From molecular insights and chemical technologies to communications and expert systems: A few short thermodynamic stories

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Being the 53rd Huffman Memorial Award Lecture of the Calorimetry Conference delivered on 27 June 2005 at its 60th annual conference held at Gaithersburg, MD, USA.

Abstract

This Hugh M. Huffman Memorial Award Lecture illustrates the power of phenomenological and statistical thermodynamics and the unique role of thermochemical data by a variety of studies in very diverse scientific and industrial fields ranging from conformational analysis to optimization of high-tech space and mass-scale chemical technologies and from data communications to data expert systems for chemical process design.

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"...So muss das alles eines werden, alles aus Einem entsprungen und zu Einem zurückkehren ..."

"...Everything should be (a part of) the One, originating from the One, and coming back to the One ..."

Johann Wolfgang von Goethe (1749 to 1832)

1. Introduction

It is my great pleasure and honor to be selected as the 2005 recipient of the Hugh M. Huffman Memorial Award by the Calorimetry Conference. I would like to thank the Calorimetry Conference and its Board of Directors and share this honor and pleasure with my mentors, colleagues, students, many collaborators worldwide, as well as with my family. It is also important for me to acknowledge the contributions of my predecessors at the Thermodynamics Research Center (TRC), Frederick Rossini, Bruno Zwolinski, Kenneth Hall and Kenneth Marsh, whose vision, in many different ways, determined the conceptual research "portfolio" of the TRC.

In preparation for this lecture, I realized that there are two principal ways this lecture could be structured: either focusing on one particular project that would be the "dearest" to my heart or selecting a number of the thermodynamic projects (or "short thermodynamic stories" as I named them) I had a privilege to be a part of and contributed to during my career. At the end, I concluded that the latter is definitely the preferable, though challenging, choice for me, in part, because of the very diverse nature of the research projects I was involved in, and, in part, because selecting such a structure for the lecture provides an opportunity to illustrate the universal nature and a power of the thermodynamic approach originating from a very limited number of the fundamental principles and capable of describing, interpreting, and predicting an enormous variety of the natural phenomena. Obviously, the selection of the epigraphy is determined by this decision. I also think that this structure will allow me to acknowledg---

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edge better the contributions of the collaborators I was very lucky to work with throughout my career.

Following this decision, for this lecture I selected seven short thermodynamic stories ranging from conformational analysis to optimization of high-tech space and mass-scale chemical technologies, and from data communications to data expert systems for chemical process design.

2. Story #1 (conformational)

The results described in this story were obtained in close cooperation with my mentor Prof. G.J. Kabo of Byelorussian State University. There are two principal questions at the core of this story:

- How significant might be the differences between thermodynamic properties of stereoisomers and conformers?
- Is it possible to obtain thermodynamic property data for stereoisomers and conformers based on results of experimental studies?

Obtaining the answer to the first question is important since most of the group contribution predictive methods for enthalpies of formation of organic compounds assume that there is no difference in thermochemical properties of stereoisomers and conformers [1].

The intuitive answer to the second question seems to be negative. Indeed, it is commonly known that conducting highly accurate experimental thermodynamic studies requires the availability of highly pure samples to be subjected to measurements. However, in the case of stereoisomers and conformers, obtaining highly pure samples in quantities required for thermochemical experiments is often a very challenging task because their physical and chemical properties are so close that the stereoisomer, or even more so the conformer mixtures, are very difficult to separate to a significant degree to obtain highly pure samples of individual species. The results of this study prove this intuitive answer to be wrong.

In order to find out how significant might be the differences between thermodynamic properties of stereoisomers, the thermochemical equilibria of the isomerization reactions of stereoisomers for a series of acyclic, monocyclic, and bicyclic alcohols were studied experimentally [2,3]. The equilbrium for acyclic alcohols was represented by the stereoisomerization of threo- and erythро-isomers of 3-methylpentanol-2 [4]. The thermodynamics of stereoisomerization of monocyclic alcohols was studied for diastereomers of 2-, 3-, and 4-methylcyclohexanols [5–7] as well as for the menthol isomers [8,9]. The bicyclic alcohol isomerization was studied for borneol-to-isoborneol transformation [10–13].

The stereoisomers can contain a number of conformers and optical isomers in their composition. The complex nature of the conformational composition for 2-, 3-, and 4-methylcyclohexanols is illustrated on figure 1. The 2-methylcyclohexanol (figure 1a) exists in cis- and trans-dia-
FIGURE 1. Conformational composition of methylcyclohexanols: (a) 2-methylcyclohexanols; (b) 3-methylcyclohexanols; and (c) 4-methylcyclohexanols.

ance. It was found that in the process of dehydrogenation reactions at $T = 500$ K, the material balance approximated (1 to 2) mole per cent. The equilibria of 3-methylpentanol-2 isomers as well as of isomers of methylcyclohexanols were achieved over a temperature range exceeding 140 K. However, in the case of borneols and menthols, with their high boiling temperatures and non-selectivity of dehydrogenation reactions at high temperatures, the investigation was limited to the single temperature of 503 K. The equilibria were achieved over the catalyst containing a mixture of copper and magnesium oxides. The analysis of the equilibrium mixtures of isomers was performed with the use of the gas-liquid chromatography method.

The results of this study are shown in table 1 [2,3]. As it follows the results represented in table 1, in the equilibrium mixture of 3-methylpentanol-2 isomers the erythroform prevails but the difference in the enthalpies of threo- and erythro-forms deduced from the experimental results is very small. In the series of methylcyclohexanols, the enthalpies of stereoisomerization are substantially higher than the possible experimental uncertainties and amount to (1.7 to 3.9) kJ·mol$^{-1}$. The values of cis-to-trans
isomerization enthalpies of 2- and 3-methylcyclohexanols can be interpreted from the point of view of conformation analysis exactly in the same way as was done by Pietzer and co-workers for dimethylcyclohexanes [16]. It was noted [17] that for 4-methylcyclohexanol there is a stabilization of the $\alpha_{CH_2}\alpha_{OH}$ form. This is a possible reason for the lower isomerization enthalpy compared with 2-methylcyclohexanol as seen from our experimental results. Since both borneol and isoborneol are present in the form of only one conformer (D,L pair), the entropies of borneols should be close and in this case $\Delta_rG^\circ \approx \Delta_rH^\circ \approx 9.6$ kJ·mol$^{-1}$. Examination of the differences in the enthalpies of similar stereoisomeric pairs makes it evident that they grow progressively from acyclic towards monocyclic and bicyclic alcohols. Qualitatively, these differences can be explained in the following way. Each of the diastereoisomers of acyclic alcohol $R_1R_2CH=CH(OH)R_3$ is represented by three rotational isomers moving around the C–C bond while the ring in methylcyclohexanols decreases the number of possible conformers to two (a’e and a’u or a’a and e’e). For bicyclic alcohols, a further simplification of the conformation picture takes place (each stereoisomer exists as only one conformer).

The above-mentioned dependence probably illustrates the more general regularities. Possibly one of the reasons for good $\Delta_rH$ additivity in the series of acyclic compounds is the great number of degrees of freedom of internal rotation, which causes substances to exist as mixtures containing many energetically non-equivalent conformers.

