Deciphering the hidden Pascal code of Guggenheims quasichemical model. Overcoming computational limitations by use of Pascal's triangle

Jo Fenstad

Abstract   A general description is given of the mathematical modelling of physical properties of liquid mixtures, with an emphasis on the early progress in mathematical representation of mixtures' thermodynamics. The core issue is employing long polynomials to represent mixing data accurately, without having to optimise a large number of independent parameters. This is for instance done by deriving the long polynomials from explicit (analytical) models with few independent parameters. It is shown that this field evolved not by gradual changes in model complexity and accuracy, but rather in bursts, followed by pausing for several years or decades whenever researchers hit computational or conceptual limitations. One such limitation that still exists is the Taylor expansion of the above mentioned analytical models. This article presents a novel use of Pascal's triangle that turns this computationally "hard" problem into a trivial iterative procedure, suitable for standard office spreadsheets. The process of transforming this hard problem into a soft problem may be described as *deciphering*. The present author conjectures that for every parametric function for which a polynomial expansion can be made, there is a corresponding coefficient pattern involving Pascal's triangle and/or other binomial sequences and matrices.

1 Introduction

The history of modelling the physical properties of liquid mixtures stretches more than 100 years back in time, and from the start the prime focus was on binary mixtures (i.e. two liquids), since these were the first to be studied experimentally, and

J. Fenstad (✉)
Department of Materials Science and Metallurgy, University of Cambridge, Cambridge, CB2 3QZ, UK
e-mail: fenstadj@yahoo.co.uk

corresponding models could be kept relatively simple. To bring more system into this, the mixing ratios would be given as atomic (or molecular) fractions, and the sum of all molecular fractions is always one. In the early days, the letter "n" was typically used to denote fractions, while modern terminology prefers the letter X. Thus, for mixture of liquids A + B, the fractions $X_A + X_B = 1$, and the x-axis is by convention reserved for the variable X_B over the range from 0 (pure A) to 1 (pure B).

Gradually, all aspects of mixing became subject to studies; densities, viscosities, electrical conductivities, heat-of-mixing, vapour pressures, etc. These are customarily assigned to the y-axis. For the simplest cases it was found that the property in question varied linearly with X_B, assuming the value corresponding to pure A and pure B at fraction 0 and 1, respectively. This gave rise to a number of "laws" that simply reflect this rather mundane observation, which in many respects might serve as a sufficient definition of "ideal behaviour". And the linear approximation is sufficiently accurate for many purposes. However, as experimental studies gradually became more precise, it was found that some properties of some mixtures would deviate from the linear relationship. In it's simplest form the deviation would form a symmetrical "∪" (or "∩"), but it could also exhibit asymmetrical shape. Any deviation (from linearity) needed to be modelled separately, thus giving rise to the concept "excess mixing property", which is essentially the observed deviation from the linear "ideality" (Fig. 1), i.e. the observed property as function of atom fraction, minus the weighted average of the properties of the two pure components.

Before proceeding, one complication should be pointed out: A mixture which composition dependency is linear with respect to e.g. electrical conductivity will not be linear with respect to the inverse property (resistivity), and *vice versa*. It is not immediately obvious which of them (conductivity or resistivity) to choose, and this type
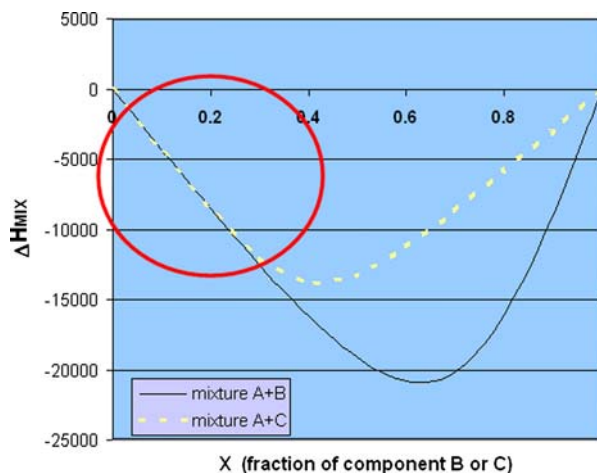

