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ORIGINAL PAPER

Uniqueness of equilibrium in the Haber synthesis of ammonia

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Abstract We report a rigorous examination of the gas phase equilibrium for the Haber synthesis of ammonia. In a setting of intensive variables and parameters we prove the existence and uniqueness of an equilibrium solution that corresponds to positive mole fractions for the constituents of the equilibrium. The uniqueness proof is established via the Sturm theorem of real algebraic geometry by exhausting all possible cases of vanishing denominators in the Sturm sequence.

Keywords Sturm theorem · Uniqueness of equilibrium · Haber synthesis

1 Introduction

Stoichiometry of chemical equilibrium is determined by three classes of equations. The conservation of total number of atoms of a given element, the conservation of total charge, and the equilibrium constants. Equations that fall into the first and second classes are linear in nature. On the other hand the equilibrium constants usually constitute nonlinear but algebraic equations. Then the equilibrium solution is found through a simultaneous solution of this system of equations. When an equation is nonlinear two major issues to be dealt with are the existence and uniqueness of solutions. True, by Gauss' fundamental theorem of algebra [1], an algebraic equation has exactly as many complex roots as its degree, counted with multiplicities. However, this is not sufficient for the chemist. Negative concentrations, complex pressures, and mole fractions that are not in the interval (0, 1) are superfluous. An existence proof must guarantee that there is at least one "acceptable" solution of the equilibrium that assigns

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values to the relevant variables of the problem in their proper ranges. Usually, a more difficult question is the issue of uniqueness of this "acceptable" solution. This issue is rarely addressed in the literature partly because of the fact that many equilibrium systems require resolutions of equations that are of lower degrees where analytical solutions are readily available.

Two different methods of uniqueness proofs of equilibrium are present in the literature which are related with the problem that is tackled in this paper, namely the equilibrium in the Haber synthesis of ammonia. (1) The deficiency zero theorem [2–4] in chemical reaction network theory states that "nothing exotic happens" in a chemical reaction network with deficiency zero. That is, there is only one steady state which is stable and there are no cyclic oscillations that remain in the physically realizable domain of concentrations. The physical setting is the one where one starts with the kinetic rate equations that are not necessarily of mass action type and deduce uniqueness of the steady state. (2) More recently, Powers and Paolucci [5] have extended a less known uniqueness proof by Zel'dovich [6]. While Zel'dovich's proof applies to isothermal–isochoric homogenous mixtures of ideal gases, these authors gave a proof for the adiabatic case as well. In this method the setting is that of thermodynamics of ideal systems, where the reactions are reversible. Consequently, approach to the equilibrium state from arbitrary initial conditions within the dynamics generated by kinetic rate equations is replaced by the well justified assumption that the system will sooner or later reach the equilibrium state. The machinery of the proof relies on the observation that the Hessian matrices of thermodynamic potentials are positive definite and full rank, therefore their minima are unique.

Here, we offer a non conventional proof of uniqueness for isothermal-isochoric, ideal, and reversible systems by the tools of real algebraic geometry. Specifically, the moderately complex case of Haber synthesis of ammonia is considered, although the method can be generalized to any reversible reaction or system of reactions. In this sense our work is in the setting of Zel'dovich's [6] proof. However, unlike Zel'dovich we do not inquire the nature of the Hessian of Helmholtz free energy, but try to classify the roots of a polynomial that arises from equilibrium problem itself. We remark that a uniqueness proof for the adiabatic case, cannot rely upon the constancy of equilibrium constant and in that case one needs to resort the method suggested by Powers and Paolucci [5].

There are efficient techniques of numerical analysis, such as that of Raphson and Newton, to approximately compute the roots of a given equation, be it algebraic or another kind. However, a computation for a set of specific parameters is never a surrogate for a generic proof of existence or uniqueness. Because the equations are algebraic in nature, it makes sense to resort to the powerful tools of real algebraic geometry in the context of root classification. In fact the core message of this paper is that real algebraic geometry is an adequate language to address the question of chemical equilibrium, rigorously. These tools have been proved to be very useful in the examination of stability in control research through the famous Routh–Hurwitz [1,7] problem. They have been applied to artificial intelligence [8]. They do have a role to play in chemical equilibrium.

A quorum of questions that are pertinent to root classification and chemical equilibrium is as follows [1,9]. Given a polynomial with real coefficients, how many of its

roots are real, real positive, real negative, or complex with negative real parts? What are the multiplicities of those roots? These questions can be conclusively settled by the following tools of real algebraic geometry. Descartes' rule of signs gives estimates (upper bounds) for the number of distinct positive and negative roots of a real polynomial. Budan–Fourier theorem also gives an estimate (upper bound) of the number of distinct real roots of a real polynomial in a given interval (a, b). Euclidean division algorithm for polynomials can detect if a given polynomial has multiple roots without computing the root itself. Repeated application of Euclidean division algorithm also identifies the multiplicities of all roots. The powerful Sturm's theorem [10] gives the exact number of distinct real roots of a real polynomial in a given finite or infinite interval (a, b). In this sense it is a major improvement of Descartes' rule of signs and the Budan–Fourier theorem. More recently techniques have been developed to increase the efficiency of Sturm's theorem that rely on Sturm–Habicht sequences [11] or Sylvester's discrimination matrix [12,13]. They have been extended to polynomials with complex coefficients [14], counting the positive roots of a polynomial [15], and efficient computations of Tarski query [16]. We remark that all of these algorithms terminate after finite number of operations, require finite memory, and with the exceptions of Descartes's rule of signs and Budan–Fourier theorem, they are powerful enough to give exact results. This contrasts with the iterative techniques of root computations in numerical analysis where convergence is achieved only up to a prescribed numerical precision.

Although some of the aforesaid tools are relatively old, the problem of root classification is by no means trivial today. For instance a complete root classification for a fourth order equation has only been given in 1988 by Arnon [8] in the context of artificial intelligence. In the context of stability Jury and Mansour [7] gave the positivity and non negativity conditions for a quartic equation in 1981. This is despite the fact that analytical solutions of quartic (fourth order) equations are known since the time of Cardano and Ferrari ca. 1500 AD. Root classification of a depressed quintic (fifth order) equation is given by Yang et al. [12] in 1996. Yang [13] also gave the root classification of a sextic (sixth order) polynomial. Why the century long lag between the proof and exploitation of Sturm's theorem? The answer lies within the long expressions that quickly run out of hand during the computation of Sturm sequence. The tedious work in Sect. 3 and 4 where factorizations of expressions that are of degree 17 are involved, as well as the 296 sign examinations of Table 1 demonstrate this. One can disentangle these obstacles by a computer algebra system (CAS). In our computations we relied on open-axiom [17] CAS.