The results obtained provide a very definitive answer to the first question of this story: the differences between thermodynamic properties of stereoisomers and conform-
ers can be very significant. It may be held that the application without change of group contribution methods that are quite effective for acyclic substances will result in gross mistakes in the calculation of monomeric and polycyclic compound enthalpies. This is not only due to angle strain in rings, but is also a consequence of the limitation of degrees of freedom of internal rotation and of the specifics of the conformational composition of individual diastereomers.

The equilibria of conformers are commonly studied by spectroscopic methods. Indeed, we showed that an NMR signal of the hydroxyl proton in tertiary 1-methycyclohexanol is split into a doublet at low temperatures (isopentane solution coalescence temperature is 222 K) with the components corresponding axial and equatorial positions of the hydroxyl group (figure 5) [18]. The Gibbs free energy of this conformational transition, \( \Delta G^\circ \) (222 K), found on the basis of the equilibrium constant calculated using signal areas, was approximately 1.8 kJ mol\(^{-1}\). The NMR spectra of secondary methycyclohexaols do not show similar splitting of either the hydroxyl group protons or protons geminal to the hydroxyl group (we shall designate the latter ones as H-COH protons). We observed measurable changes of the chemical shifts of H-COH protons as a function of temperature in spectra of less stable diastereomers (figure 6), which was caused by temperature-induced changes of their conformational compositions. Indeed, as temperature decreases, the ratio of \( \delta_{\text{CH}_2\text{OH}} \) and \( \delta\text{CH}_3\text{OH} \) (comprising less stable diastereomers: cis- for 2- and 4-methycyclohexanols, trans- for 3-methycyclohexanol) changes resulting in increase of the concentration of \( \delta_{\text{CH}_2\text{OH}} \) conformer as the relatively "bulky" methyl group tends to occupy equatorial position. That leads in turn to a change in chemical shift of the signal towards lower magnetic field. At significantly low temperatures (close to \( \approx 170 \text{ K} \)), methyl groups occupy equatorial positions in nearly all molecules. Therefore temperature decrease in the range 180 K to 160 K causes no further changes of chemical shift. The values of chemical shift at these temperatures can be assigned as ones for conformers with equatorial position of H-COH proton, \( \delta_{\text{H-COH}} \). Chemical shifts of H-COH protons in more stable diastereomers (trans- for 2- and 4-methycyclohexanols, cis- for 3-methycyclohexanol) do not exhibit any changes as temperature decreases since these diastereomers consist of predominantly of \( \delta_{\text{CH}_2\text{OH}} \) conformers at temperatures as high as ambient (figure 6). These chemical shifts can be identified as those for conformers with an axial position of H-COH proton, \( \delta_{\text{H-COH}} \).

Following a similar procedure previously described [19], we determined the equilibrium concentrations of the conformers:

\[
[\delta_{\text{CH}_2\text{OH}}] = \frac{\delta_a - \delta_{\text{H-COH}}}{|\delta_a - \delta_e|}, \tag{1}
\]

\[
[\delta_{\text{CH}_3\text{OH}}] = \frac{\delta_{\text{H-COH}} - \delta_e}{|\delta_a - \delta_e|}, \tag{2}
\]

where \([\delta_{\text{CH}_2\text{OH}}]\) and \([\delta_{\text{CH}_3\text{OH}}]\) are equilibrium mole fractions of \( \delta_{\text{CH}_2\text{OH}} \) and \( \delta_{\text{CH}_3\text{OH}} \) conformers, \( \delta_a \) and \( \delta_e \) are chemical shifts of H-COH protons in axial and equatorial positions, and \( \delta_{\text{H-COH}} \) is an unresolved chemical shift of H-COH proton in a mixture of conformers.

Using (1) and (2), the equilibrium constant \( K \) can be calculated as:

\[
K = \frac{\delta_a - \delta_{\text{H-COH}}}{\delta_{\text{H-COH}} - \delta_e}. \tag{3}
\]

The calculated values of the equilibrium constant were used to estimate the Gibbs free energy of the conformational transformation of \( \alpha'\epsilon \leftrightarrow \epsilon'\alpha \) type (table 2).

The samples of stereoisomer mixtures of well-defined composition could be used in bomb calorimetry to determine the enthalpy of their formation. On the other hand, the results of the equilibrium studies of stereoisomers make it possible to determine the enthalpies of stereoisomeric transformations. The combination of the calorimetric and equilibrium studies provides an opportunity to determine the enthalpies of formation of the individual stereoisomers, \( \Delta H_{m,i} \).

**FIGURE 5.** Temperature dependence of NMR hydroxyl group spectrum of 1-methycyclohexanol (in isopentane, JEOL PNS-100): 1-axial hydroxyl group; 2-equatorial hydroxyl group [18].
TABLE 2
NMR study of cis-trans equilibrium (T = 301 K, in pentane) [18]

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta$H$_j$/Hz</th>
<th>$\delta$/Hz</th>
<th>$\delta^{1H}$COH$_j$/Hz</th>
<th>[H$\delta$H, $\delta$OH]/%</th>
<th>K</th>
<th>$\Delta_rG^\circ$ (kJ·mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-Methylocyclohexanol</td>
<td>300</td>
<td>380</td>
<td>374</td>
<td>93</td>
<td>12.3</td>
<td>6.2</td>
</tr>
<tr>
<td>3-Methylocyclohexanol</td>
<td>336</td>
<td>390</td>
<td>384</td>
<td>89</td>
<td>8.0</td>
<td>5.1</td>
</tr>
<tr>
<td>4-Methylocyclohexanol</td>
<td>330</td>
<td>390</td>
<td>378</td>
<td>80</td>
<td>4.0</td>
<td>3.4</td>
</tr>
</tbody>
</table>

$$\sum_{i=1}^{n} x_i \Delta H_{m,i} = \Delta H_j (\text{exp., calor.}),$$  
$$\sum_{i=1}^{n} v_i \Delta H_{m,i} = \Delta H_j (\text{exp., equil.}),$$

where $\Delta H_j (\text{exp., calor.})$ is the enthalpy of formation of the mixture of stereoisomers of a particular composition; $\Delta H_j (\text{exp., equil.})$ is the enthalpy of $j$th reaction derived from equilibrium constants; $x_i$ is a mole fraction of the stereoisomer $i$, $n$ is a total number of stereoisomers; $v_i$ are stoichiometric coefficients (all $v_i = 1$ in case of isomerization equilibria). The values obtained for the enthalpies of formation of the stereoisomers could further have been used in combination with the results of conformational equilibrium studies to determine the enthalpies of formation of individual conformers.

The demonstrated results prove that it is possible to obtain thermodynamic property data for individual stereoisomers and conformers based on results of experimental studies.

3. Story #2 (conformational again)

The results described in this story were obtained in close cooperation with Prof. G.J. Kabo and Dr. Peter Poleshchuk. The principal question of this story is:
• Is it possible to determine the heat capacity of conformer mixing analytically (not numerically)?

Studying thermodynamic properties of organic compounds is commonly complicated by the existence of the substances as equilibrium mixtures of conformers or of tautomers, which are either impossible or extremely difficult to separate. In these cases, the thermodynamic formulae that apply to the individual chemical species may not be valid, and the reconciliation of the results of the statistical mechanical calculations with the experimental data becomes very challenging.