Fig. 1 Two imagined mixtures A + B and A + C drawn in order to explain why polynomial approximations expanded around $X = 0$ may be preferable to explicit Quasichemical Model equations: The parameters of the explicit equations are very different for these two mixtures, thus giving no indication that they are very similar in the region $X = 0.0$ to $X = 0.3$. But the two polynomials expanded around $X = 0$ will exhibit coefficients (*for the lower terms*) that immediately reveals the similarity (*circle*)

of dilemma has led to some scientific debate [1]. The convention is to describe the property on a form that correspond to thermodynamic ideality (or to any other measure for ideality at the atomic level). It should be noted finally, that for a selected few mixing properties (i.e. entropy ΔS_{MIX} and Gibb's energy ΔG_{MIX}), the thermodynamic ideality does not generate a linear "baseline" but a curved one. But for the vast number of mix properties, the ideal "baseline" is linear, and the curved deviation can be analysed in the form in which it is commonly available. In this respect, the mixing property heat-of-mixing (ΔH_{MIX}) is particularly uncomplicated, since the ideal "baseline" is flat (zero) for all molecular fractions, i.e. the heat-of-mixing and the excess-heat-of-mixing are identical.

Approaching from the fundamental side, Herzfeld and Heitler [2] used atomistic considerations to derive a primitive symmetrical quasichemical model that effectively treats the mixing entropy and the mixing enthalpy separately. This model, which successfully accounted for the symmetrical U shape of the heat-of-mixing for a large number of binary mixtures, has later been inappropriately attributed to Hildebrand, whose contribution was merely to coin a term ("Regular solutions") for mixtures that fit Herzfeld's model, and to assemble and summarise some empirical case evidence. This case evidence suggested that Herzfeld's "regular" model is fulfilling for mixtures of two fairly similar liquids, while the "ideal" model (when applied to heat-of-mixing) required the two liquids to be near identical. While the 2nd order polynomial derived from Herzfeld's model represents no computational challenge, problems were to emerge when Guggenheim [3–6] took the obvious next steps, which were to generate successive model modifications that account for the heat-of-mixing of increasingly dissimilar liquids; the ones that tend to exhibit V shapes. These shapes are not easily dealt with by using polynomials, which is why other (analytical) formulae came to prominence. This article will show how polynomials can be generated for these cases of V shaped deviations from ideal mixing, but will limit the discussion to the simpler case of symmetrical V shapes. The more complicated case of asymmetrical V shapes is to be discussed in an upcoming article.

Between 1935 and 1940, with contributions from Rushbrooke [4] and Fowler, Guggenheim came up with a set of refined "quasichemical" thermodynamic formulae, where the subtle interactions between heat-of-mixing and entropy had been taken into account [5]. Like Herzfeld's formulae, this model was derived from atomistic considerations of perfect mix-crystals under constant volume assumptions, but also employed approximations from gas theory (the "lattice gas" approximation). This led to a slightly schizophrenic model, which on its own could not make quality predictions for the mixed crystals from which it was derived, and also was not really relevant for gases. However, if one was willing to accept empirical use of these formulae, e.g. let the parameter for "atomic coordination" assume impossible values like 50, then the Guggenheim formulae had an empirical potential for describing liquid mixtures with unprecedented high precision. In light of the potential for high precision, Guggenheims rather humble term for his model, "the first order approximation", may in retrospect seem understated or even paradoxal, since for the next 40 years (or so) all work derived from his model would be approximations to his "approximation".

In the following decade or two, many scientists with interest in theoretical (mathematical) chemistry pursued the empirical potential of Guggenheim's so-called "first

order approximation" formulae, by deriving Taylor polynomial expansions (Eq. 10). One particular and important advantage of using approximate polynomials it that polynomial empirism is readily extended to ternary and higher order mixtures (i.e. multi-component liquids). In this era, scientific computers (of any type) were absent, pocket calculators had not been invented, so available computational devices were restricted to pen, paper and slide rules. Thus, scientists [7] were bound to embark on a lenghty pencil-and-paper Taylor expansion journey; this was straightforward but "increasingly tedious and complicated" [8]. In fact, this tedious task turned out to be outright mountainous, and work eventually petered out; from the late 1950 s and onwards, researchers would settle for using only the first three or so polynomial terms. By the 1960 s, a technique was developed and flourished briefly [9], whereby the mixture's composition range (fractions between 0 and 1) was divided into several smaller ranges that were modelled separately. This kind of empirism was so far removed from the direction Guggenheim and Herzfeld must have envisioned, that one can definitely say the development had come "off the tracks".