In this paper we study ammonia synthesis from nitrogen and hydrogen for two reasons. First, ammonia is a precursor in the industrial synthesis of many nitrogen containing compounds including ammonium nitrate, a compound that can act as an artificial fertilizer and of great importance in agricultural production [18]. Therefore an understanding of the industrial production of ammonia is always of interest. Secondly, ammonia synthesis with its few constituents is elementary enough to demonstrate the application of Sturm's theorem. And since the equilibrium yields a fourth order equation, it is also complicated enough to be counted as nontrivial. While thermodynamics allows the formation of ammonia from its elements particularly at high pressures, since the days of Haber [19], the focus of research has been to find an adequate catalyst or

Table 1 Signs of the polynomials in Sturm sequence of $P(Y)$ of Eq. (24) evaluated at $-1/4$ and 0

	D_1	D_2	D_3	D_4	D_5	$P_0(\frac{-1}{4})$	$P_1(\frac{-1}{4})$	$P_2(\frac{-1}{4})$	$P_3(\frac{-1}{4})$	$P_4(\frac{-1}{4})$	$w(\frac{-1}{4})$	$P_0(0)$	$P_1(0)$	$P_2(0)$	$P_3(0)$	$P_4(0)$	$w(0)$	Count
A, E	−	−	−	−	−	+	−	+	+	−	3	−	+	+	+	−	2	1
B, F	−	−	+	−	−	+	−	+	+	−	3	−	+	+	−	−	2	1
C, G	+	−	+	−	−	−	+	−	−	+	3	+	−	−	+	+	2	1
D	−	−	−	+	−	+	−	+	−	−	3	−	+	+	+	−	2	1
H, M, P	−	+	−	−	−	+	−	+	+	−	3	−	−	+	−	−	2	1
I, N, Q	−	+	+	−	−	+	−	+	+	−	3	−	−	+	+	−	2	1
J	+	+	+	−	−	−	+	−	−	+	3	+	+	−	−	+	2	1
K	−	+	−	+	−	+	−	+	−	−	3	−	−	+	−	−	2	1
L, S	+	+	+	−	+	−	+	−	−	−	2	+	+	−	−	−	1	1
O, R	−	+	+	−	+	+	−	+	+	+	2	−	−	+	+	+	1	1
α_1	−	−	0	−	−	+	−	+	+	−	3	−	+	+	0	−	2	1
α_2	−	+	0	−	−	+	−	+	+	−	3	−	−	+	0	−	2	1
β_1	−	−	−	0	−	+	−	+	0	−	3	−	+	+	+	−	2	1
β_2	−	+	−	0	−	+	−	+	0	−	3	−	−	+	−	−	2	1
γ_1	+	+	+	−	0	−	+	−	−	0	2	+	+	−	−	0	1	1
γ_2	−	+	+	−	0	+	−	+	+	0	2	−	−	+	+	0	1	1
δ_1						+	−	+	+		2	−	+	+	+		1	1
δ_2						+	−	+	−		3	−	−	+	−		2	1
δ_3						−	+	−	−		2	+	+	−	−		1	1
δ_4						+	−	+	+		2	−	−	+	+		1	1
η_1						+	−	+	−		3	−	+	+	−		2	1
η_2						+	−	+	+		2	−	−	+	+		1	1
η_3						−	+	−	−		2	+	+	−	−		1	1

In all cases the number of distinct roots of $P(Y)$ in this interval, which is given by the "count", i.e. $w(-1/4) - w(0)$, in the last column is 1 which establishes the uniqueness of equilibrium. Latin labels signify the 2-D regions in Fig. 2 whereas Greek labels signify the 1-D level sets that are obtained by setting D_{3-5}, E, and p to zero

to improve a known one for the process to overcome kinetic barriers. Accordingly, research in engineering has focused on [20,21] reactor optimization through kinetic models, while theoretical research in physical sciences recently applied first principles calculations [22,23] to investigate the catalytic properties of nano particles and there have been experimental studies to eliminate the high pressure requirement [24] via electrochemical reactors. By proving the uniqueness of equilibrium in the Haber process, we hope to fill a void that has not been addressed in the theoretical studies of ammonia synthesis.

The rest of the paper is organized as follows. In Sect. 2 we describe the system to be studied in detail and give a short and easy proof of existence for the equilibrium solution. Sections 3 and 4 exploit Sturm's theorem for the proof of uniqueness of the equilibrium solution by exhausting all possible cases. Section 5 closes the paper with a discussion.

2 Background

The gas phase synthesis of ammonia from molecular nitrogen and hydrogen is given by the following equilibrium reaction.

$$\mathrm{N_2(g)} \;+\; 3\mathrm{H_2(g)} \;\rightleftharpoons\; 2\mathrm{NH_3(g)} \tag{1}$$

Assuming the ideal behavior for the gases, we have the following equilibrium constant given in terms of mole ratios

$$\kappa := \frac{x_{\mathrm{NH_3}}^2}{x_{\mathrm{N_2}} x_{\mathrm{H_2}}^3} \tag{2}$$

where x_{X} signifies the mole ratio of the compound (or element) X and κ is the equilibrium constant. Equation (2) must be provided with two more equations in order to solve for the three unknowns. Those remaining equations can be easily retrieved through the law of conservation of mass. Since the reaction tank is closed, the total number of hydrogen and nitrogen atoms are fixed. This gives us two linear equations.

$$n := 2N_{\mathrm{N_2}} + N_{\mathrm{NH_3}} \tag{3}$$

$$h := 2N_{\mathrm{H_2}} + 3N_{\mathrm{NH_3}} \tag{4}$$

Here n and h are the total number of nitrogen and hydrogen atoms, respectively. N_{X} signifies the number of X molecules in the equilibrium. κ, n, and h are invariants (parameters) of the system. These three numbers provide a complete description of the problem. Define the total number of molecules as follows.

$$N_{\mathrm{T}} := N_{\mathrm{H_2}} + N_{\mathrm{N_2}} + N_{\mathrm{NH_3}} \tag{5}$$

It is easy to deduce that $n + h = 2N_{\mathrm{T}} + 2N_{\mathrm{NH_3}}$. If one divides both sides of Eq. (3) by $n + h$, exploits Eq. (5), and uses the fact that $x_{\mathrm{N_2}} := N_{\mathrm{N_2}}/N_{\mathrm{T}}$, then one arrives at the following equation

$$x_{N_2} = \nu + \left(\nu - \frac{1}{2}\right) x_{NH_3} \tag{6}$$

where

$$\nu := \frac{n}{n+h}. \tag{7}$$

Obviously, $\nu \in (0, 1)$. Note that the definition of ν given in Eq. (7) will reduce the number of parameters from three to two. Furthermore, unlike the set of parameters (κ, n, h), the new set of parameters (κ, ν) consists of intensive quantities only. In a similar fashion, if one divides both sides of Eq. (4) by $n + h$ and observes the fact that the left hand side is nothing but $1 - \nu$, then after a simple rearrangement one obtains that

$$x_{H_2} = 1 - \nu - \left(\nu + \frac{1}{2}\right) x_{NH_3}. \tag{8}$$

Although, at this point we can substitute Eqs. (6) and (8) into Eq. (2) and solve for x_{NH_3}, in our experience it is better to study the problem in the quantity

$$x := \frac{N_{NH_3}}{n+h} = \frac{x_{NH_3}}{2 + 2x_{NH_3}}. \tag{9}$$

Since $x_{NH_3} \in (0, 1)$, this implies that $x \in (0, 1/4)$. It is a simple exercise to rearrange Eq. (9) to read

$$x_{NH_3} = \frac{2x}{1 - 2x}. \tag{10}$$

The transformation in Eq. (10) is a monotonic one in the interval $x \in (0, 1/4)$, i.e. the correspondence between x and x_{NH_3} is one to one. Hence, uniqueness of the solution in one variable implies the uniqueness for the other.