The heat capacities of conformational and tautomeric mixtures can be determined from the following equation:

\[ C_p = \sum_{i=0}^{n} x_i C_{pi} + \sum_{i=0}^{n} \frac{\delta x_i}{\delta T} \Delta H_{T(0-\theta)}^i, \]  

(6)

where \( C_{pi} \) is a molar heat capacity of the mixture; \( C_{pi} \) and \( x_i \) are molar heat capacity and mole fraction of the conformer (tautomer) \( i \), respectively; \( \Delta H_{T(0-\theta)} \) is a standard molar enthalpy of the transition from the most stable conformer (tautomer) designated as a conformer (tautomer) 0 to any other conformer (tautomer) \( i \); \( n \) is a total number of conformers (tautomers) in the mixture.

In most cases, \( (\delta x_i/\delta T) \) is usually determined numerically based on equilibrium compositions using the approximation of \( (\delta x_i/\delta T) \approx (\Delta x_i/\Delta T) \) for the temperature range \( \Delta T \leq 1 \) K. This approximation leads quite often to an increase in the uncertainties in calculated heat capacity values that commonly cannot be well estimated.

Aston [20], Lielnitz and Bondi [21], and Compton [22] developed a procedure for calculating the contributions to the thermodynamic functions for the elementary transition between conformers \( A_0 \) and \( A_1 \):

\[ A_0 \rightarrow A_1. \]  

(7)

Conformational mixtures of this type are not very common. Therefore, there is a need for more general approach to the calculation of the contributions to the thermodynamic functions related to the conformation mixing.

We shall assume that the compound consists of a set of conformers \( (A_0, A_1, A_2, \ldots) \), one of which \( (A_0) \) is energetically the most stable. Then its concentration in the mixture, expressed in mole fractions, is \( x_0 \rightarrow 1 \) at \( T \rightarrow 0 \). It has been shown [23] that two equivalent expressions can be obtained for the reduced enthalpy when this multicomponent mixture passes from the state \( \{T_1, x_0(T_1), x_1(T_1), x_2(T_1), \ldots \} \) to the state \( \{T_2, x_0(T_2), x_1(T_2), x_2(T_2), \ldots \} \):

\[ \frac{H_f^2 - H_f^0}{T} = \sum_{i=0}^{n} x_i(T) \frac{[H_f^2 - H_f^0]}{T} + \sum_{i=1}^{n} x_i(T) \frac{\Delta H_{T(0-\theta)}^i}{T}, \]  

(8)

\[ \frac{H_f^1 - H_f^0}{T} = \frac{[H_f^1 - H_f^0]}{T} + \sum_{i=1}^{n} x_i(T) \frac{\Delta H_{T(0-\theta)}^i}{T}, \]  

(9)

where \( \Delta H_{T(0-\theta)} \) is the enthalpy of transition of the conformer \( A_0 \) into the conformer \( A_i \).

Differentiation of equations (8) and (9) with respect to temperature produces [23-25] an expression for the heat capacity of a system containing an arbitrary number of conformers (tautomers) \( n \):

\[ C_p = \sum_{i=0}^{n} x_i C_{pi} + \frac{1}{RT^3} \sum_{i=0}^{n} x_i \sum_{j<i} x_j \left( \frac{\Delta H_{T(0-\theta)}^i}{T} \right)^2, \]  

(10)

where \( \Delta H_{T(0-\theta)} \) is the enthalpy of transition from the conformer \( i \) to conformer \( j \), \( C_{pi} \) is the molar heat capacity of the conformer mixture at constant pressure, \( C_{pi} \) is the molar heat capacity of the conformer \( i \) at constant pressure, and the \( R \) is universal gas constant.

Notably, equation (10) is an entirely analytical equation as a difference to equation (6), containing numerical differentiation. In equation (10), all possible pairs of conformer transformations have to be counted, not only those that are linearly independent. Therefore, the second term in equation (10) contains \( n(n - 1)/2 \) contributions. Using the approach described above, one can obtain the well-known expression for the entropy of mixing:

\[ S_T = \sum_{i=0}^{n} x_i S_{T,i} - R \sum_{i=0}^{n} x_i \ln x_i. \]  

(11)

The effectiveness of the use of equations (8) to (10) has been demonstrated in statistical mechanical calculations of the thermodynamic functions of cyclohexanol and cyclohexanone in the ideal gas state [24]. The contributions of external rotation of cyclohexanol to its thermodynamic properties were determined using a product of its three principal moments of inertia obtained from rotational spectra [26]. Vibrational components of the thermodynamic functions were determined by the wave-numbers obtained by normal coordinate analysis [27]. Conformational contributions were calculated with equations (8) to (10) based on the set of conformers represented in table 3.

For cyclohexanol, the principal moments of inertia were calculated for the most stable chair conformer with the hydroxyl group on the equatorial position based on structural information [14]. The vibrational frequencies were estimated from a comparison of the results of spectral analysis of cyclohexanol [28,29] and the frequencies assigned for cyclohexane [30] and cyclohexanethiol [31]. The contribution of rotation of the \( \text{OH}\)-top was calculated from Pitzer’s tables [32] by use of the values of the assumed threefold symmetry of the potential function. The formation of rotational isomers due to the \( \text{OH}\)-top rotation was considered in combination with other conformations for calculating their contributions to the thermodynamic properties of this compound. It was assumed that cyclohexanol, similar to cyclohexanethiol, had conformations as shown in table 4 with symmetry number \( \sigma = 1 \) for each conformation.

The calculated thermodynamic properties of cyclohexanol and cyclohexanone allowed us to evaluate equilibrium constants as a function of temperature for the reaction of...
TABLE 3
Enthalpy and entropy changes for transformation of the chair form of cyclohexanone into other conformations [24]

<table>
<thead>
<tr>
<th>Conformer</th>
<th>Symmetry group, optical isomers</th>
<th>$\Delta H_{T=0}^{f}$ (kJ·mol$^{-1}$)</th>
<th>$\Delta S_{T=0}^{f}$ (J·K$^{-1}$·mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{2}$</td>
<td></td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$C_{3}(\sigma = 2)$; d,l</td>
<td>8.3</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>$C_{1}$; d,l</td>
<td>23.5</td>
<td>5.76</td>
<td></td>
</tr>
<tr>
<td>$C_{1}$; d,l</td>
<td>8.3</td>
<td>5.76</td>
<td></td>
</tr>
<tr>
<td>$C_{2}$</td>
<td></td>
<td>23.0</td>
<td>0</td>
</tr>
</tbody>
</table>

FIGURE 7. Plot of equilibrium constant of the dehydrogenation reaction of cyclohexanol against reciprocal temperature [24]; (a) previous calculated [32], (b) results calculated with the use of equations (8) to (10) +, experimental data [24].

(10) for determinations of conformational contributions to thermodynamic functions are in very good agreement with reliable experimental data.

4. Story #3: "...Something about Nylon"

The results described in this story were obtained in close cooperation with Prof. G.J. Kabo and Dr. Isaac Kantorovich (currently of Intel Corporation). This story demonstrates a critical role of the thermodynamic property data in chemical process design.

