GEOMETRIC PROGRAMMING AS A GENERAL METHOD FOR PHASE AND REACTION EQUILIBRIUM CALCULATIONS

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ABSTRACT

Geometric programming has been used to calculate a large number of different ideal and non-ideal equilibria, including, for the first time, combined non-ideal reaction and phase equilibria. For non-ideal systems the primal program is solved a number of times with the non-ideal terms fixed each time. After each primal solution, the non-ideal terms are updated using the corresponding dual solution. This iteration generally converges. We have included one counter-example, where the failure is caused by the equation of state, which cannot give correct roots.

Keywords: Multi-phase equilibrium calculations; reaction equilibrium calculations; geometric programming; UNIFAC.

INTRODUCTION

Calculation of phase and/or reaction equilibria is generally complex, since the functions are highly nonlinear, the variables may have very small values, and phases may appear and disappear during the calculations. No one method can guarantee solution in all cases, and there is probably no single method that is always best. Nevertheless, geometric programming is a powerful optimization method that may be used for all kinds of equilibrium calculations.

However, there has not been much published literature on applying it to equilibrium calculations. Previously, publications were more numerous (Passy and Wilde 1968; Dinkel and Lakshamanan 1979; Geana 1981a,b; Ruda and Thompson 1985), but except for one set of papers they were all for ideal systems. The three papers (I-III) on non-ideal systems, (Ohanomah and Thompson, 1984) treated only phase equilibria. Rather few publications have addressed simultaneous phase and reaction equilibrium calculation. Some of the other contributions include those by Smith and Missen (1988) and McDonald and Floudas (1995a, b).

The purpose of this paper is not to derive new algorithms, but rather to apply the geometric programming, and to show its ability in describing non-ideal systems. As part of this, we will write down the equations in a more typical chemical engineering notation, since the general notation chosen by most authors (Wilde and Beightler, 1967) make it a bit hard to see how to formulate the equilibrium equations.

In most of the introductory literature on geometric programming (Wilde and Beightler, 1967; Converse, 1970; Zahradnik, 1971) it is pointed out how the dual program is most often much easier to solve. For phase and reaction equilibria, the opposite is the case. Formulating the equilibrium in the customary manner and then manipulating it slightly gives a dual program in geometric programming, from which a primal program can be written down and solved.

The connection between the primal and the dual program can be found using either Lagrange multipliers. The multipliers for the primal are the variables for the dual and vice versa. Alternatively the arithmetic-geometric inequality (which gives the method its name) is used. However, when the primal or dual is solved, the Lagrange multipliers are not used during the calculations.

PROBLEM FORMULATION

Phase and/or reaction equilibria at fixed temperature (T) and pressure (P) are formulated in the most general way as a minimization of Gibbs energy (G) with respect to the mole numbers. It is simpler to use mole numbers and not mole fractions, since the former are all independent of each other. Mole fractions have to be used in subroutines for calculating the non-ideal contributions (fugacity coefficients, activity coefficients), but the mole fractions are of course found easily from the mole numbers. Thus, the starting point is

$$\min G(\mathbf{n}) = \min \sum_{k} \sum_{j} \mu_j^k n_j^k \qquad (1)$$

subject to non-negativity of all mole numbers $nj^k \geq 0$

and the abundance equations (constancy of the constituent atoms),

$$\sum_{j} a_{ij} \left(\sum_{k} n_j^k \right) = b_i \qquad (2)$$

Here, μ_j^k is the chemical potential of component ***j*** in phase ***k***, and we use ***j*** as a component (species) subscript, k as a phase superscript, and ***i*** as an element (atom or species in the case of phase equilibria) subscript. The indices ***i, j, k*** all start at 1. In the abundance equations, a_{ij} are the number of ***i***-atoms in component ***j***, and b_i the total moles of atom ***i***. If the calculations are for only phase equilibria, the components are the natural building blocks, so then $a_{ij} \equiv \delta_{ij}$ (the Kronecker delta) and $b_i \equiv b_j$ the total number of moles of component ***j***. However, it is fully possible in this case also to let the components arise from reactions, which might be quicker with many components made up of few atoms. Alternatively, the species can be made up of groups, or combinations of atoms and groups.