Since the late 1970 s, computational resources became increasingly available and affordable to the scientific communities, and by early 1990 they were available even to students, and were about to permeate and eventually become ubiquitous within all scientific disciplines. There was (and is) still development on Quasichemical Modelling (QM), which was now the common term for derivatives of Guggenheim's "first approximation", and also a lot of developments on the use of polynomials for modelling the effects of mixing. It therefore seems a bit surprising that no progress was made regarding Taylor expansions of the symmetrical quasichemical formulae of Guggenheim.

2 Formulae to be studied

To clarify this absense of progress, this author undertook a computational Taylor expansion, employing software that could do exact algebraic calculations (including integration and derivation) in seconds, that would have taken days or months back in the 1940 s. The goal was to generate a large polynomial for Guggenheims formula for the two mixing deviations known as *excess Gibbs free energy of mixing* (ΔG^E_{MIX}), and the *heat-of-mixing* ΔH_{MIX}. For reasons of formulaic clarity, this article will deal with the quantities $\Delta G^E_{MIX}/zRT$ and $\Delta H_{MIX}/zRT$. For the purposes of this article, zRT is just a scaling constant. Guggenheims's $\Delta G^E_{MIX}/zRT$ and $\Delta H_{MIX}/zRT$ are similar in that (for specific parameter values) both can exhibit those difficult V shapes, the latter typically more than the former. But from a computational perspective, the immediate and seemingly easier task was to expand a related quantity known as the *partial molar free energy* of liquid B, for which Guggenheim's Quasichemical Model provided the following explicit ("exact") formula (written in modern notation)

$$\frac{\Delta \overline{G}^E_B}{zRT} = \ln \sqrt{\frac{\beta - 1 + 2X_B}{(\beta + 1) X_B}} \tag{1}$$

This $\frac{\Delta \overline{G}_B^E}{zRT}$ is proportional to the natural logarithm of *the activity coefficient* for component B, and is derived from the Gibbs free energy of mixing (ΔG_{MIX}^E) by the following universally valid relation

$$\frac{\Delta \overline{G}_B^E}{zRT} = \Delta G_{MIX}^E/zRT + (1 - X_B)\frac{\partial \Delta G_{MIX}^E/zRT}{\partial X_B} \tag{2}$$

Fairly obviously, the *partial molar free energy* is defined for both liquid components (A and B), and the corresponding quantity for component A is (conveniently) given by substituting A for B in Eq. 2, to obtain

$$\frac{\Delta \overline{G}_A^E}{zRT} = \Delta G_{MIX}^E/zRT - X_B\frac{\partial \Delta G_{MIX}^E/zRT}{\partial X_B} \tag{3}$$

Thus, Guggenheim's model is not only physically symmetric, but also formalistically symmetric. Once polynomial expansions have been made for these two quantities, using Eq. 1, the polynomial formula for the excess Gibbs free energy of mixing can (in principle) be made explicit by means of the following much simpler formula

$$\Delta G_{MIX}^E/zRT = X_B\frac{\Delta \overline{G}_B^E}{zRT} + (1 - X_B)\frac{\Delta \overline{G}_A^E}{zRT} \tag{4}$$

but in practice, formula this Eq. 4 does not always work well with approximate polynomials. Special precautions may be needed to counteract truncation errors, which arise when high order terms are omitted. This will be detailed in an upcoming article. The term β is a function of composition and the "ordering" parameter λ

$$\beta = \sqrt{1 + 4(1 - X_B)X_B\lambda} \tag{5}$$

Thus, $\frac{\Delta \overline{G}_B^E}{zRT}$ is a function of variable X_B, with only one parameter (λ). Moreover, a polynomial expansion of $\frac{\Delta \overline{G}_B^E}{zRT}$ (and consequently its parent $\Delta G_{MIX}^E/zRT$) may have any number of polynomial terms but is still defined only by X_B and the λ parameter. Note that when the ordering parameter λ approaches -1 (which happens for many real mixtures) then the two deviations (ΔG_{mix}^E and ΔH_{mix}) both begin to exhibit the challenging V shapes. Obviously, each of the Eqs. 1–5 have an analogue involving ΔH_{mix} (instead of ΔG_{mix}^E), such as

$$\frac{\Delta \overline{H}_B}{zRT} = \Delta H_{MIX}/zRT + (1 - X_B)\frac{\partial \Delta H_{MIX}/zRT}{\partial X_B} \tag{6}$$