The sequence of chemical reactions shown in figure 8 represents the chemistry of large-scale Nylon production.

\[
\text{Benzene} + \text{H}_2 \rightarrow \text{Cyclohexane} \rightarrow \text{Cyclohexanol} \rightarrow \text{H}^+ \rightarrow \text{e-Caprolactam} \rightarrow \text{Cyclohexanone oxime} \rightarrow \text{Cyclohexanone} \rightarrow \text{Nylon}
\]

FIGURE 8. Chemistry of Nylon production.
from benzene, commonly used in industry. One of the critical stages of this process is the stage of cyclohexanol dehydrogenation:

\[
\begin{align*}
\text{OH} & \quad \overset{\text{Cu/Mg catalyst}}{\longleftrightarrow} \quad \text{O} \\
& + \quad \text{H}_2
\end{align*}
\]

(12)

It is obvious that any increase of the yield on this stage would lead to an increase of efficiency of the overall production process. Reaction (12) is an endothermic reaction. Therefore, it is usually run under elevated temperatures. In industry, this reaction is conducted in the reactor schematically illustrated in figure 9. Heating gas coming from the combustion chamber proceeds into the space between the inner tubes filled with the catalyst getting into a heat exchange process with the reaction mixture flowing through the tubes (figure 9). Here we shall analyze possible options of the reactor settings to optimize its functioning. In order to do that, mathematical modeling of the heat and mass exchange processes within the reactor has been undertaken [33].

Since the convection flow for the reaction mixture is much higher than that for the diffusion of the reaction components under industrial conditions, the motion equation for cyclohexanol (13) and the continuity-of-flow equation in the cylindrical tube (14) are

\[
\frac{\partial}{\partial x} (c_i v) + r = 0, \quad (c_1 + c_2 + c_3) v S = \text{const.} = G,
\]

(13)
(14)

where the indices “1”, “2”, and “3” are related to cyclohexanol, cyclohexanone, and hydrogen, respectively; \( x \) is a reactor coordinate (m); \( c_i \) (mol · m\(^{-3}\)) is a concentration of the reaction component \( i \); \( v \) (m · s\(^{-1}\)) is a linear velocity of the reaction mixture; \( r \) (mol · m\(^{-3}\) · s\(^{-1}\)) is a reaction rate; \( S \) (m\(^2\)) is a cross-section area for the reaction mixture flow; and \( G \) (mol · s\(^{-1}\)) is a reaction mixture flow rate through the reactor.

Based on the equation of chemical reaction (12)

\[
c_2 = c_1,
\]

(15)

In equations (13) and (14) we assume that gas movement in the radial direction is negligible.

In the equations for heat transfer, we assume both thermal conductivity of the heating gas and the heat transfer over the tubes negligible (we have proven the validity of these assumptions). Then, the energy balance within a system can be expressed by equation (16) for the reaction mixture and (17) for the heating gas (index “g” corresponds to the heating gas):

\[
G C_p \frac{\partial T}{\partial x} = -r S \Delta H + \alpha (T_g - T),
\]

(16)
\[
G C_p \frac{\partial T}{\partial x} = \alpha (T_g - T),
\]

(17)

where \( C_p \) (J · mol\(^{-1}\) · K\(^{-1}\)) is the composition-dependent heat capacity at constant pressure for the reaction mixture; \( T \) (K) is a reaction mixture temperature; \( \Delta H \) (J · mol\(^{-1}\)) is an enthalpy of the reaction; \( \alpha \) (J · m\(^{-1}\) · K\(^{-1}\) · s\(^{-1}\)) is a thermal conductivity coefficient between a reaction mixture and heating gas; and \( C_g, T_g, \) and \( G_g \) are heat capacity, temperature, and flow rate of heating gas through the reactor, respectively.

Using the ideal-gas equation of state and assuming that the total pressure dependence over the length of the reactor is linear, under the condition of chemical equilibria we obtain the following equation for the reaction mixture:

\[
\frac{\partial T}{\partial x} = \frac{2 \Delta H \cdot \frac{\partial P}{\partial x} \cdot \frac{K P}{(P + P)^2 (K P + K)^2}}{C_p \left[ 1 - \frac{\Delta H K P}{R c_g T^2 (P + P)^2 (K P + K)^2} \right]},
\]

(18)

where

\[
P_p = P + 2 K - 2 (K P + K)^{1/2},
\]

(19)

where \( P \) (Pa) is the total pressure; \( K \) (Pa) is an equilibrium constant; and \( R \) (J · mol\(^{-1}\) · K\(^{-1}\)) is the gas constant.

It is obvious that the use of equation (18) requires a knowledge of thermodynamic and transport property data of the components, as well as the enthalpy of reaction (12) [34]. The process of obtaining some of these property data for cyclohexanol and cyclohexanone was described in Story #2 above. The equilibrium composition for reaction (12) was determined on the basis of these property data [35].

The algorithm described above was used to analyze two settings of the reactor for the process of cyclohexanol dehydrogenation: unidirectional (figure 10a), where the heating gas and the reaction flow are along the same direction, and counter directional (figure 10b), where the heating gas and the reaction flow are along opposite directions. The results of this analysis are illustrated in figure 11. In both cases, the initial temperature of the heating gas was 543 K and the initial temperature of cyclohexanol was 498 K. The initial total pressure was 0.15 MPa, the final total pressure was 0.12 MPa. As it follows from figure 11, the final temperature of the reaction mixture in case of the counter directional setting is higher by about 15 K than that in the case of the unidirectional setting. That corresponds to an increase in the yield of the cyclohexanone by about 9%. The results of this analysis were implemented in the
5. Story #4: gas-generators and applications

The results described in this story were obtained in close cooperation with Prof. G.J. Kabo and Dr. Isaac Kantorovich. This story illustrates the critical role that thermodynamic property data might play in non-traditional chemical process design applications.

A gas-generator can be defined as a technical device designed to generate gaseous products from liquid and solid materials. Gas-generators have a broad range of applications in various fields of technology, such as maintenance of “controllable” environments [37], pneumatic engines, and rocket propulsion systems [38,39]. Gas-generating systems of the “fuel-coolant” type have been of particular interest for a long time due to their high efficiency [40]. “Fuel-coolant” gas-generating systems deploy solid fuels, combustion of which generates a bulk of the gaseous products. These gaseous products are then “cooled down” as a result of an endothermic chemical decomposition of the “coolants” such as carbonates or oxalates of ammonium. However, the decomposition of ammonium salts commonly leads to formation of ammonia, water, and carbon dioxide. At moderate temperatures, these products interact chemically, form solutions, and transform into a liquid phase, resulting in decreased gas-production, which can be defined as a ratio of the total volume of the gaseous products at normal conditions either to the gas-generator mass or to the mass of the gas-generating fuel (propellant).

We have used methods of chemical thermodynamics to analyze the possibility of a catalytic conversion of the multicomponent mixtures of the coolant decomposition products in order to increase overall gas-production of the “fuel-coolant” gas-generating systems. We have calculated equilibrium compositions of the products of chemical interaction of the thermolysis components of the “coolants” (bicarbonate and oxalate of ammonium). These calculations were performed using an isobaric-isothermal potential minimization [40] method. The approximations of the ideal gas and the condensed “large” molecules [41] were used for the gaseous and condensed phases, respectively. Deploying the undetermined Lagrange multiplier method [42], this algorithm leads to a solution of m non-linear algebraic equations with regard to Lagrange multipliers $\lambda_j$:

$$\sum_{i=1}^{k} \left( a_{ij} - \frac{n_i n_j}{N_j} \right) \exp(x_i) = P \delta_{ij}, \quad j = 1, \ldots, m, \quad (20)$$

where

$$P_i = \exp(x_i), \quad \text{and} \quad (21)$$

$$x_i = -A_i \left[ \Phi_i(T) + \sum_{j=1}^{m} n_{ij} \lambda_j \right] / R, \quad (22)$$

The development of the counter directional setting reactor technology for the cyclohexanol dehydrogenation stage in the synthesis of Nylon from benzene [36].
The $n_j$ is the number of atoms of the $j$th element in molecule of the $i$th reaction participant; $N_j$ is the amount (moles) of the $j$th element per one kilogram of the reaction mixture; $m$ is the total number of elements in the reaction mixture; $k$ is the total number of participants, $A_i$ is a constant equal to 1 for gaseous participants or to a certain large number for condensed participants; $\Phi_i(T)$ is the reduced Gibbs free energy of the $i$th participant; $P_i$ is the partial pressure of the $i$th participant; $P$ is the total pressure; $\delta_{ij}$ is the Kronecker symbol ($\delta_{ij} = 1$ for all $i = j$; $\delta_{ij} = 0$ for all $i \neq j$); $R$ is the gas constant.