The individual chemical potentials may be written as,

$$\mu_j^k = \mu_j^{k,o} + RT \ln \frac{f_j^k}{f_j^{k,o}}$$

$$f_j^k = y_j^k \varphi_j^k P \quad or \quad f_j^k = x_j^k \gamma_j^k P_j^s \qquad (3)$$

$$and \quad f_j^{k,o} = P^o$$

Where f is fugacity, φ is fugacity coefficient, ***x*** and ***y*** are mole fractions, γ is activity coefficient and P^s is the pure component vapor pressure. Superscript ***o*** denotes standard state, which for fluids is ideal gas at pressure P^o. In the alternative using activity coefficients there should in principle also be a Poynting correction and a fugacity coefficient for the pure component vapor. However, we only apply this model at low to moderate pressures as is customary, and then the simplification used is usual and acceptable. The models implemented here are only for non-electrolytes, and also do not include the use of Henryan activity coefficients, but geometric progamming can handle all models. Equations of state models are used for the vapour phase, but may be applied even for the liquid phases.

We now rewrite the expression for the component chemical potential as follows to separate the mole fraction term from the others, and we also change the sign:

$$-\frac{\mu_j^k}{RT} = \ln c_j^k - \ln \frac{n_j^k}{n_t^k} \qquad (4)$$

where: $n_t^k = \sum_{j} n_j^k$ and

$$c_j^k = \exp\left\{ -\left(\frac{\mu_j^{k,o}}{RT} + \ln \varphi_j^k \frac{P}{P^o} \right) \right\} \qquad (4(i))$$

$$\text{or } c_j^k = \exp\left\{ -\left(\frac{\mu_j^{k,o}}{RT} + \ln \gamma_j^k \frac{P_j^s}{P^o} \right) \right\} \qquad (4(ii))$$

The letter ***c*** indicates that we treat also the non-idealities as constants at the given T and P. This is of course not so, but they are updated after each solution of the primal problem. Otherwise for ideal or pure condensed phases, the non-ideality terms vanish.

Substituting equation (4) into the Gibbs energy expression (1) gives:

$$-\frac{G}{RT} = \sum_{k} \sum_{j} n_j^k \left\{ \ln c_j^k - \ln n_j^k + \ln n_t^k \right\} (4(iii))$$

which on combining the first two terms and rearranging the expression gives:

$$-\frac{G}{RT} = -\sum_{k}\sum_{j} n_j^k \ln\frac{c_j^k}{n_j^k} + \sum_{k} n_t^k \ln n_t^k \quad (5)$$

Exponentiating equation (5) gives instead:

$$\exp\left(-\frac{G}{RT}\right) = \prod_{k}\prod_{j}\left(\frac{c_j^k}{n_j^k}\right)^{n_j^k}\left(n_j^k\right)^{n_t^k} \qquad (6)$$

This is a maximization formulation, referred to as F5 by Smith and Missen (1988). The right hand side of equation (6) with the product is almost the standard geometric programming dual. However, the product for the phases should go from ***0*** and not from ***1*** to be of standard form. This cannot be fixed just by renumbering. Instead, a zero-phase is introduced with mole numbers n_j^0. To have no change in the value of the objective function (6), this means the *cs'* for the zero phase must be equal to the **n**s', i.e. $c_j^0 = n_j^0$. Since the last factor contains the sum of the mole numbers in each phase, it is also necessary that

$$\sum n_j^0 = 1 \qquad (6(i))$$

which becomes the normalization equation of the standard dual program.

Finally, the abundance equations have to be made into the standard orthogonality equations of the dual. First we write the abundance equations as,

$$\sum_{k}\sum_{j} a_{ij} n_j^k - b_i = 0 \qquad (4(ii))$$

Defining the zero-phase abundance by $a_{ij} = -b_i$ we can write for $k = 0$,

$$-b_i = \sum_{j} a_{ij} n_j^o \text{ since}$$

$$\sum_{j} -b_i n_j^0 = -b_i \sum_{j} n_j^o = -b_i \qquad (4(iii))$$

and the abundance equations can then be written (summing the phases from 0) as,

$$\sum_{k=0}\sum_{j=1} a_{ij} n_j^k = 0 \qquad (7)$$

The definition of a dummy phase is not necessary if one uses primal NLP formulation. The problem is now formulated as a standard dual program of geometric programming. The corresponding primal program is then,

$$\min \prod_{i} u_i^{-b_i} \qquad (8)$$

where, u are the primal variables, one for each element in the dual. The restrictions on the primal variables are that $u_i > 0$. (In the general formulation of geometric programming the primal objective function has the same form as the constraints here (eq. 9), but because of the special properties of the artificial zero phase we get the simple objective function in eq. (8). Furthermore, the primal objective function is subject to the following kind of constraint, one for each phase

$$g^k = \sum_{j} c_j^k \prod_{i} u_i^{a_{ij}} \leq 1 \qquad (9)$$

with $c_j^k > 0$.