Now, if one substitutes Eqs. (6, 8, 10) into Eq. (2) and rearranges so that $\kappa x_{N_2} x_{H_2}^3 - x_{NH_3}^2 = 0$, one obtains a rational function in x. The denominator of this rational function is $(x - 1/2)^4$ and since $x \in (0, 1/4)$ this denominator (which is always a positive number) is not singular in the interval of interest. Therefore it is justified to focus on the numerator only. It is

$$Ax^4 - Ax^3 + Bx^2 + Cx + D = 0 \tag{11}$$

where the coefficients are defined as follows.

$$A := \frac{27}{16}\kappa - 1, \tag{12}$$

$$B := \frac{9}{8}\kappa(1 - \nu)(\nu + 1/2) - \frac{1}{4}, \tag{13}$$

$$C := -\frac{1}{2}\kappa(1 - \nu)^2(\nu + 1/8), \tag{14}$$

$$D := \frac{1}{16}\kappa\nu(1 - \nu)^3. \tag{15}$$

In this setting two major cases manifest themselves for separate exploration. Case I: $A = 0$, i.e. $\kappa = 16/27$. Then the degree of Eq. (11) suffers a reduction and one studies a simpler equation of degree 2. It is

$$f(x) := ax^2 + bx + c = 0 \tag{16}$$

where

$$a := -2\nu^2 + \nu + \frac{1}{4}, \tag{17}$$

$$b := -\frac{8}{9}(1-\nu)^2(\nu + 1/8), \tag{18}$$

$$c := \frac{1}{9}\nu(1-\nu)^3. \tag{19}$$

Again, it is possible to split this case into two. Case I.a: $a = 0$, i.e. $\nu = \nu_\mp := (1 \mp \sqrt{3})/4$. $\nu_- \notin (0, 1)$ and hence it can be disregarded. On the other hand when $\nu = \nu_+$, the solution of the linear equation $bx + c = 0$ reads $x = \nu_+(1-\nu_+)/(8\nu_+ + 1) = 1/(16 + 8\sqrt{3}) \in (0, 1/4)$. Case I.b: $a \neq 0$. We have the following factorization for the discriminant of Eq. (16).

$$b^2 - 4ac = \frac{8}{81}(1-\nu)^3(\nu + 1/2)^3 > 0 \tag{20}$$

Thus there are two (distinct) real roots of Eq. (16). Furthermore, since

$$f(0)f(1/4) = -\frac{\nu}{81}(1-\nu)^3\left(\nu^4 - \nu^3 + \frac{3\nu^2}{8} - \frac{\nu}{16} + \frac{7}{64}\right) \tag{21}$$

and the quartic term in Eq. (21) has no real roots as can be verified easily by a CAS, $f(0)f(1/4) < 0$ which means Eq. (16) has at least one real root in $(0, 1/4)$ by the mean value theorem. It cannot have two real roots, for otherwise we would have a positive sign in Eq. (21). This proves the uniqueness for case I.b.

The other major case and the focus of the remaining part of the paper is realized when $A \neq 0$, i.e. $\kappa \neq 16/27$. Then it is possible to reduce Eq. (11) to a monic equation by dividing both sides by A and x is the root of

$$P(X) := X^4 - X^3 + \frac{B}{A}X^2 + \frac{C}{A}X + \frac{D}{A}. \tag{22}$$

Polynomial $P(X)$ allows us to give a generic proof for the existence of equilibrium: *There exists an* $x \in (0, 1/4)$ *such that* $P(x) = 0$. To prove this statement observe that

$$P(0)P(1/4) = -\frac{\kappa\nu(1-\nu)^3(\kappa(4\nu-1)^4 + 16)}{256(16 - 27\kappa)^2} < 0 \tag{23}$$

where $P(0)$ and $P(1/4)$ can be evaluated and factorized by a CAS. By the intermediate value theorem, the continuous function $P(X)$ has a root in the interval $(0, 1/4)$.

While the existence proof is easy, the uniqueness requires more work. We begin with bringing Eq. (22) to its depressed form. To that end we define $X =: Y + 1/4$ and substitute this into Eq. (22) to read

$$P(Y; \kappa, \nu) := Y^4 + pY^2 + qY + r \tag{24}$$

where the coefficients p, q, and r are defined as follows.

$$p := \frac{9\kappa(4\nu - 1)^2 - 16}{8(16 - 27\kappa)}, \tag{25}$$

$$q := \frac{\kappa(4\nu - 1)^3}{8(16 - 27\kappa)}, \tag{26}$$

$$r := \frac{\kappa(4\nu - 1)^4 + 16}{256(16 - 27\kappa)}. \tag{27}$$

When there is no ambiguity, we will drop the κ and ν dependence of P in Eq. (24). It is obvious that we must seek the root of $P(Y)$ in the interval $(-1/4, 0)$.

3 Application of Sturm's theorem

Given a polynomial with real coefficients, the powerful Sturm's theorem gives the *exact* count of distinct roots in the interval (a, b). When this interval is infinite, Sturm theorem yields the number of distinct real roots. When it is semi infinite, one can deduce the number of distinct positive or negative roots. While we recapitulate the theorem here for completeness, the details of the proof can be found in elsewhere [1,9,10].

Let $P(Y)$ be a polynomial with real coefficients. Define $P_0(Y) := P(Y)$ and $P_1(Y) := P'(Y)$ where the prime signifies the derivative. The Sturm sequence of $P(Y)$ is $\text{Sturm}(P(Y)) := \{P_0(Y), P_1(Y), \ldots, P_n(Y)\}$ where the rest of the polynomials in this sequence are defined through the Euclidean division.

$$P_k(Y) = A_k(Y)P_{k+1}(Y) - P_{k+2}(Y) \tag{28}$$

Here $P_{k+1}(Y)$ is the divisor, $P_{k+2}(Y)$ is the remainder, and $A_k(Y)$ is the quotient which [together with $P_{k+2}(Y)$] is uniquely determined by the requirement that $\deg(P_{k+2}) < \deg(P_{k+1})$ where deg signifies the degree of a polynomial. The sequence terminates when one reaches a constant (or zero) remainder in Eq. (28). Define $w(y) := \text{Var}\{\text{sgn}(P_0(y)), \ldots, \text{sgn}(P_n(y))\}$ as the total number of sign disagreements between the consecutive terms of Sturm sequence at a specific value y. Here $\text{sgn}(x)$ is the usual signum function that returns the sign of x. Then the number of distinct real roots of $P(Y)$ in the interval (a, b) is given by $w(a) - w(b)$.