3 The wagner polynomial formalism

The particular interest in Taylor expanding both Eq. 1 and its heat-of-mixing equivalent Eq. 13 around $X_B = 0$ (i.e. $X_A = 1$) arise partially because $X_A = 1$ was the basis

of the widespread polynomial description of mixtures' thermodynamics established by Wagner since the early 1950 s. Unlike Guggenheim's model, the empirical Wagner polynomials are inherently asymmetric; since one component is defined as solvent, and all other components as solutes. This "Wagner formalism" [10] was invented and intended for steel and other multi-component metals (alloys) where one component (the solvent metal) dominates. The composition of the alloys was naturally defined by the amount of alloying elements, thus for the pure solvent $X_B = X_C = X_D = \cdots = 0$. One advantage of the Wagner polynomial formalism (and derivated formalisms) is illustrated in Fig. 1. In this Figure, two imagined mixtures A+B and A+C behave very similarly close to the pure solvent (component A), but the two mixtures become very different when the amount of A decreases. In this case, the parameters of the explicit Quasichemical equations are very different for these two mixtures, thus giving no indication about their similarity between $X = 0.0$ and $X = 0.3$ (circle). But two polynomial approximations expanded around $X = 0$ will exhibit coefficients (for the lower terms) that immediately reveals the similarity.

The applicability of Wagner formalism is strictly limited to low-alloyed metals, but was later extended to higher alloys and other concentrated mixtures, but this process saw some disarray in the 1970 s and fell short of accurate prediction for all possible mixtures, which remains the ultimate goal, to this day. Instead, various ways of re-formulating the polynomials (and there are numerous different ways) were explored, usually to make some specific calculation more straightforward, but invariably at the expense of slowing down some other type of calculation. Despite this, the polynomial approximations remained attractive for modelling mixtures due to the potentially large benefits and the ever increasing availability of computing resources. However, effective penetration of the polynomial methods into the realms of high-accuracy multi-component mixture prediction did not gain momentum until the late 1980 s, when Pelton & Bale's invention of the "coefficiently efficient" formalism UIPF[1] [11] and Pelton & Blander's revival of the (explicit) Quasichemical Models [12] fortuitously coincided with the advent of students desktop computing from the early 1990 s onwards.

4 The computations

During the 1990 s, this author undertook a computational Taylor expansion, employing Maple V software on early Intel pentium PC's. This software can do exact algebraic calculations, including integration and derivation, in seconds, that would have taken days or months back in the 1940 s. These computations were repeated recently, with state of the art computers.

The author applied the above equation by substituting Eq. 5 into Eq. 1, and Taylor expanding the result around $X_B = 0$, thus the following six polynomial terms in X_B were generated (from Guggenheim's formula) before the capabilities of the author's PC were exhausted.

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[1] As it is known today. Its unique characteristic is that it makes super-efficient use of its coefficients. Unlike all other polynomial formalisms, UIPF coefficients have the same name and same value regardless of which component is defined as the "solvent". It's very convenient, like keeping your phone number when you switch network supplier.

$$\frac{\Delta \overline{G}_B^E}{zRT} = \ln \sqrt{1+\lambda} +$$

$$X_B \cdot \frac{-1}{1} \cdot \lambda +$$

$$X_B^2 \cdot \frac{1}{2} \left(3\lambda^2 + \lambda\right) +$$

$$X_B^3 \cdot \frac{-1}{3} \left(10\lambda^3 + 6\lambda^2\right) + \qquad (7)$$

$$X_B^4 \cdot \frac{1}{4} \left(35\lambda^4 + 30\lambda^3 + 3\lambda^2\right) +$$

$$X_B^5 \cdot \frac{-1}{5} \left(126\lambda^5 + 140\lambda^4 + 30\lambda^3\right)$$

The three last terms were novel, going further than any previously published series of terms derived by expanding polynomials of X_B. The above expression contains the following sub-series that is computationally hard to expand further:

$$\lambda +$$
$$\left(3\lambda^2 + \lambda\right) +$$
$$\left(10\lambda^3 + 6\lambda^2\right) + \qquad (8)$$
$$\left(35\lambda^4 + 30\lambda^3 + 3\lambda^2\right) +$$
$$\left(126\lambda^5 + 140\lambda^4 + 30\lambda^3\right)$$

Subsequent attention was focused on this sub-series. One can clearly see indications of a pattern, yet the coefficients for each λ^n rapidly become unpredictable as n increases, and no particular pattern immediately comes to mind as being overwhelmingly convincing. For brevity, we may re-write this series as a matrix of the coefficients from each term (Fig. 2).

