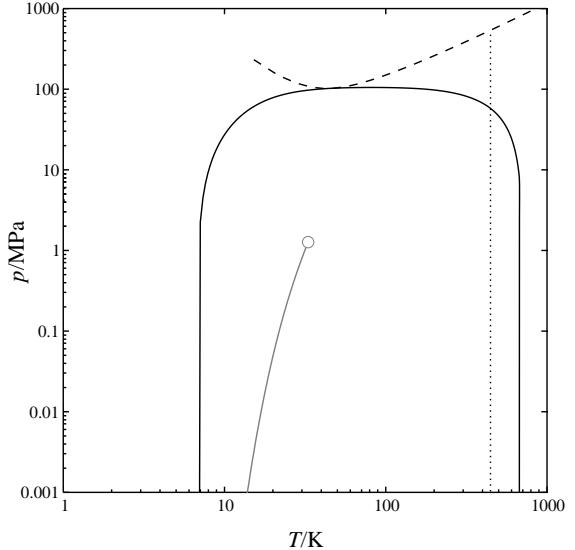


Figure 2. Amagat (Joule inversion) curve of hydrogen, calculated with several equations of state. —: “soft SPHCT equation” (temperature dependence of the size parameter based on perturbation theory) [5], – – : PC-SAFT equation [6], ····· : Peng–Robinson equation (its Joule inversion curve is an artifact of the temperature function of its attraction term.) [7]; grey line: vapour pressure curve with critical point.

satisfactorily. But is it safe to conclude that an equation that performs well up to 20 MPa will also perform well at 200 MPa? An easy-to-use test is the calculations of Brown’s characteristic curves [3,4]. Along these curves, one of the thermodynamic properties of a real fluid is the same as that on an ideal gas. Here we restrict ourselves to the discussion of the Amagat curve, also known as Joule inversion curve. Its mathematical conditions are either one of

$$\left(\frac{\partial Z}{\partial T} \right)_V = 0 \quad \left(\frac{\partial Z}{\partial p} \right)_V = 0 \quad \left(\frac{\partial p}{\partial T} \right)_V = \frac{p}{T} \quad \left(\frac{\partial U}{\partial V} \right)_T = 0. \quad (15)$$

In a pT diagram, the Amagat curve should have a single maximum and no inflection points, as indicated in Fig. 2. The pressure at the maximum is extremely high, usually 50–100 times the critical pressure. For some compounds, however, this is still in the technically relevant range, e.g., for hydrogen.

But even users not interested in such high pressures are advised to check the Amagat curve, for if there is anything amiss, deviations or odd behaviour of thermodynamic functions can already make themselves felt at lower pressures.

1. As a rule, equations of state containing a hard-sphere term with a temperature-independent size parameter (this applies to most cubic equations of state) do not show a correct Amagat curve, or they do not have an Amagat curve at all. Such equations should be used with caution at high pressures, for some of their derivative properties behave wrongly. The commonly used remedy, namely devising a more complicated temperature dependence of the *attraction term*, invariably fails when the pressure are high enough.
2. Equations of state containing a hard-sphere term with a simplistic temperature dependence of the size parameter

²The situation can be remedied by using scaling factors with appropriate dimensions. An axiomatic derivation of Eq. (11) shows that these must exist. But they are usually omitted in the literature.