Several remarks are in order. (1) In the count of sign variations zeros are disregarded. Thus $\text{Var}\{+-0++\} = \text{Var}\{+0-++\} = \text{Var}\{+-++\} = 2$. (2) If the coefficients

of P_0 are rational, then so are the coefficients of all polynomials in the Sturm sequence of P_0. While this closure is a nice property for abstract algebra, in the numerical computations these rational coefficients turn out to be ratios of two very long and mutually prime integers as one progresses in the Sturm sequence. Therefore special data structures for long numbers are required in the numerical implementations. (3) When the coefficients are literal or symbolic the algorithm is very demanding on the memory and can be intractable even for polynomials of moderate degree. Yang et al. [12] report that for a polynomial of degree 7, their computation suffered memory overflow after running approximately 1,000 s. (4) The Sturm sequence can be computed after finite number of operations.

In what follows we will assume that $\kappa \neq 16/27$, $p \neq 0$, $E \neq 0$ where

$$E := 8pr - 9q^2 - 2p^3, \tag{29}$$

and compute the Sturm sequence of $P(Y) =: P_0(Y)$ as defined in Eq. (24). This is indicated as case II in the tree depicted in Fig. 1. Now, $P_1(Y)$ is particularly easy.

$$P_1(Y) = 4Y^3 + 2pY + q \tag{30}$$

The rest of the terms in the Sturm sequence can be computed with a CAS and well known in the literature [9]. They are

$$P_2(Y) = -\frac{p}{2}Y^2 - \frac{3q}{4}Y - r, \tag{31}$$

$$P_3(Y) = \frac{(8pr - 9q^2 - 2p^3)Y - q(p^2 + 12r)}{p^2}, \tag{32}$$

$$P_4(Y) = \frac{p^2 Z}{4(8pr - 9q^2 - 2p^3)^2} \tag{33}$$

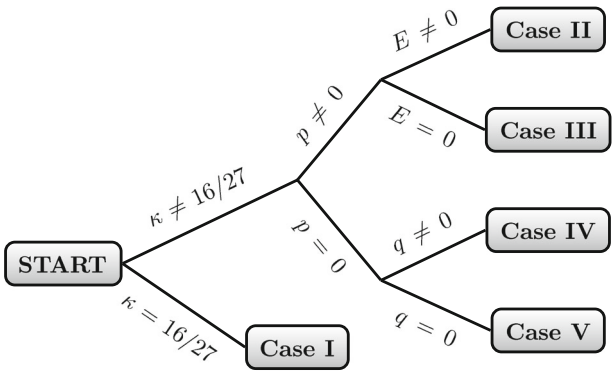

Fig. 1 There a total of five distinct cases in the examination of the uniqueness of solutions in the synthesis of ammonia. This binary tree depicts the paths of realizations for those cases. For the definitions of p, q, and E see Eqs. (25), (26), and (29), respectively

where

$$Z := 256r^3 - 128p^2r^2 + 144prq^2 + 16p^4r - 27q^4 - 4q^2p^3. \tag{34}$$

(Note that the $+16p^4r$ term in Z has an incorrect sign in Basu, Pollack, and Roy. See page 21 in their text [9]).

With the Sturm sequence given above we need to compute $w(-1/4)$ and $w(0)$. This necessitates the evaluation of the polynomials in the Sturm sequence of $P(Y)$ at $-1/4$ and 0. We start with the relatively easy case of $Y = 0$. $P_0(0) = r$ and $\mathrm{sgn}(r) = \mathrm{sgn}(D_1)$ where

$$D_1 := 16 - 27\kappa. \tag{35}$$

It is obvious that $D_1 \neq 0$. $P_1(0) = q$ and $\mathrm{sgn}(q) = \mathrm{sgn}(D_2/D_1)$ where

$$D_2 := 4\nu - 1. \tag{36}$$

$P_2(0) = -r$ and $\mathrm{sgn}(-r) = -\mathrm{sgn}(D_1)$. $P_3(0) = -q(p^2 + 12r)/p^2$ and the denominator is irrelevant for the sign determination. Now, through a CAS we deduce that

$$-q(p^2 + 12r) = -\frac{\kappa(4\nu - 1)^3 D_3}{(16 - 27\kappa)^3}. \tag{37}$$

where

$$D_3 := 3\kappa(\nu - 1)(2\nu + 1)(4\nu^2 - 2\nu + 1) + 2. \tag{38}$$

Clearly $\mathrm{sgn}(P_3(0)) = -\mathrm{sgn}(D_2D_3/D_1)$. Note that $\mathrm{sgn}(P_4(0)) = \mathrm{sgn}(P_4(-1/4)) = \mathrm{sgn}(Z)$ and the sign analysis of this expression is explored in the next paragraph.

Secondly, we evaluate the Sturm sequence at $Y = -1/4$. Through a CAS we find that

$$P_0(-1/4) = \frac{\kappa\nu(\nu - 1)^3}{16 - 27\kappa}. \tag{39}$$

Since by definition $\nu \in (0, 1)$, $\mathrm{sgn}(P_0(-1/4)) = -\mathrm{sgn}(D_1)$. Likewise

$$P_1(-1/4) = \frac{\kappa(\nu - 1)^2(8\nu + 1)}{16 - 27\kappa} \tag{40}$$

and clearly $\mathrm{sgn}(P_1(-1/4)) = \mathrm{sgn}(D_1)$. As for $P_2(-1/4)$ we have

$$P_2(-1/4) = -\frac{\kappa(\nu - 1)^2(4\nu - 1)^2}{16(16 - 27\kappa)} \tag{41}$$

and $\mathrm{sgn}(P_2(-1/4)) = 0$ if $\nu = 1/4$. Otherwise, $\mathrm{sgn}(P_2(-1/4)) = -\mathrm{sgn}(D_1)$. The next item in our list is $P_3(-1/4)$ and as before we disregard the p^2 term that appears in the denominator of Eq. (32) as it is inconsequential in the sign designation.

$$p^2 P_3(-1/4) = \frac{\kappa(\nu - 1)^2 D_4}{(16 - 27\kappa)^3} \tag{42}$$

Here D_4 is defined as follows.

$$D_4 := 64\nu(\nu-1) - 3\kappa(2\nu+1)(4\nu-1)^2(16\nu^2-14\nu+1) \tag{43}$$

The sign of $P_3(-1/4)$ is given by $\mathrm{sgn}(D_4/D_1)$. The final expression for sign determination is Z as given in Eq. (34). With the aid of a CAS we have the following factorization.

$$Z = \frac{16\kappa^2(\nu-1)^3(2\nu+1)^3 D_5}{(16-27\kappa)^5} \tag{44}$$

Here D_5 is defined as follows.

$$D_5 := \kappa(\nu-1)(2\nu+1)(4\nu-1)^4 + 16\nu(2\nu-1) \tag{45}$$

Clearly, $\mathrm{sgn}(Z) = -\mathrm{sgn}(D_5/D_1)$.