The author believed that repeating the Taylor expansion on a larger computer system would add more coefficients to this matrix. Such attempts led to the disappointing conclusion that the computational limitation was in the software itself. The larger computer system calculated polynomial terms more swiftly, but the software was unable to allocate enough memory to proceed beyond six polynomial terms. Other QM formulae, such as Guggenheims formula for the Enthalpy of mixing, would yield one or two terms more, but again the memory capabilities of Maple V would inevitably become exhausted.

$$
\begin{matrix}
126 & 35 & 10 & 3 & 1 \\
 & 140 & 30 & 6 & 1 \\
 & & 30 & 3 &
\end{matrix}
$$

Fig. 2 Matrix of coefficients from each term of the computationally hard part of the Taylor polynomial expansion for Eq. 1 around $X_B = 0$

Part of the problem is that expanding Guggenheims formula for $\frac{\Delta \overline{G}_B^E}{zRT}$ around $X = 0$ lead to 0/0 expressions.

$$
\begin{aligned}
f^{(0)} &\equiv \frac{\Delta \overline{G}_B^E}{zRT} = \ln \sqrt{\frac{\beta - 1 + 2X_B}{(\beta + 1) \ X_B}} \\
f^{(1)} &\equiv \frac{\partial f^{(0)}}{\partial X_B} \\
f^{(2)} &\equiv \frac{\partial f^{(1)}}{\partial X_B} \\
&\cdots \\
f^{(n)} &\equiv \frac{\partial f^{(n-1)}}{\partial X_B}
\end{aligned}
\tag{9}
$$

which are required for the Wagner type Taylor polynomial expansion

$$
\begin{aligned}
\frac{\Delta \overline{G}_B^E}{zRT} &= f^{(0)}(x_B = 0) + X_B \frac{f^{(1)}(x_B = 0)}{1!} + X_B^2 \frac{f^{(2)}(x_B = 0)}{2!} + \cdots \\
&\quad + X_B^n \frac{f^{(n)}(x_B = 0)}{n!} + \cdots
\end{aligned}
\tag{10}
$$

To circumvent this, MAPLE was set to calculate the limit (of these expressions) as $X \to 0$. This seems to require exponentially larger memory as the order of the desired term is increased. Thus, even the leaping progress in computer and software capability during the 1990 s could only add three extra terms beyond the three that had been known for decades.

5 Pascal's triangle

As seen in the displayed polynomial (7), the Taylor expansion of various formulae generates arrays of coefficients. As is well known, such coefficient arrays often presents a pattern. Two well known examples are the expansion of the e^X function (around $X = 0$)

$$
e^X = 1 + \frac{X}{1!} + \frac{X^2}{2!} + \frac{X^3}{3!} + \frac{X^4}{4!} + \cdots .
\tag{11}
$$

and the $\ln(X)$ function (around $X = 1$)

$$
\ln(X) = (X - 1) - \frac{(X - 1)^2}{2} + \frac{(X - 1)^3}{3} - \frac{(X - 1)^4}{4} + \cdots .
\tag{12}
$$

which both yield very obvious coefficient patterns. With parametric functions such as Guggenheims's, patterns are likely to be more complex (and less obvious), and it is no

```
 1   1   1   1   1   1
 6   5   4   3   2   1
15  10   6   3   1
20  10   4   1
15   5   1
 6   1
```

Fig. 3 Matrix of the first (lowest) numbers of the remarkably versatile Pascal triangle

surprise that the three terms that [9] expanded from Guggenheim's model, were too few to indicate a pattern of coefficients.

However, the three additional terms identified by the initial Taylor expansion for the present article, provided just enough coefficients to reveal a faint trace of a pattern, but not enough to identify it with any certainty. Thus, further efforts were justified. But at this point, there was no obvious cure for the software limitations that halted the computational polynomial expansion.

Thus, after reaching a dead end with Guggenheim's ΔG^E_{MIX} formula, present Eq. 2 was instead applied to Guggenheim's ΔH_{MIX} formula, to generate a derivative quantity (analogous to Eq. 1), being suitable for Taylor expansion. This derivative quantity, also defined by the variable X_B and only one non-scaling parameter (λ), was much more complicated in appearance than (1). Despite this apparent complexity, the Taylor expansion proceeded at blazing speed and yielded 14 polynomial terms before the expected slow-down, providing about 60 coefficients. When these were arranged in a matrix of coefficients, a pattern emerged : Row after row was compellingly familiar, each having an unmistaken counterpart within the Pascal's triangle, only mildly obscured by a factorial scaling factor. Apparently, this triangle (Fig. 3) was first described [13,14] by indian mathematician Pingala, and much later (around year 1100) studied by persians Karaji and Khayyam, and chinese Yanghui. Later, Chinese Zhu Shijie provided the most famous early illustration of the triangle. In the 1600s, frenchman Blaise Pascal demonstrated its versatility, by applying it to successfully develop the then novel field of probability theory.