The calculated results [43-45] (figure 12) show that the temperature range of 900 K to 1100 K is optimal to achieve high gas-production. On another hand, we have proven that the experimental results of the catalytic conversion of the mixtures of the (NH$_3$_H$_2$O-CO$_2$) type performed with the use of commercial catalysts for ammonia synthesis are very close to the results of the thermodynamic analysis [40] (table 5).

The studied catalytic processes are slow at temperatures below ~750 K. Therefore, the concept of multistage cooling was proposed (figure 13). Final and intermediate parameters of the process based on this concept can be calculated under the condition of entropy constancy. For the first stage of this process, we calculated a ratio of the masses of the coolant $m_1$ and the fuel (propellant) $m_2$ as a function of the temperature $T_2$:

$$m_1 = \frac{\sum_{i=1}^{n_a} \beta_i m_i Y_i(T_1)}{\beta Q + \sum_{i=1}^{n_a} \beta_i m_i Y_i(T_1)}$$

where $n_a$ and $n_p$ are the numbers of the components in the high-temperature gas coming out of the combustion chamber, and in the products of the coolant decomposition, respectively; $\alpha_i$ are ratios of the mole numbers of the components of the high-temperature gas; $\beta$ and $\beta_i$ are ratios of the mole numbers of the coolant and the products of its decomposition; $c_{p,i}$ is the isobaric heat capacity of component $i$; $\mu_i$ is the molar mass of the $i$th component; $T_a$ is the temperature of decomposition of the coolant; $T_1$ is the temperature of the high-temperature gas; $T_2$ is the temperature of the reaction mixture after coolant decomposition.

$$Q = \int_{T_a}^{T_2} c_{p,coolant} dT + \Delta_r H + \Delta_n H,$$

where $c_{p,coolant}$ is the heat capacity of the coolant, $\Delta_r H$ is the reaction enthalpy of the decomposition, and $\Delta_n H$ is the sum of the enthalpies of phase transitions.

For the second stage of the process, there is a chemical conversion of the gaseous mixture. We assume the constancy of the entropy on this stage:

$$S = \sum_{i=1}^{n_a} c_i S_i(T) - R \sum_{i=1}^{n_p} c_i \ln P_i(T) = \text{const.},$$

where $S$ is a total entropy, $c_i$ is the concentration of the $i$th component, $k$ is the total number of the components, and $\kappa_b$ is the number of the gaseous components.

Simultaneous solution of $m$ equations (20) and (25) allows determination of the equilibrium composition and theoretical temperature $T_3$ of the system. The values of $c_{p,coolant}$, $T_3$ and $\Delta_r H$ for the selected coolants were obtained experimentally.

As follows from the results represented in figure 14, gas-production of the outgoing gas $T_3$ exceeds gas-production of the incoming high-temperature gas for a broad range of the mass ratios of coolant to propellant. That clearly indicates the efficiency of the multistage cooling process. The range of the coolant-to-propellant ratios, $m_1/m_2 \approx 0.2$ to 0.3, corresponds to the maximum of the gas production $T_3$ and the temperature range of $T_3 \approx 900 K$ to 1000 K. At such a high temperature, kinetic limitations become insignificant, and the chemical conversion is controlled by thermodynamic factors. The two-stage cooling with low
values of the \( m_1/m_2 \) ratio at the first stage of the process (figure 13) provides an opportunity for additional cooling stage (stage 3, figure 13) in order to obtain temperatures \( T_4 \) suitable for a variety of the applications (such as pneumatic devices). Notably, as it follows from the data presented in figure 14, the chemical conversion of the high-temperature incoming gas leads to an increase of the gas production by about 15%, even if no coolant is used. The technology developed on the basis of thermodynamic analysis outlined above was used in a number of space program-related applications.

6. Story #5: plastic crystals and their nature

The results described in this story were obtained in close cooperation with Prof. G.J. Kabo and members of his group (Prof. Kozyro, Drs. Krasulin, Sevruk, and Blokhin), Prof. Alan Marchand of North Texas State University, and Dr. Vladimir Diky, my former graduate student and now colleague at NIST/Boulder. The principal question of this story is:

- What is happening in the nodes of the plastic crystalline lattice?

Timmermans [46] used the following logical line to define liquid and plastic crystals: since most typical crystals are anisotropic and typical liquids are isotropic, liquid crystals can be defined as “fluidized” but still anisotropic while plastic crystals are “not fluidized” but isotropic. Even though it was generally understood that the formation of plastic crystals is caused by a partial removal of prohibitions of reorientational motion, the nature of the plastic crystalline state remained unknown for a long time. Historically, it was shown that a number of monocyclic hydrocarbons tend to exist in the plastic crystalline state [46,47]. Our studies of two representatives of the multicyclic (“cage”) hydrocarbons, heptacyclotetradecane and pentaeyclounde-

cane [48,49] (figure 15), proved that they can also form plastic crystals. Interestingly, a comprehensive analysis of the thermodynamic properties of the mono-, bi-, and multicyclic compounds allowed us to predict [50] that the enthalpy of sublimation of cubane should be about one half the value reported previously derived from experimental measurements of the vapor pressure [51]. Because of the critical importance of cubane in determining parameters for molecular mechanical and quantum mechanical calculations of the properties of strained hydrocarbons [50], this prediction led to the initiation of new measurements [52] resulting in a value fairly close to the predicted one within the limits of the uncertainties (table 6).

Comprehensive studies of the thermodynamic properties of 1-chloro-1-methylcyclohexane [53] and cyclohexane provided new insights into the nature of the plastic crystalline state [54]. The measurements of the heat capacity of 1-chloro-1-methylcyclohexane by the method of adiabatic calorimetry resulted in observing two phase transitions: one at \( T = 214.37 \) K, corresponding to the (rigid crystal)-to-(plastic crystal) transformation, and the other one at \( T = 234.52 \) K corresponding to the (plastic crystal)-to-liquid transformation (figure 16). The enthalpies and entropies of these transitions are summarized in table 7. The IR spectra of the compound recorded at the temperatures 293 K, 223 K, and 205 K indicated the presence of both conformers (one with the methyl group in the equatorial position towards the cyclohexane ring (a doublet 545 cm\(^{-1}\) to 565 cm\(^{-1}\)), and the other with the methyl group in the axial position (a singlet at 658 cm\(^{-1}\)) in gaseous, liquid, and plastic crystal states), while only one conformer with a methyl