Expressions D_{1-5} and their signs are quintessential in the root counting. To that end we first prepared Fig. 2 where the level sets, i.e. the solutions of $D_i = 0$, of these expressions are displayed in the $\nu\kappa$ plane. The level sets of D_1 and D_2 are particularly easy. They are displayed as horizontal and vertical bold lines in Fig. 2, respectively. On the other hand $D_3 = 0$ level set yields the following relation between κ and ν.

$$\kappa_3(\nu) := \frac{2}{3(1-\nu)(2\nu+1)(4\nu^2-2\nu+1)} \tag{46}$$

$\kappa_3(\nu)$ has two real singularities at $\nu = -1/2$ and $\nu = 1$ which are both out of the interval $(0, 1)$. $D_4 = 0$ yields another level curve $\kappa_4(\nu)$. It is

$$\kappa_4(\nu) := \frac{64\nu(\nu-1)}{3(2\nu+1)(4\nu-1)^2(16\nu^2-14\nu+1)}. \tag{47}$$

Unfortunately, some of the singularities of $\kappa_4(\nu)$ fall into the interval $(0, 1)$. This function is singular at the points $\{-1/2, \nu_1 \approx 0.07846484, 1/4, \nu_2 \approx 0.79653517\}$. With the exception of the singularity at $-1/2$, the rest are visible in Fig. 2. Finally, $D_5 = 0$ gives

$$\kappa_5(\nu) := \frac{16\nu(2\nu-1)}{(1-\nu)(2\nu+1)(4\nu-1)^4}. \tag{48}$$

Function $\kappa_5(\nu)$ has singularities at points $\{-1/2, 1/4, 1\}$. However, at the singularity at $\nu = 1/4$, κ_5 tends to $-\infty$ and it cannot be seen in Fig. 2. Also note that, since the κ axis is in logarithmic scale, the root of the numerator at $\nu = 1/2$ appears as a singularity even though the function simply vanishes at $1/2$.

Once the regions that are in the $\nu\kappa$ plane are labeled, one must proceed to the designation of the signs of D_{1-5} in these regions. This is best illustrated for D_1 and D_2. Now, by Eq. (35) $D_1 < 0$ for all $\kappa > 16/27$. Therefore all regions that are above the $\kappa = 16/27$ line in Fig. 2 yield a negative sign for D_1. While those below this line produce a positive sign. Likewise, by Eq. (36) in the regions where $\nu < 1/4$, sign of D_2 is negative. These regions fall to the left of $\nu = 1/4$ line in Fig. 2. Arguments

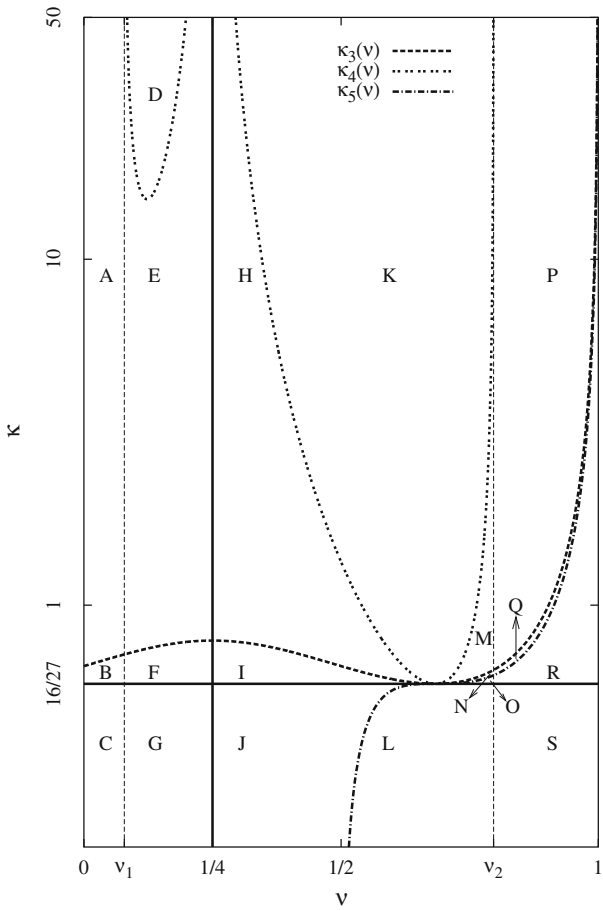

Fig. 2 Illustration of the level sets of D_{1-5} in the $\nu\kappa$ plane. The κ axis is on the logarithmic scale. ν_1 and ν_2 are the singularities of κ_4. (For their values, refer the text.) There are a total of 19 different regions labeled with *capital letters* in which the signs of D_{1-5} must be determined in the application of Sturm's theorem. They are ordered from *top* to *bottom* so that the small region *N* is *sandwiched* in between the regions *M* and *O*

similar to these can be made for D_{3-5}. Since the signs of P_i at $-1/4$ and 0 simply depend on D_{1-5} or their products, one can easily determine $w(-1/4)$ and $w(0)$. Table 1 gives the signs of the polynomials in the 19 regions as depicted in Fig. 2. However, in the sign designation it turns out that there are only 10 distinct cases. In each case the last column of Table 1 gives the number of distinct roots of $P(Y)$ as 1 in the interval $(-1/4, 0)$. This proves that the equilibrium solution of the Haber process when the values of the parameters ν, κ fall into the 2-D regions as labeled in Fig. 2 is unique.

This exercise is incomplete. The signum function also returns the value of 0 when its argument vanishes. Those cases must be studied, too. With the exception of case I, all other cases of Fig. 1 follow the situation $\kappa \neq 16/27$. Therefore $D_1 \neq 0$.

(1) $D_2 = 0$ implies that $\nu = 1/4$. This specific case simplifies Eq. (24) to the following form.

$$P(Y;\kappa,1/4) = Y^4 - \frac{2}{16-27\kappa}Y^2 + \frac{1}{16(16-27\kappa)} \tag{49}$$

Although $P(y;\kappa,1/4) = 0$ is still a fourth order equation, it can be analyzed by the well known techniques that are developed for the second order equations if one substitutes the transformation $T := Y^2$. Through simple algebra we have the solutions of $P(y;\kappa,1/4) = 0$ rearranged in the following form.

$$y_{1,2,3,4} = \pm\frac{1}{4}\sqrt{\frac{1}{1\pm\sqrt{\frac{27\kappa}{16}}}} \tag{50}$$

It is a simple exercise to verify that only the sign combination $-+$ (from left to right) provides a solution for y in the interval $(-1/4, 0)$ which establishes the uniqueness for this case.