6 Deciphering the polynomial "code" within Guggenheim's $\frac{\Delta \overline{G}^E_B}{zRT}$

In short, from the above calculations the present author concluded that Pascal's triangle was an "ingredient" in the pattern obtained from the coefficient array yielded by the Taylor expansion. The obvious next step was to "divide" the coefficient matrix with the Pascal matrix, or (in more correct terms) perform an *array division*. i.e. divide each element of the coefficient matrix by the corresponding element of the Pascal matrix. Once this was done, a rather simple pattern emerged, and subsequent terms for this polynomial could easily be predicted, using any spreadsheet software, requiring only the most basic functionality. More importantly, the author had learnt how to decipher the disguised patterns.

$$126 \quad 35 \quad 10 \quad 3 \quad 1$$
$$35 \quad 10 \quad 3 \quad 1$$
$$10 \quad 3$$

Fig. 4 Matrix of coefficients from Fig. 2, after each term is divided by the corresponding term of the Pascal matrix. The resulting pattern is comparatively trivial, as it spells out another sequence hidden within Pascal's triangle

Using this same approach on the original six polynomial terms expanded from Eq. 1 immediately unveiled an unambiguous pattern that had been only vaguely indicated by the original matrix.

Intriguingly, the 1, 3, 10, 35, 126,.. binomial series (Fig. 4) can itself be derived from the versatile Pascal triangle, in the same way as the "higher" order Fibonacci series [15], and the nth term of the series is given by $(2n-1)!/[n!\,(n-1)!]$. The sequence, which is also known as the binomial coefficient "$2n-1$ over $n-1$" [16], is a convolution of the Catalan sequence and the central binomial sequence [17], and it appears in a multitude of other combinatorial situations, such as polygon mathematics [18].

Following this discovery, it is a trivial task to derive (say) 100 polynomial terms for Eq. 6 by literally any spreadsheet software. It is also conceptually straightforward to show that a polynomial with terms derived from this binomial series (and Pascal's triangle), agrees with the corresponding "exact" expression (Eq. 1) from Guggenheim to any desired accuracy, provided that a sufficient number of terms were included. The coefficients for the first ~ 15 polynomial terms of the expansion of Eq. 1 are identified by means of an OpenOffice CALC spreadsheet shown in Fig. 5.

7 An accidental discovery

To summarise the present discovery, Eq. 2 was applied to Guggenheim's ΔH_{MIX} formula, after which a Taylor expansion yielded a high number of terms, forming a very obvious pattern, from which Pascal's triangle was identified as the deciphering "key", allowing identification of the polynomial coefficients.

Subsequent deciphering of the polynomial patterns emerging from (1) (i.e. Eq. 2 applied to Guggenheim's ΔG_{MIX}^{E} formula) was now straightforward. However, it was later found that when applying Eq. 2 to Guggenheim's ΔH_{MIX} formula, a typing error had been made. Thus the Taylor expansion produced a polynomial that is irrelevant for Guggenheims model. The Taylor expansion was therefore repeated, using the correct formula (Eq. 13), this time producing fewer coefficients and no obvious pattern. Thus, a philosophical paradox has occured ; if that typing mistake had not been made, then the role of Pascal's triangle as a deciphering "key" would probably not have been discovered. Thus, this author encountered the same kind of accidental discovery that repeatedly pushes science forward. It is well known that coincidents and sometimes accidents leads to scientific progress in experimental disciplines such as chemistry. But there are till now few (if any) published cases of progress occurring this way within the more mathematically oriented disciplines, such as modelling.