The latter is fulfilled from the definition of c_j^k in the dual. There are as many terms in each constraint summation as there are components in that phase, and each term in the constraint corresponds to what we may call a calculated mole fraction. That is, if the constraint is binding, i.e. $g^k = 1$, the calculated mole fractions sum to one and the calculated phase is present. If the constraint is <1, the calculated mole fractions do not sum to one, and the phase is not present.

This is the same kind of test used in other stability or equilibrium calculations. Consider a typical example for bubble point calculation: If the calculated equilibrium mole fractions in the vapour sum to less than one the liquid is below its bubble point, if they sum to one it is at its boiling point, if they sum to more than one the liquid phase is really all vapour. Also tangent plane calculations, as described by Michelsen (1982), use a calculated mole fraction which sum to one when the new phase is at equilibrium with the old.

It should be pointed out that in geometric programming, new phases are not introduced into the calculations as they proceed. The phases one wish to test for must be assumed present from the start, and then the constraint value will tell if a phase is physically present or not.

To calculate for non-ideal systems, the geometric programming must be used iteratively. First, the primal program is solved using ideal-system values of the c's. The calculated mole fractions and mole numbers are then used in the dual to update the cs' and so on. There is no *a priori* guarantee that such iterations will succeed, but our experience is that they indeed do so.

NUMERICAL EXAMPLES

The proposed method has been tested successfully with several examples, some of which are shown in Tables 1-7. When a phase is indicated as absent, it means the phase was included in the calculations but it is not present at equilibrium. The geometric programming code used was made by Dembo (1972) and provided by the Department of Chemical Engineering at the Technion, Israel. We modified and updated the code to allow for the iterative calculations needed for non-ideal systems. The UNIFAC code was provided by the Department of Chemical Engineering at DTU, Denmark. We made the SRK code. In addition, we have implemented the NRTL model as an alternative to UNIFAC, with the gas phase predicted by the SRK equation and have included some results for comparison. Physical properties for the components were taken from Poling et al. (2001).

Table 1. Solid-Gas Equilibrium in a Blast Furnace at 1363 K, 1 atm. Feed moles: FeO 1.00, C 2.00, CO 0.75, H_2 0.75 and O_2 0.5

Specie	Phase	Equilibrium mole fractions		
		This work*	Lantagne et al. (1988)*	Castilo and Grossmann (1981)*
Fe	Solid (s)-1	1.0	1.0	1.0
FeO	Solid (s)-2	0.0	0.0	0.0
C	Solid (s)-3	1.0	1.0	1.0
CO	Gas	0.7834D+00	0.7834D+00	0.7834D+00
CO_2	Gas	0.1754D-02	0.1736D-02	0.1736D-02
H_2	Gas	0.2139D+00	0.2139D+00	0.2139D+00
O_2	Gas	0.1239D-17	0.2864D-11	0.2864D-11
H_2O	Gas	0.8643D-03	0.8556D-03	0.8567D-03

- Ideal gas and pure solids

Table 2. Chemical Equilibrium of an Equimolar Mixture of EtOH-HAc at 358 K, 1 atm. Feed, moles: EtOH 0.5 and HAc 0.5

Specie	Phase	Equilibrium mole fractions			
		This work*	Lantagne et al. (1988)#	Castilo and Grossmann (1981)+	McDonald and Floudas (1995b)$
EtOH	Vapour	0.06995	0.13841	0.07536	0.07531
HAc	Vapour	0.06995	0.13841	0.07536	0.07531
Water	Vapour	0.43190	0.36159	0.42464	0.42469
EtAc	Vapour	0.43190	0.36159	0.42464	0.42469
	Liquid-1	Absent	Absent	Absent	Absent
	Liquid-2	Absent	Absent	Absent	Absent

* Vapor SRK, Liquids UNIFAC; # Vapour SRK, Liquids UNIQUAC; +Vapour Ideal, Liquids Wilson's equation; $Liquids NRTL.