(2) $D_3 = 0$ implies the relation $\kappa = \kappa_3(\nu)$ as given in Eq. (46). Since $\kappa_3(\nu) > 16/27$ as can be verified from Fig. 2, $\mathrm{sgn}(D_1) = -$ along this curve. Likewise, $\mathrm{sgn}(D_2)$ is not affected by this situation and it is $-$ when $\nu \in (0, 1/4)$ and $+$ when $\nu \in (1/4, 1)$. To designate the signs of D_4 and D_5 along the $\kappa_3(\nu)$ curve, one substitutes $\kappa = \kappa_3(\nu)$ into Eqs. (43) and (45). Upon factorization with a CAS we have

$$D_4 = \frac{2(2\nu+1)(8\nu^2-4\nu-1)^2}{(\nu-1)(4\nu^2-2\nu+1)}, \tag{51}$$

$$D_5 = -\frac{2(8\nu^2-4\nu-1)^2}{3(4\nu^2-2\nu+1)}. \tag{52}$$

Neither D_4 nor D_5 has any singularities in the interval of interest. Both have the same root at $\nu = \nu_+$. However, since $\kappa_3(\nu_+) = 16/27$ we can safely disregard this situation. Hence $\mathrm{sgn}(D_4) = \mathrm{sgn}(D_5) = -$. Therefore along the $\kappa_3(\nu)$ curve we have two segments, i.e. 1-D point sets. They are $\alpha_1 = \{\nu \in (0, 1/4),\ \kappa = \kappa_3(\nu)\}$ and $\alpha_2 = \{\nu \in (1/4, 1)\backslash\{\nu_+\},\ \kappa = \kappa_3(\nu)\}$. Table 1 gives the sign situations of polynomials and along both segments uniqueness of the root is established.

(3) $D_4 = 0$ implies that $\kappa = \kappa_4(\nu)$ as given in Eq. (47). First, we note that $\kappa \in (0,\infty)\backslash\{16/27\}$ only if $\nu \in (\nu_1, \nu_2)\backslash\{1/4, \nu_+\}$. Therefore our analysis is restricted to this interval. Since $\kappa_4(\nu) > 16/27$, $\mathrm{sgn}(D_1) < 0$ when ν is in the interval of interest. As before the value of κ is immaterial for $\mathrm{sgn}(D_2)$. If $\nu \in (\nu_1, 1/4)$ then $\mathrm{sgn}(D_2) < 0$, whereas if $\nu \in (1/4, \nu_2)$ then $\mathrm{sgn}(D_2) > 0$. As for the signs of D_3 and D_5 we follow the usual procedure of substituting $\kappa = \kappa_4(\nu)$ into Eqs. (38) and (45) and factorize the results to read

$$D_3 = \frac{2(2\nu+1)(8\nu^2-4\nu-1)^2}{(4\nu-1)^2(16\nu^2-14\nu+1)}, \tag{53}$$

$$D_5 = \frac{16\nu(8\nu^2-4\nu-1)^2}{3(16\nu^2-14\nu+1)}. \tag{54}$$

Though there are singularities in D_3 and D_5 at $\{1/4, \nu_1, \nu_2\}$, these cases are disregarded in our analysis. Likewise, both of these expressions have a positive root at $\nu = \nu_+$ which is also excluded since $\kappa_4(\nu_+) = 16/27$. Thus in the interval $(\nu_1, \nu_2)\backslash\{1/4, \nu_+\}$, $\mathrm{sgn}(D_3) = \mathrm{sgn}(D_5) = -$. Finally we divide $\kappa_4(\nu)$ curve into two segments. $\beta_1 = \{\nu \in (\nu_1, 1/4),\ \kappa = \kappa_4(\nu)\}$ and $\beta_2 = \{\nu \in (1/4, \nu_2)\backslash\{\nu_+\},\ \kappa = \kappa_4(\nu)\}$. Table 1 summarizes the sign situations for this case and its last column establishes the uniqueness.

(4) $D_5 = 0$ or equivalently $\kappa = \kappa_5(\nu)$. Equation (48) or Fig. 2 reveals that when $\nu \in (0, 1/2)$, $\kappa_5(\nu) < 0$. Likewise, $\kappa_5(\nu_+) = 16/27$. Hence we focus on the interval $(1/2, 1)\backslash\{\nu_+\}$. Since $\kappa_5(\nu) < 16/27$ when $\nu \in (1/2, \nu_+)$, $\mathrm{sgn}(D_1) = +$ when ν is in this interval. Likewise, when $\nu \in (\nu_+, 1)$, $\mathrm{sgn}(D_1) = -$. Obviously $\mathrm{sgn}(D_2) = +$ when $\nu \in (1/2, 1)$. Upon substitution of $\kappa = \kappa_5(\nu)$ into Eqs. (38) and (43) and factorization we have

$$D_3 = \frac{2(8\nu^2-4\nu-1)^2}{(4\nu-1)^4}, \tag{55}$$

$$D_4 = \frac{16\nu(8\nu^2-4\nu-1)^2}{(\nu-1)(4\nu-1)^2}. \tag{56}$$

The singularities of D_3 and D_4 do not fall into the interval of $(1/2, 1)$. Furthermore their common root at $\nu = \nu_+$ is also excluded from our analysis. We divide $\kappa_5(\nu)$ curve into two segments. $\gamma_1 = \{\nu \in (1/2, \nu_+),\ \kappa = \kappa_5(\nu)\}$ and $\gamma_2 = \{\nu \in (\nu_+, 1),\ \kappa = \kappa_5(\nu)\}$. The situation of signs and the uniqueness of the root is established in Table 1.

4 Specializations

Although the Sturm sequence computed in Eqs. (30–33) is used in the analysis of the previous section the results do not apply if, say, $p = 0$ since the denominator of $P_3(Y)$ is p^2. In the cases of zero denominators, Sturm sequence must be calculated anew. In this section we explore those exceptional cases. In the parlance of algebraic geometry these exceptional cases are called specializations.

4.1 Case III: $\kappa \neq 16/27 \wedge p \neq 0 \wedge E = 0$

By Eq. (29) $E = 0$ implies that

$$\frac{4\kappa G(\kappa, \nu)}{(27\kappa - 16)^3} = 0 \tag{57}$$

where $G(\kappa, \nu) := 27\kappa(\nu-1)\nu(2\nu-1)(2\nu+1)(4\nu-1)^2 + 2(32\nu^4 - 32\nu^3 + 48\nu^2 - 20\nu - 1)$. Clearly, for Eq. (57) to hold one must have $G(\kappa, \nu) = 0$. This yields a relation between κ and ν. It is

$$\kappa_{\mathrm{III}}(\nu) := \frac{2(32\nu^4 - 32\nu^3 + 48\nu^2 - 20\nu - 1)}{27(1-\nu)\nu(2\nu-1)(2\nu+1)(4\nu-1)^2}. \tag{58}$$

$\kappa_{\mathrm{III}}(\nu)$ has singularities at $\nu = 1/4$ and $\nu = 1/2$ in the interval of interest. Since $\kappa_{\mathrm{III}}(\nu_+) = 16/27$, $\nu = \nu_+$ must also be disregarded. Furthermore, numerator of Eq. (58) has two real roots at -0.04498992 and $\nu_\mathrm{a} \approx 0.54498992$. Consequently, in the interval $(1/2, \nu_\mathrm{a})$, $\kappa_{\mathrm{III}}(\nu)$ attains negative values and hence our analysis must exclude this interval as well as the points in $\{1/4, 1/2, \nu_+\}$.