Fig. 5 Matrix of coefficients for each term of the computationally hard part of the Taylor polynomial expansion of Eq. 1. Compare upper part with Fig. 2. The numbers shown here identifies 14 polynomial terms, but this matrix may be extended with copy and paste operations, allowing hundreds of additional terms to be identified

8 Deciphering the polynomial "code" within Guggenheim's $\frac{\Delta\overline{H_B}}{zRT}$

When the abovementioned mistake was discovered, the deciphering was repeated, by first Taylor expanding Eq. 13, which is derived by applying Eq. 2 correctly to the heat-of-mixing function from Guggenheim

$$
\frac{\Delta\overline{H_B}}{zRT} = \ln\sqrt{1+\lambda}\,\frac{(1-x_B)^2}{\left(1+\sqrt{1+4x_B(1-x_B)\lambda}\right)^2}
$$
$$
\times\left[2\frac{\sqrt{1+4x_B(1-x_B)\lambda}+1+2x_B\lambda}{\sqrt{1+4x_B(1-x_B)\lambda}}\right] \tag{13}
$$

This time, about 10 polynomial terms were analytically identified before computations slowed down. The coefficient matrix from these terms suggested a pattern that was significantly more complex than patterns found in any of the two previous cases.

$$
\frac{\Delta\overline{H_B}}{zRT} = \ln\sqrt{1+\lambda}\left[1 - x_B\cdot(2\lambda+2) + x_B^2\cdot\left(6\lambda^2+7\lambda+1\right)\right.
$$
$$
- x_B^3\cdot\left(20\lambda^3+28\lambda^2+8\lambda\right) + x_B^4\cdot\left(70\lambda^4+115\lambda^3+48\lambda^2+3\lambda\right)
$$
$$
- x_B^5\cdot\left(252\lambda^5+476\lambda^4+260\lambda^3+36\lambda^2\right)
$$
$$
+ x_B^6\cdot\left(924\lambda^6+1974\lambda^5+1330\lambda^4+290\lambda^3+10\lambda^2\right)
$$
$$
- x_B^7\cdot\left(3432\lambda^7+8184\lambda^6+6552\lambda^5+1960\lambda^4+160\lambda^3\right)
$$
$$
+ x_B^8\cdot\left(12870\lambda^8+33891\lambda^7+31416\lambda^6+11970\lambda^5+1610\lambda^4+35\lambda^3\right)
$$
$$
\left. - \cdots\right] \tag{14}
$$

In fact, it seems so complex (Fig. 6) that this author might not have detected the presence of Pascal's triangle within this matrix. But what had been learnt in the earlier runs could not be unlearnt, and the author now assumed that the same "key" and procedure would hold with only slight changes. By duly dividing with respect to the Pascal matrix, the following matrix emerges (Fig. 7)

While this is still not a trivial matrix, it looks a lot more orderly than its parent. Although its asymmetry makes it much less orderly than the very simple matrix (Fig. 4) that was derived from Eq. 1, the progression of the above series' are still entirely logical and unambiguous. An OpenOffice CALC spreadsheet is shown in Fig. 8, identifying the coefficients for the first ~20 polynomial terms of the expansion of Eq. 13.

The uppermost sequence of Fig. 7 increases monotonously as (1, 6/3, 6, 20, 210/3, ..) and is defined by $a_0 = 1$ and the recursive formula $a_n = a_{n-1}(4n-2)/n$ where n is (1, 2, ..). The lowermost sequence of Fig. 7 is (1, 9/3, 10, 35, ..) and is given

					1
				2	2
			6	7	1
		20	28	8	
	70	115	48	3	
252	476	260	36		
1974	1330	290	10		
6552	1960	160			
11970	1610	35			

Fig. 6 Matrix of coefficients from each term of the computationally hard part of the Taylor polynomial expansion (around $X_B = 0$) for Eq. 13, as derived by applying Eq. 2 to Guggenheims model for the heat-of-melting. The inherent numeric sequences of this figure are not obvious

					1
				6/3	1
			6	7/3	1
		20	7	8/3	
	210/3	23	8	9/3	
252	238/3	26	9		
282	266/3	29	10		
312	294/3	32			
342	322/3	35			

Fig. 7 Matrix of coefficients from Fig. 6, after each term is divided by the corresponding term of the Pascal matrix. The resulting pattern is still markedly complex compared to Fig. 4, but the inherent numeric sequences are sufficiently long to be decipherable

by $b_0 = 1$ and the recursive formula $b_n = b_{n-1}(4n + 2)/(n + 1)$ where n is (1, 2, ..) The intermittent numbers are found by linear interpolation, as is evident from Fig. 7.

One motivation for employing Guggenheim's ΔH_{MIX} (heat-of-mixing) formula (through Eq. 13) rather than his ΔG^E_{MIX} (through Eq. 1) to derive a polynomial approximation, is that the former is more adept at describing the difficult V-shaped mixing properties. Expressed differently, the former would require fewer polynomial terms to successfully approximate a given V shape than the latter would, an obvious advantage from a practical point of view. Thus, the V-shaped polynomial approximation for ΔH_{MIX} (heat-of-mixing) may describe data from ΔG^E_{MIX} experiments more accurately than Guggenheim's explicit model for ΔG^E_{MIX} (and its polynomial approximation)! This is the essence of empirism; that a function is applied according to where it works best, not according to how it originated.