Table 3. L-L Equilibrium of a Mixture of Toluene-Water at 298 K, 1 atm. Feed moles: Toluene 0.35251, Aniline 0.59846 and Water 0.04633

Specie	Phase	Equilibrium mole fractions				
		This work*	Castilo and Grossmann (1981)+	McDonald and Floudas (1995b)+	Previous work+	PRO/II (1991)#
	Vapour	Absent	Absent	Absent	Absent	Absent
Toluene	Liquid-1	0.35262	0.36692	0.34629	0.37585	0.10669
Aniline	Liquid-1	0.61530	0.61738	0.57666	0.61207	0.81254
Water	Liquid-1	0.02208	0.01569	0.07575	0.01231	0.08047
Toluene	Liquid-2	0.00006	0.00046	0.00007	0.00000	0.00074
Aniline	Liquid-2	0.00001	0.02510	0.00496	0.00015	0.00618
Water	Liquid-2	0.99993	0.97444	0.99364	0.99984	0.99378

*Liquids UNIFAC; +Liquids NRTL Equation; #SimSci International commercial code (NRTL

Table 4. V-L-L Equilibrium of a Mixture of Benzene-Acetonitrile-Water at 333 K, 0.769 atm: Feed moles: Benzene 0.34359, Acetonitrile 0.30923 and Water 0.34718

Specie	Phase	Equilibrium mole fractions					
		This work*	Lantagne et al (1988)#	Castilo and Grossmann (1981)+	McDonald and Floudas 1995b#	Previous work#	PRO/II (1991)$
C_6H_6	Vapour	0.45557	0.46972	0.46937	0.47848	0.43479	0.41043
CH_3N	Vapour	0.34512	0.28920	0.28997	0.28180	0.36983	0.35167
H_2O	Vapour	0.19931	0.24108	0.24066	0.23970	0.19538	0.23789
C_6H_6	Liquid-1	0.00099	0.00265	0.00268	0.00256	0.00112	0.00159
CH_3N	Liquid-1	0.07589	0.07929	0.08008	0.07617	0.07420	0.09136
H_2O	Liquid-1	0.92312	0.91810	0.91724	0.92127	0.92467	0.90706
C_6H_6	Liquid-2	0.39735	0.45340	0.45336	0.47880	0.34390	0.40383
CH_3N	Liquid-2	0.52823	0.47030	0.47092	0.45409	0.54413	0.51031
H_2O	Liquid-2	0.07442	0.07634	0.07572	0.06728	0.11120	0.08560

*Vapour SRK, Liquids UNIFAC; #Vapour ideal, Liquids NRTL; +Vapour ideal, Liquids NRTL; $SimSci code

Table 5. V-L-L Equilibrium of a Mixture of Benzene-Acetonitrile-Water at 300 K, 0.10 atm.

Specie	Phase	Equilibrium mole fractions					
		This work*	Lantagne et al (1988)#	Castilo and Grossmann (1981)+	McDonald and Floudas 1995b)#	Previous work#	PRO/II (1991)$
C_6H_6	Vapour	0.39866	0.34950	0.34756	0.34928	0.39837	0.34592
CH_3N	Vapour	0.35482	0.31402	0.31246	0.31382	0.34507	0.31119
H_2O	Vapour	0.24652	0.33649	0.33998	0.33257	0.24657	0.34289
C_6H_6	Liquid-1	0.00044	0.00020	0.00019	0.00018	0.00018	0.00015
CH_3N	Liquid-1	0.02634	0.02995	0.02958	0.02997	0.02016	0.01887
H_2O	Liquid-1	0.97322	0.96985	0.97023	0.96985	0.97966	0.98098
	Liquid-2	Absent	Absent	Absent	Absent	Absent	Absent

Table 6. V-L-L Equilibrium of a Mixture of n-Decane Carbon dioxide at 342.9 K, 50.83 atm: Feed moles: Carbon dioxide 0.650, n-Decane 0.3350