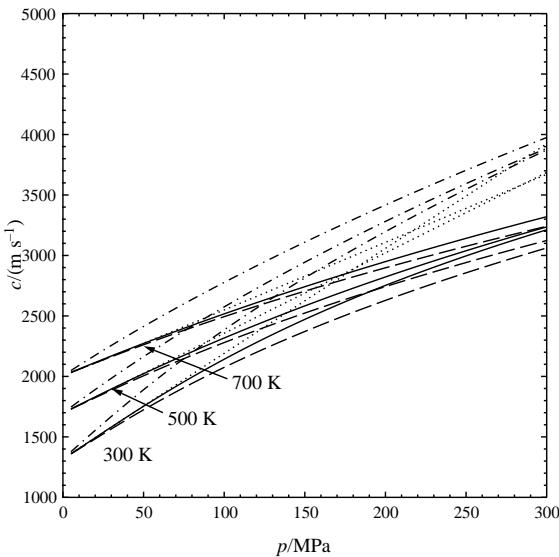


Figure 3. The speed of sound of hydrogen computed with several equations of state. —: reference equation [11], - - : “soft SPHCT” [5], --- : PC-SAFT [6], - · - : Peng–Robinson equation [7] (using an acentric factor of 0.0). The parameters of the soft SPHCT, PC-SAFT, and PR equations were determined from the critical temperature and pressure.

(usually a T^{-1} dependence or a Boltzmann factor, e.g., BACK [8] or PC-SAFT [6]) usually give distorted Amagat curves. They are not safe at high pressures, too. Moreover, it is known that a temperature dependence of the size parameter may lead to isotherm crossing [9, 10].

3. Using a temperature dependence of the size parameter derived from perturbation theory can lead to equations of state with correctly shaped Amagat curves and a very wide pressure range. With modern computers, the numerical overhead for the calculation of the temperature functions is affordable.

The effect on an important thermodynamic property, the speed of sound, is shown in Fig. 3: The curve of the Peng–Robinson equation starts at low pressures with the correct slope, but departs from the reference equation [11] as soon as softness effects make themselves felt. The PC-SAFT equation deviates even more. Only the “soft SPHCT” equation [5], which has a temperature dependence based on Weeks–Chandler–Andersen perturbation theory, can match the behaviour of the reference equation reasonably well³.

Admittedly, the underlying SPHCT equation is too simple for really accurate work. But the principle of the softness correction used for the “soft SPHCT” equation can easily be applied to other equations of state. This adds a numerical complication, but it is desirable to not let real or perceived difficulties of the computational implementation let the design of thermodynamic models too much. In the long run, it is better to use advanced numerical techniques and to keep the better model.

CONCLUSION

Solving scientific or engineering problems can often be regarded as a three-step process, namely

- devising a mathematical model,
- solving it,
- and interpreting the results.

Ideally, solving and model making should be distinct steps: It is not wise to let our (sometimes insufficient) capabilities to solve equations influence the way how we devise models. Of course, sometimes we cannot avoid it. But if we have to make compromises, we must remember so and look for ways to remedy the situation. Overcoming limitations of models by merely adding one more adjustable parameter usually helps for a while, but not in the long run.

We should not introduce simplifications and approximation at a too early stage of the model making. We should especially avoid making obsolete simplifications and retain exact thermodynamic relations as long as possible.

Over the previous decades, our computing power has become enormous. We can afford to use theories beyond cubic equations of state. But our higher computing power is not only caused by higher processor clock frequencies. Much of it is owed to the availability of high-level programming languages and program libraries. If we formulate our thermodynamic problems in a modern and clear way, using tools of differential geometry, we can efficiently make use of the available numerical tools.

Let us cease honing our stone axes and try to get chainsaws instead!

NOMENCLATURE

A	Helmholtz energy; \hat{A} : its Hessian matrix
f	fugacity
G	Gibbs energy
K	chemical equilibrium constant
N	number of components of a mixture
p	pressure
R	gas constant
S	entropy
T	temperature
U	internal energy
V	volume
x	mole fraction; \vec{x} : vector of all mole fractions of a phase
Z	compression factor, $Z = pV_m/(RT)$
μ	chemical potential; $\vec{\mu}$: vector of all μ_i of a phase
v	stoichiometric coefficient; \vec{v} : vector of v_i for a chemical reaction
ρ	molar density; $\vec{\rho}$: vector of all densities
Ψ	Helmholtz energy density, $\Psi = A/V$; $\hat{\Psi}$: its Hessian matrix

Subscripts

i	component i of a mixture
m	molar property
r	chemical reaction

Superscripts

\ominus	reference value
$'$, $"$	phase indicators

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³The reference equation is probably beyond its range of validity at 700 K and 300 MPa.

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