<table>
<thead>
<tr>
<th>Source</th>
<th>Method</th>
<th>( \Delta_{sub}H/\text{kJ} \cdot \text{mol}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kybett et al. [51]</td>
<td>Effusion</td>
<td>79.1</td>
</tr>
<tr>
<td>Diky et al. [50]</td>
<td>Predicted</td>
<td>44.1 ± 5.0</td>
</tr>
<tr>
<td>Bashir-Hassani et al. [52]</td>
<td>g.i.e.</td>
<td>55.2 ± 2.0</td>
</tr>
</tbody>
</table>
group in the equatorial position is present in the rigid crystal (figure 17). This observation leads to the conclusion that the prohibition of cyclohexyl ring inversion with a potential barrier of about 50 kJ·mol⁻¹ obtained by the MM2(87) program is removed at the (rigid crystal) ↔ (plastic crystal) transition. So, it is highly probable that the methyl group rotation is also excited at this transition, because the potential barrier of this rotation is lower than that of the cyclohexyl ring inversion (an estimate of 19.2 kJ·mol⁻¹ was obtained by MM2(87) calculations). The contributions of ring inversion (≈14.6 J·K⁻¹·mol⁻¹) and CH₃-top rotation (≈4.8 J·K⁻¹·mol⁻¹) to the entropy at the temperature of transition (214.37 K) were calculated by the methods of statistical thermodynamics (non-interacted molecules). As the sum of these two values is considerably less than the value of the entropy of the phase transition, 43.76 J·K⁻¹·mol⁻¹, it is plausible to assume a possibility of existence of both internal rotation and over-all rotation of molecules in the plastic crystals of 1-chloro-1-methylcyclohexane.

The entropy of the over-all rotation of the molecule in the absence of a potential barrier ("free rotation") was estimated as follows:

\[
S°_{\text{free}} = R \left[ \ln \frac{8\pi^2}{\sigma} \left( \frac{2\pi kT}{\hbar^2} \right)^{1/2} \left( I_{A} I_{B} I_{C} \right)^{1/2} + \frac{3}{2} \right].
\]

where \( I_{A} I_{B} I_{C} \) is the product of the principal moments of inertia; \( \sigma \) is the symmetry number of the over-all rotation; \( h \) is the Planck constant; \( k \) is the Boltzmann constant; and \( R \) is the gas constant. The principal moments of inertia were determined based on the geometrical parameters of 1-chloro-1-methylcyclohexane obtained by molecular mechanics methods. The free over-all rotation entropy calculated using equation (26) was determined to be 116.19 J·K⁻¹·mol⁻¹ at \( T = 214.37 \) K (table 8). The difference between the entropy of the phase transition and the sum of the entropies of ring inversion and CH₃-top rotation is significantly smaller than the entropy of free over-all rotation. This leads to the conclusion that the over-all
TABLE 8
Rotational contributions to entropy for 1-chloro-1-methylcyclohexane at T = 214.37 K [53]

<table>
<thead>
<tr>
<th>Contribution</th>
<th>Barrier/ (kJ · mol⁻¹)</th>
<th>Value/ (J · K⁻¹ · mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ring inversion</td>
<td>50</td>
<td>14.61</td>
</tr>
<tr>
<td>CH₂group rotation</td>
<td>19.2</td>
<td>4.76</td>
</tr>
<tr>
<td>Over-all molecule free rotation</td>
<td>0</td>
<td>116.19</td>
</tr>
</tbody>
</table>

rotation of the molecules in the nodes of the plastic crystals of 1-chloro-1-methylcyclohexane is significantly hindered.

Based on experimental results discussed above, we can summarize that ring conversion, internal rotation, and over-all rotation (orientational contribution) are contributing to the heat capacities and entropies of the (plastic crystal)-to-(rigid crystal) phase transition. In addition, the entropy of such a transition is dependent on isothermal expansion of the rigid crystalline phase at the temperature of transition. Assuming that other contributions, such as those related to variations of the vibration frequencies and of lattice defect distributions, are much smaller in magnitude, we have:

$$\Delta_{\text{inv}} C_s = \Delta_{\text{int}} C_s + \Delta_{\text{orient}} C_s,$$

$$\Delta_{\text{inv}} S_m = \Delta_{\text{int}} S_m + \Delta_{\text{orient}} S_m,$$

where $\Delta_{\text{inv}} C_s$ and $\Delta_{\text{inv}} S_m$ are the molar saturated heat capacity and entropy of the (rigid crystal)-to-(plastic crystal) transition; $\Delta_{\text{int}} C_s$ and $\Delta_{\text{int}} S_m$ are ring inversion contributions to the molar saturated heat capacity and entropy in the plastic crystal state; $\Delta_{\text{orient}} C_s$ and $\Delta_{\text{orient}} S_m$ are orientational contributions to the molar saturated heat capacity and entropy in the plastic crystal state; $\Delta_{\text{orient}} S_m$ is the isothermal expansion contribution to the entropy of the phase transition.

The isothermal expansion contribution to the entropy of the (rigid crystal)-to-(plastic crystal) transition can be calculated as

$$\Delta_{\text{s,m}} S_m = \int_{V_1}^{V_2} \left( \frac{\partial P}{\partial T} \right)_V dV = \int_{V_1}^{V_2} \beta_{\text{f}}(V) dV,$$

where $V_1$ and $V_2$ are the molar volumes of a rigid crystal and plastic crystal, respectively, at the temperature $T_{\text{trs}}$.

This equation can be simplified [55,56] if it is assumed that the mean pressure coefficient is constant in the range from $V_1$ to $V_2$ at different pressures. Then

$$\Delta_{\text{s,m}} S_m = \beta_{\text{f}} \Delta V,$$

where $\Delta V = V_2 - V_1$.

If the molecules in the plastic crystalline phases undergo hindered over-all rotation from one preferable orientation $E_{\text{plast,ij}}$ to another having the local minima of energy, we assume that the lowest energy (basic) orientation in a plastic crystal is the one existing in the rigid crystal and the corresponding energy level is $E_{\text{bas}}$. The diagram of the energy levels due to the orientation disorder in plastic crystals is given in figure 18.

Applying equations (25) to (28) to analyze (rigid crystal)-to-(plastic crystal) transition in cyclohexane [34], one obtains:

$$\Delta_{\text{orient}} C_s = 7.6 \text{ J · K}^{-1} \cdot \text{mol}^{-1},$$

$$\Delta_{\text{orient}} S_m = 13.1 \text{ J · K}^{-1} \cdot \text{mol}^{-1}.$$  

On the other hand, $\Delta_{\text{orient}} S_m$ and $\Delta_{\text{orient}} C_s$ can be expressed in terms similar to those used in the Story #2 (equations (10) and (11)):

$$\Delta_{\text{orient}} C_{s,m} = \sum_{i=1}^{n} \frac{\partial x_i}{\partial T} \Delta E_i = \frac{1}{RT^2} \sum_{i=1}^{n} x_i \sum_{j=1}^{n} x_j (\Delta E_i)^2,$$

$$\Delta_{\text{orient}} S_{s,m} = -R \sum_{i=1}^{n} x_i \ln(x_i),$$

where $x_i$ and $x_j$ are mole fractions of molecules with $i$th and $j$th orientations; $\Delta E_i = (E_{\text{plast,ij}} - E_{\text{bas}})$ is the energy difference between the plastic and basic orientations.

A combination of equations (31) to (34) allows determination of the number of orientations, $n$, and the average energy difference, $\Delta E$, simultaneously. It was found for cyclohexane (figure 19), that $n = 7$ and $\Delta E = 2.9 \text{ kJ · mol}^{-1}$.