The Sturm sequence given in Eqs. (30–33) are valid except that $P_4(Y)$ is no more needed and $P_3(Y)$ is now a constant. It is

$$P_3(Y) = -\frac{q(p^2 + 12r)}{p^2}. \tag{59}$$

In the coefficients p, q, and r one substitutes $\kappa = \kappa_{\mathrm{III}}(\nu)$.

At $Y = 0$ the polynomials in the Sturm sequence are evaluated and factorized as follows.

$$P_0(0) = -P_2(0) = -\frac{(4\nu-1)^2 J(\nu)}{6912(8\nu^2 - 4\nu - 1)^3}, \tag{60}$$

$$P_1(0) = \frac{(1-\nu)^2(4\nu-1)^2 H(\nu)}{16}, \tag{61}$$

where $H(\nu) := (32\nu^4 - 32\nu^3 + 48\nu^2 - 20\nu - 1)/(8\nu^2 - 4\nu - 1)^3$ and $J(\nu) := 512\nu^6 - 768\nu^5 + 192\nu^4 + 128\nu^3 + 408\nu^2 - 228\nu - 1$. Evaluation of $P_3(0) = P_3(-1/4)$ is skipped to the next paragraph. Now, denominators of $H(\nu)$, $P_0(0)$, and $P_2(0)$ switch sign at $\nu = \nu_+$. Furthermore the numerator of $H(\nu)$ switch sign at $\nu = \nu_\mathrm{a}$ in the interval of interest. As for $J(\nu)$, it has two real roots as well. They are -0.00435212 and $\nu_\mathrm{b} \approx 0.50435212$. Note that $J(\nu)$ suffers a sign change in the interval $(1/2, \nu_\mathrm{a})$ which is excluded from our analysis.

At $Y = -1/4$ we have the following polynomial evaluations and factorizations by a CAS.

$$P_0(-1/4) = (1-\nu)^3 \nu H(\nu), \tag{62}$$

$$P_1(-1/4) = -(1-\nu)^2(8\nu+1)H(\nu), \tag{63}$$

$$P_2(-1/4) = \frac{1}{16}(1-\nu)^2(4\nu-1)^2 H(\nu), \tag{64}$$

$$P_3(-1/4)p^2 = P_3(0)p^2 \tag{65}$$

$$= \frac{(1-\nu)^3\nu(2\nu-1)(2\nu+1)^3(4\nu-1)^5 H(\nu)}{18(8\nu^2 - 4\nu - 1)^4}. \tag{66}$$

These expressions switch sign at $\{1/4, 1/2, \nu_\mathrm{a}, \nu_+\}$ in the interval of interest.

Having clarified the sign situations of the polynomials in the Sturm sequence, there appear four distinct sets to examine. $\delta_1 = \{\nu \in (0, 1/4),\ \kappa = \kappa_{\mathrm{III}}(\nu)\}$, $\delta_2 = \{\nu \in (1/4, 1/2),\ \kappa = \kappa_{\mathrm{III}}(\nu)\}$, $\delta_3 = \{\nu \in (\nu_\mathrm{a}, \nu_+),\ \kappa = \kappa_{\mathrm{III}}(\nu)\}$, and

$\delta_4 = \{\nu \in (\nu_+, 1),\ \kappa = \kappa_{\mathrm{III}}(\nu)\}$. Signs of the polynomials over these sets as well as the uniqueness of the solution is displayed in Table 1.

4.2 Case IV: $\kappa \neq 16/27 \wedge p = 0 \wedge q \neq 0$

$p = 0$ implies that

$$\kappa_{\mathrm{IV}}(\nu) = \frac{16}{9(4\nu - 1)^2} \tag{67}$$

by Eq. (25). Upon substitution of this into Eqs. (26) and (27) we have

$$q = \frac{(4\nu - 1)^3}{72((4\nu - 1)^2 - 3)}, \tag{68}$$

$$r = \frac{(4\nu - 1)^2((4\nu - 1)^2 + 9)}{2304((4\nu - 1)^2 - 3)}. \tag{69}$$

The singularities of q and r at $\nu = \nu_+$ do not bother us, because in this case $\kappa_{\mathrm{IV}}(\nu_+) = 16/27$. Likewise, we also exclude the case where $\nu = 1/4$, since it is the singularity of κ by Eq. (67). The corresponding Sturm sequence is as follows.

$$P_0(Y) = Y^4 + qY + r, \tag{70}$$

$$P_1(Y) = 4Y^3 + q, \tag{71}$$

$$P_2(Y) = -\frac{3q}{4}Y - r, \tag{72}$$

$$P_3(Y) = \frac{256r^3 - 27q^4}{27q^3}. \tag{73}$$

At $Y = 0$ we have $P_0(0) = -P_2(0) = r$. Now, the numerator of r is always positive and its sign is determined through its denominator easily. If $\nu \in (0, \nu_+)\backslash\{1/4\}$, then $\mathrm{sgn}(P_0)(0) = -$. Whereas if $\nu \in (\nu_+, 1)$, then $\mathrm{sgn}(P_0(0)) = +$. This also takes care of the sign situations of $P_2(0)$. Since $P_1(0) = q$, it suffers a sign change at $\nu = 1/4$ and $\nu = \nu_+$. Accordingly, if $\nu \in (0, 1/4)$ or $\nu \in (\nu_+, 1)$, then $\mathrm{sgn}(P_1(0)) = +$. Otherwise, i.e. if $\nu \in (1/4, \nu_+)$, then $\mathrm{sgn}(P_1(0)) = -$. For the sign designations of $P_3(0) = P_3(-1/4)$ see the next paragraph.

At $Y = -1/4$ we have the following factorizations through a CAS for the values of the polynomials in Eqs. (70–73).

$$P_0(-1/4) = \frac{\nu(\nu - 1)^3}{18(8\nu^2 - 4\nu - 1)}, \tag{74}$$

$$P_1(-1/4) = \frac{(\nu - 1)^2(8\nu + 1)}{18(8\nu^2 - 4\nu - 1)}, \tag{75}$$

$$P_2(-1/4) = -\frac{(\nu - 1)^2(4\nu - 1)^2}{288(8\nu^2 - 4\nu - 1)}, \tag{76}$$

$$P_3(-1/4) = \frac{8(\nu-1)^3(2\nu+1)^3(4\nu^2-2\nu+1)}{27(4\nu-1)^3(8\nu^2-4\nu-1)}. \tag{77}$$

Observe that all of the expressions in Eqs. (74–77) suffer a sign change at $\nu = \nu_+$ due to the common quadratic factor in their denominators. Furthermore, $P_3(-1/4)$ suffers another sign change at $\nu = 1/4$. These two points are the only points of interest to our analysis.