The discovery of the close relationship between these patterns and Pascal's Triangle, do not amount to a mathematical proof. The discovery bears more resemblance with deciphering of secret codes. Indeed, as was verified using a spreadsheet software,

	C	D	E	F	G	H	I	J	K
49									
50									
51									
52	1	2	1						
53	2	7	8	3					
54	6	28	48	36	10				
55	20	115	260	290	160	35			
56	70	476	1330	1960	1610	700	126		
57	252	1974	6552	11970	13020	8442	3024	462	
58	924	8184	31416	68376	92400	79464	42504	12936	1716
59	3432	33891	147576	372372	600600	642642	456456	207636	54912
60	12870	140140	682110	1956240	3663660	4684680	4144140	2505360	990990
61	48620	578578	3111680	9991410	21295560	31651620	33489456	25233780	13273260
62	184756	2385032	14041456	49984120	119167620	201753552	248312064	223924272	146881020
63	705432	9817262	62783448	244432188	646646000	1227980754	1722664944	1808022216	142034616
64	2704156	40354328	278528068	1179012016	3420757340	7198463272	11333117796	13564046496	1240396572
65	10400600	166666700	1227270800	5611123700	17712221800	40900359500	71389718400	95929934100	100073087400
66	40116600	679307760	5375624400	26396722800	90048394800	226337857200	433692539280	646331914800	757240941600
67	155117520	2782420515	23422745520	122930634600	450616395600	1224536482260	2554940671920	4181270310360	5434542313200
68	601080390	11385169740	101592585910	567419888160	2223997443000	6496476855120	14659148551320	26130166714080	37304251164180
69	2333606220	46542479610	438717969360	2598470525970	10843490235600	33879295101960	82198945493280	158500090199880	246517493866360
70	9075135300	190100202600	1887628142400	11815826160600	5230000473390	17402479451280	45172393469280	9367717662072	1.58E+015

Fig. 8 Matrix of coefficients for each term of the computationally hard part of the Taylor polynomial expansion of Eq. 13. Compare upper part with Fig. 6. The numbers shown here identifies 14 polynomial terms, but this matrix may be extended with copy and paste operations, allowing hundreds of terms to be identified

the numeric disagreement between Eq. 1 or 13 and their polynomial approximations converges steadily towards zero with increasing numbers of polynomial terms, and at 32 terms the Model and the present approximations can be shown to be virtually indistinguishable, as will be the topic of an upcoming article.

These patterns and the binomials defining them make it possible to determine any desired number of coefficients for quasichemical polynomials with comparatively little efforts. Any commercial mathematical worksheet may be used. Even the paper, pencils and slide rules of the 1940 s would have yielded 10 or 100 times more polynomial terms, for no extra effort. Finally, the Taylor expansion of Guggenheim's formula for $\frac{\Delta \overline{G}_B^E}{zRT}$ was repeated recently, yielding one more analytical term than had been achieved with a late 1990 s computer. It was no surprise to observe that this extra term, obtained by analytical means, is identical to what is predicted numerically by the matrix patterns published herein.

9 Concluding remark

Long polynomials can be employed to accurately represent the physical properties of liquid mixtures. By deriving the long polynomials from explicit (analytical) models with few independent parameters, the co-optimisation of a large number of independent parameters can be avoided. For the thermodynamics of mixtures, the derivation of such long polynomials by Taylor expansion is sometimes computationally "hard". This article presents a novel use of Pascal's triangle that turns this computationally "hard" problem into a trivial iterative procedure. This iterative procedure is used to expand two equations that Guggenheim derived from his symmetric "First approximation" Quasichemical model. This Taylor expansion, which in the past had required thousands of man–hours of tedious work, and pushes even today's algebraic software to its limitations, can now be performed with ordinary spreadsheet software, requiring only its most basic functionality, and producing any desired number of polynomial terms, only limited by the allowed spreadsheet size. The process of transforming this hard problem into a "soft" problem may be described as deciphering. The discovery of this Pascal deciphering was aided by an initial mistake by the author, and it is likely that without this mistake, the author would not have discovered neither this deciphering procedure, nor its key (Pascal's triangle).

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