7. Story #6: data legacy, storage, and delivery

The results described in this story were obtained in close cooperation with my colleagues at the NIST Thermodynamics Research Center; Drs. Rob Chirico, Vladimir Diky, and Chris Muzny, as well as members of the IUPAC Task Group for the project 2002-055-3-024, “XML-based IUPAC Standard for Experimental and Critically Evaluated Thermodynamic Property Data Storage and Capture,” [57] and a number of experts representing both the “data supply” and “data consumption” sides of the data delivery process, including Drs. A.R.H. Goodwin of
There is a great demand for the establishment of efficient global data delivery processes [58]. Until recently, such a process did not exist in the field of thermodynamics. In fact, there are only two well known processes of this nature outside the field of thermodynamics: submission and retrieval of protein structures from the Protein Data Bank (PDB) [59] and submission and retrieval of crystal structures for smaller molecules from the Cambridge Structural Database (CSD) [60].

It is clear that establishing a global data delivery process in thermodynamics is a very challenging task in comparison with the PDB and CSD processes because of the necessity to communicate information related to the hundreds of thermophysical, thermochemical, and transport properties commonly reported. Moreover, communicating these property data is further complicated by the extensive system of thermodynamic metadata (variables, constraints, phases, methods, and uncertainties) required.

Efforts to develop a standard for thermophysical and thermochemical property data exchange [58] were initiated in the early 1980s, reflecting a new trend in data collection through design of electronic databases, which became possible due to the rapid development of computer technology. During 1980s and 1990s, a number of projects, such as CODATA COSTAT [61], Global CAPE Open [62], CODATA IUCOSPED [63], and DIPPR 991 [64], were initiated with the goal of establishing standard for thermodynamic data communications. Though all these projects played a positive role in attracting the attention of the international scientific community to core issues related to thermophysical data standardization, for various reasons none of them resulted in establishing an internationally recognized standard.

In 2002, IUPAC approved project 2002-055-3-024, “XML-based IUPAC Standard for Experimental and Critically Evaluated Thermodynamic Property Data Storage and Capture,” and established a Task Group to carry out the project (Michael Frenkel, USA – Chair; John Dymond, UK; Erich Königsberger, Australia; Kenneth Marsh, New Zealand; Stephen Stein, USA; William Wakeham, UK – members). This project has recently been successfully completed with the establishment of the new IUPAC standard for thermodynamic data communications, ThermoML [65]. The “ThermoML” namespace is now reserved on the IUPAC Website [66].

ThermoML (Markup Language for Thermodynamics) is based on XML (Extensible Markup Language) technology. Advantages of XML technology include its “native” operability, modular nature, assured legacy of the information expressed within the ASCII code system, and transparent readability by both humans and computers [67]. It is also critical that this technology is supported strongly by both the hardware and software industries. The ThermoML structure represents a balanced combination of hierarchical and relational elements. The ThermoML schema structure explicitly incorporates structural elements related to basic principles of phenomenological

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**FIGURE 19.** Orientational contributions to molar saturated heat capacity and entropy in plastic crystalline phase of cyclooctane [54].

Schlumberger Technology Corporation (Sugar Land, TX, USA), J.W. Magee and W.M. Haynes of NIST/Boulder, M. Thijsse of Elsevier (Amsterdam, Netherlands), S. Watanasiri of Aspen Technology (Cambridge, MA, USA), M. Satyro of Virtual Materials Group (Calgary, Canada), M. Schmidt of FIZ CHEMIE (Berlin, Germany), and A.I. Johns of the National Engineering Laboratory (Glasgow, UK). The principal question of this story is:

- How to efficiently communicate thermodynamic property data from “data producers” to “data users”, from “data producers” to “data producers”, and from “data users” to “data users”?

Thermodynamic property data represent a key resource for development and improvement of all chemical process technologies (examples are illustrated by Stories #3 and #4 above). However, rapid growth in the number of custom-designed software tools for engineering applications has created an interoperability problem between the formats and structures of thermodynamic data files and required input/output structures for the software applications. Establishment of efficient means for thermodynamic data communications is absolutely critical for provision of solutions to such technological challenges as elimination of data processing redundancies and data collection process duplication, creation of comprehensive data storage facilities, and rapid data propagation from measurement to data-management system and from data-management system to engineering application. Taking into account the diversity of thermodynamic data and numerous methods for their reporting and presentation, standardization of thermodynamic data communications is very complex.
thermodynamics: thermochemical and thermophysical properties (equilibrium and transport), state variables, system constraints, phases, and units. Meta- and numerical data records are grouped into ‘nested blocks’ of information corresponding to data sets. The structural features of the ThermoML metadata records ensure unambiguous interpretation of numerical data and allow data-quality control based on the Gibbs Phase Rule. ThermoML covers essentially all experimentally determined thermodynamic and transport property data (more than 120 properties) for pure compounds, multicomponent mixtures, and chemical reactions (including change-of-state and equilibrium) [68].

ThermoML consists of four major blocks, as shown in figure 20: Citation, describing the source of the data; Compound, characterizing the chemical system; PureOrMixtureData, providing information for meta- and numerical data for a pure compound or multicomponent mixture; and ReactionData, providing information for meta- and numerical data for a chemical reaction with thermodynamic state change or in a state of chemical equilibrium. Definitions and descriptions of all quantities related to the expression of uncertainty in ThermoML [69] conform to the Guide to the Expression of Uncertainty in Measurement (ISO, 1993) [70]. In order to implement this extension of ThermoML, an interpretation of the Guide to the Expression of Uncertainty in Measurement for the field of thermodynamics was made. All properties are characterized with the most comprehensive measure of data quality, the combined expanded uncertainty. In addition, there is a provision for the properties, variables, and constraints to be characterized with the commonly used measures of precision such as repeatability, specifications of measuring device, and deviation from a fitted curve (figure 21). ThermoML currently covers all major data types: experimental, predicted, and critically evaluated. Data prediction types encompass all major types of the thermophysical and thermochemical data prediction methods (figure 22), such as group contribution, correlation, corresponding states, statistical mechanics, empirical or semi-empirical quantum chemical methods, molecular dynamics, and ab initio [71]. Three principal types of critical data evaluation are repre-

FIGURE 20. ThermoML: major structural blocks [68].

FIGURE 21. ThermoML: specification of uncertainties [69].
presented in ThermoML: (1) single property critical data evaluation; (2) multiple property critical data evaluation; and (3) critical data evaluation performed with the use of an equation of state (figure 23). Communication of the parameters of regression equations was accomplished (figure 24) by linking the ThermoML-EquationDefinition schema to MathML [72] (The Mathematical Markup Language). Schema elements in ThermoML for equation representation provide for storage of the equation components required for the specific equation definition. The nature or scope of the equations is not restricted in any way.

The role of ThermoML in thermodynamic data communications is reflected through its impact on development of efficient chemical engineering applications, including chemical process design; provision of new capabilities for data delivery from “data producers” to “data users”, from “data producers” to “data producers”, and from “data users” to “data users”; establishment of software “tools” such as NIST Guided Data Capture Software [73], designed to improve the quality of published experimental data; as well as new mechanisms for development of a variety of data products serving the scientific and engineering communities. The development of ThermoML and the software infrastructure supporting it has led to a unique cooperation (figure 25) between five major journals in the field (Journal of Chemical and Engineering Data [75], The Journal of Chemical Thermodynamics [76], Fluid Phase Equilibria [77], Thermochimica Acta [78], and International Journal of Thermophysics [79], three scientific publishers (ACS, Elsevier, and Springer), NIST, IUPAC, and leading chemical process design companies [65].)