It is apparent that there are a total of three segments that is of interest in this case. They are $\eta_1 = \{\nu \in (0, 1/4), \kappa = \kappa_{\mathrm{IV}}(\nu)\}$, $\eta_2 = \{\nu \in (1/4, \nu_+), \kappa = \kappa_{\mathrm{IV}}(\nu)\}$, and $\eta_3 := \{\nu \in (\nu_+, 1), \kappa = \kappa_{\mathrm{IV}}(\nu)\}$. The sign situations and the uniqueness of the root for this case is also summarized in Table 1.

4.3 Case V: $\kappa \neq 16/27 \wedge p = 0 \wedge q = 0$

By Eq. (26) $q = 0$ is realized for $\nu = 1/4$ only. However in this case $p \neq 0$. Hence the common solutions of $p = q = 0$ constitute an empty set for positive κ and $\nu \in (0, 1)$ and this case is trivial.

5 Discussion

We have presented a thorough analysis of the equilibrium of ammonia synthesis by exploring 5 major cases and signs of 296 expressions. Existence and uniqueness of the equilibrium solution are established. In the proof of uniqueness the use of the intensive quantity ν reduced the dimensionality of the parameter space from three to two. This enabled an easy illustration of the various cases for the signs of the polynomials in the Sturm sequence through a 2-D diagram. When the number of distinct chemical elements that appear in the equilibrium system is two, such an easy visualization can always be produced. This applies to the formation equilibria of all binary compounds in the gas phase. On the other hand when the number of distinct elements that appear in a reaction exceeds two, the diagrams for the signs of the polynomials are more than 2-D. In that case visualization of the level sets becomes difficult if not entirely impossible.

An alternative route to the uniqueness proof given in this paper can be taken by the following observation. For a polynomial $P(X)$ of degree n, define $Y := (X-a)/(b-X)$ and

$$Q(Y) := (1+Y)^n P\left(\frac{a+bY}{1+Y}\right). \tag{78}$$

The number of positive roots of $Q(Y)$ is equal to the number of roots of $P(X)$ in (a, b). Indeed as X varies in (a, b), Y varies in $(0, \infty)$. Counting positive roots in a Sturm sequence requires the evaluation of the polynomials at 0 and ∞. However, $\mathrm{sgn}(P(0))$ is the sign of the constant term of $P(X)$ and $\mathrm{sgn}(P(\infty))$ is the sign of its leading coefficient for any polynomial. Therefore an extension of the interval to a positive semi infinite one without altering the root count seems to eliminate the polynomial evaluation at a and b. The price to be paid is the evaluation of a new polynomial $Q(Y)$

which is unlikely to be in a depressed form. The Sturm sequence of a polynomial that is not in its depressed form is more complicated.

Recent research in computational algebraic geometry has produced methods that have better specialization properties and do not necessitate the computation of Sturm sequence anew for each case. These methods rely on Sylvester matrices [12] and Sturm–Habicht [11] sequences. Their efficiency has a potential for exploitation in more complicated problems.

Evaluation of the signs of the polynomials in a Sturm sequence is relatively easy if the parameters that specify the equilibrium are <3. Then the algebraic sets where the signs are examined form 0-, 1-, and 2-D point sets which are easily visualized. Future research of more complicated equilibrium problems, in which visualization is impossible, must integrate or develop techniques that are not visual to identify the domains of constant sign for polynomials.

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References

1. V.V. Prasolov, *Polynomials* (Springer, Berlin, 2004). ISBN: 978-3-540-40714-0
2. M. Feinberg, Chem. Eng. Sci. **42**, 2229 (1987)
3. F.J.M. Horn, Arch. Ration. Mech. Anal. **49**, 172 (1972)
4. F.J.M. Horn, R. Jackson, Arch. Ration. Mech. Anal. **47**, 81 (1972)
5. J.M. Powers, S. Paolucci, Am. J. Phys. **76**, 848 (2008)
6. Y.B. Zel'dovich, Z.F. Khim, **11**, 685 (1938) (in Russian)
7. E.I. Jury, M. Mansour, IEEE Trans. Autom. Control **AC-26**, 444 (1981)
8. D.S. Arnon, Artif. Intell. **37**, 37 (1988)
9. S. Basu, R. Pollack, M.-F. Roy, *Algorithms in Real Algebraic Geometry*, 2nd edn (Springer, Berlin, 2006)
10. H. Dörrie, *100 Great Problems of Elementary Mathematics, Their History and Solution* (Dover, New York, 1965)
11. L. Gonzalez, H. Lombardi, T. Recio, M.-F. Roy, in *Proceedings of the ISSAC '89* (ACM Press, New York, 1989), pp. 136–146
12. L. Yang, X.R. Hou, Z.B. Zeng, Sci. China E **39**, 628 (1996)
13. L. Yang, J. Symb. Comput. **28**, 225 (1999)
14. S. Liang, J. Zhang, Sci. China E **42**, 113 (1999)
15. L. Yang, B. Xia, MM Res. Prepr. **15**, 134 (1997)
16. H. Fu, L. Yang, Z. Zeng, Sci. China E **43**, 32 (2000)
17. T. Daly, in *A*xiom: The 30 Year Horizon. A Tutorial (Lulu.com, 2005), ISBN: 1-411-66597-X
18. M.A. Sutton, J.W. Erisman, F. Dentener, D. Möller, Environ. Pollut. **156**, 583 (2008)
19. F. Haber, in *Nobel Lectures, Chemistry 1901–1921* (Elsevier, Amsterdam, 1966)
20. S.S. Elnashaie, M.E. Abashar, A.S. Al-Ubaid, Ind. Eng. Chem. Res. **27**, 2015 (1988)
21. V. Prasad, A.M. Karim, A. Arya, D.G. Vlachos, Ind. Eng. Chem. Res. **48**, 5255 (2009)
22. K. Honkala, A. Hellman, I.N. Remediakis, A. Logadottir, A. Carlsson, S. Dahl, C.H. Christensen, J.K. Nørskov, Science **307**, 555 (2005)
23. A. Hellman, E.J. Baerends, M. Biczysko, T. Bligaard, C.H. Christensen, D.C. Clary, S. Dahl, R. van Harrevelt, K. Honkala, H. Jonsson et al., J. Phys. Chem. B **110**, 17719 (2006)
24. G. Marnellos, M. Stoukides, Science **282**, 98 (1998)