8. Story #7: from data to information in one gigantic step

The late Dr. Randolph Wilhoit of Texas A&M University (College Station, TX, USA) and Prof. Ken Marsh of the University of Canterbury (Christchurch, New Zealand) were the inspiration for the efforts encompassing this story. The results described in this story were obtained in close cooperation with my colleagues at the NIST.
Thermodynamics Research Center, Drs. Rob Chirico, Vladimir Diky, Chris Muzny, Qian Dong, and Xinjian Yan. The principal question of this story is

- How to generate thermodynamic critically evaluated data on-demand?

Traditionally, critical data evaluation is an extremely time- and resource-consuming process, which includes extensive use of labor in data collection, data mining, analysis, fitting, etc. Because of this, it must be performed far in advance of a need within an industrial or scientific application. In addition, it is quite common that by the time the critical data-evaluation process for a particular chemical system or property group is complete (sometimes after years of operation of data evaluation projects involving highly skilled data experts), it must be reinitiated because significant new data have become available. This type of slow and inflexible critical data evaluation can be defined as "static." These shortcomings have become magnified dramatically within the last 5 to 10 years due to the significant increase in the rate of publication of experimental and predicted thermodynamic data that need to be analyzed during the critical data evaluation process.

To address the weaknesses of static evaluations, the concept of a dynamic data evaluation system was developed at the Thermodynamics Research Center [58,80,81]. This concept requires large electronic databases capable of storing essentially all experimental data known to date with detailed descriptions of relevant metadata and uncertainties. The combination of these electronic databases with expert-system software, designed to generate automatically recommended data based on available experimental data, leads to the ability to produce critically evaluated data dynamically or "to order" (figure 26). This concept contrasts sharply with static critical data evaluation, which must be initiated far in advance of a particular need. The dynamic data evaluation process dramatically reduces the effort and costs associated with anticipating future needs and keeping static evaluations current.

Critically evaluated data produced through the deployment of the dynamic data-evaluation concept can rigorously be characterized with their quality assessments. That, in turn, provides the ability to propagate reliable data-quality limits to all aspects of chemical process design. Implementation of the dynamic data evaluation concept consists of the solution of a number of major tasks: (1) design and development of a comprehensive database system structure based on the principles of physical chemistry and capable of supporting a large-scale data entry operation for the complete set of thermophysical, thermochemical, and transport properties for chemical systems, including pure compounds, binary mixtures, ternary mixtures, and chemical reactions; (2) development of software tools for automation of the data-entry process with robust and internally consistent mechanisms for automatic assessments of data uncertainty; (3) design and development of algorithms and software tools to assure quality control at all stages of data entry and analysis; (4) development of algorithms and computer codes to implement the stages of the dynamic data-evaluation concept; (5) development of algorithms to implement, target, and apply prediction methods depending on the nature of the chemical system and property, including automatic chemical structure recognition mechanisms; and (6) development of procedures allowing generation of output in a format suitable for application in major commercial simulation engines for chemical-process design.
The ThermoData Engine (TDE) [82,83] software incorporates all major stages of the concept implementation including data retrieval, grouping, normalization, sorting, consistency enforcement, fitting, and prediction. The SOURCE data system [84,85] is used in conjunction with TDE as the comprehensive storage facility for experimental thermophysical and thermochemical property data (figure 27). In addition, the NIST/TRC Ideal Gas Database [86] is used as a source of thermodynamic property data in the ideal-gas state.

Version 1.0, released in 2005, is limited to thermodynamic properties of pure compounds. The software architecture emphasizes enforcement of consistency between related properties (including those obtained from predictions), assumes an imperfect source of original data, provides for flexibility in the selection of default data models.
depending on the particular data scenario, incorporates a large variety of models for secondary fitting, and allows saving critically evaluated data in the ThermoML format. The latter assures compatibility of the TDE software with any engineering application equipped with a ThermoML software “reader.” The properties of the pure compounds are subdivided into four property groups: (1) phase diagram properties, (2) volumetric properties, (3) energy-related properties, and (4) other properties, including transport properties. The general algorithm of the TDE is illustrated in figure 28. Figure 29 illustrates enforcement of the thermodynamic consistency between vapor pressure, sublimation pressure, and the triple point for pyrrole [83].

**FIGURE 29.** Example of the enforcement of thermodynamic consistency by ThermoData Engine between vapor pressure, sublimation pressure, and triple point data for pyrrole [83]: (a) vapor pressure and sublimation curve without enforcement of consistency at $T_{tp}$; (b) the same data scenario with automatic enforcement of thermodynamic consistency in terms of value and relative slope at $T_{tp}$. The relative slopes are directly related to the enthalpy of the phase transition ($\Delta_{\text{melt}}H$ for the melting transition).
Full implementation of the dynamic data evaluation concept requires a continuous update of the data storage facility that can be delivered to the computer of a local user through a multi-tier Web-dissemination architecture, as shown in figure 30. The TDE software can communicate with chemical process simulation engines via ThermoML to provide critically evaluated data on demand for analyses of feasibility for conceptual processes and the improvement of existing chemical and biochemical industrial processes (figure 31) [58].

Future enhancements of TDE will include incorporation of computational tools for generating equations of state on-demand, depending on the data "scenario." Longer-term plans include expansion of the TDE to critical data evaluation for binary and ternary mixtures, as well as for chemical reactions.

![Diagram of multi-tier architecture for Web dissemination](image)

**FIGURE 30.** Multi-tier architecture for Web dissemination [58,79].

![Diagram of global data delivery and communication process linking ThermoData Engine and chemical process simulation applications](image)

**FIGURE 31.** Global data delivery and communication process linking ThermoData Engine and chemical process simulation applications [58].
Implementation of the dynamic data evaluation concept provides unprecedented opportunities in validating new experimental thermodynamic property data. Indeed, the dramatically increased rate of publishing experimental thermodynamic property data has led in many instances to situations when published data are either grossly erroneous or even inconsistent with the fundamental laws of nature. This is despite the peer-review process. This trend also magnifies the problem, among journals publishing scientific and technical data, of an absence of consensus concerning the requirements placed on authors for characterization of overall data quality and reliability. Even in reporting experimental property data with a relatively simple metadata infrastructure, such as critical temperature, comprehensive uncertainty analyses currently remain rare, particularly with regard to consideration of contributions arising from sample impurities [87]. The ThermoData Engine technology provides an opportunity to use the whole body of thermodynamic knowledge available to date to be used in validating newly obtained experimental data.

Another principal venue of deploying ThermoData Engine is related to the design of software tools for strategic measurement planning. Development of these tools would lead to elimination of unjustified redundant measurements, identification of "gaps" in the existing measurement space, as well as determination of key measurements for validation of new computational and predictive techniques, and would, therefore, play a central role in enhancing the existing knowledge base for industrial applications, with ensuing enormous potential economic benefits in the development of new chemical processes.

9. Concluding remarks

I hope the seven stories I selected for my lecture illustrate a part of the power and beauty of phenomenological and statistical thermodynamics, and the unique role that thermophysical and thermochemical property data play in science and engineering.

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