Specie	Phase Type	Equilibrium mole fractions	
		This work*	Inomata et al. (1986)+
Carbon dioxide	Vapour	0.999295	0.999
n-Decane	Vapour	0.000705	0.001
Carbon dioxide	Liquid-1	0.451294	0.377
n-Decane	Liquid-1	0.54878701	0.623
	Liquid-2	Absent	n.a

*Vapour SRK, Liquids SRK; +Experimental values

Table 7. V-L-L Equilibrium of a Mixture of n-Decane Carbon dioxide at 248.15 K, 15.89 atm: Feed moles: Carbon dioxide 0.650, n-Decane 0.3350

Specie	Phase Type	Equilibrium mole fractions	
		This work*	Kulkarni et al. (1974)+
Carbon dioxide	Vapour	0.999999	0.999
n-Decane	Vapour	0.000001	0.001
Carbon dioxide	Liquid-1	Absent	0.266
n-Decane	Liquid-1	Absent	0.734
n-Decane	Liquid-2	0.026322	0.084
Carbon dioxide	Liquid-2	0.973678	0.916

*Vapour SRK, Liquids SRK; +Experimental values

DISCUSSIONS

For all examples except CO_2-n-decane system, the geometric programming code gives comparable results to those obtained by others using different methods. Some difference, especially in very small mole numbers, are to be expected which in our case may be attributed to slight differences in the standard Gibbs free energy and/or vapour pressure values used or predicted among others. Also where non-ideality predicting model (in our case, UNIFAC) could not adequately account for the entire behaviour (such as polymerization) in the vapour phase as evidenced in Table 2, one could expect problems (McDonald and Floudas, 1995b). This was confirmed by solving the same problem, in the first case using Free energy data from Stull *et al.* (1969) and in the other from Reid *et al.* (1988) when the two results were found to vary slightly. Since the conditions were not completely identical, the observed variations are also to be expected.

The failure to calculate the correct equilibria for the system carbon dioxide - n-decane reflects a failure of the underlying equation of state. At –

25°C this system has only vapor-liquid equilibrium (VLE) at pressures below 16.10 bar according to measurements (Kulkarni et al. 1974) and as described by Baker et al (1982). At 16.10 bar there is a three-phase equilibrium (VLLE). At slightly higher pressures there is a liquid-liquid equilibrium between CO_2 mole fractions of around 0.78 to around 0.92, and a small region of VLE at mole fractions of CO_2 higher than around 0.92. This small VLE region vanishes quickly as pressure is raised, leaving only the LLE region.

Our simple SRK equation of state which does not include interaction parameters failed to give anything but VLE which is a common and sometimes expected failure of many equations of state which we tested in the commercial simulator Hysys. Baker et al. (1982) managed to calculate all the equilibria, including the three-phase equilibrium at 16.134 bar. They give no details of their calculations. Using another in-house equation of state (VRK), Vonka et al. (1993) we managed to calculate all the equilibria, including a three-phase at 16.657 bar, and with the small VLE region disappearing at 16.61 bar. The results for the various equations of state we tested are summarized in Table 8.

Table 8. Equilibria for CO_2 – n-decane: at -25°C.

Equation of state	*Equilibria*
SRK, our version	VL only
SRK, Hysys	VL only
PR, Hysys	VL only
Sour SRK, Hysys	VL only
GCEOS, Hysys	VL, LL
VRK, Own program	VL, LL, VLL

CONCLUSIONS

A Generalized Geometric programming code modified and extended by us and implementing UNIFAC model for predicting system non-idealities was tested on various equilibrium problems. The code has been found to be versatile and robust for calculating phase and/or reaction equilibria. As any other general code, it has its own strengths and weaknesses. However when consistent and correct thermodynamic data and non-ideality models are used, the code converges to the correct type of phases and equilibrium compositions.

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NOMENCLATURE

Symbols

	Description	**Units**
c^k_j	Coefficient j in phase k	[-]
f^k_j	Fugacity of j in phase k	[atm]
i	Index for chemical element	[-]
j	Index for chemical species	[-]
k	Index for phases	[-]
n	Vector of mole numbers	[-]
n^k_j	Mole number j in phase k	[-]
P	Pressure	[atm]
R	Universal gas constant	[J/mol K]
T	Temperature	[K]
x^k_j	Liquid mole fraction j in phase k	[-]
y^k_j	Vapour mole fraction j in phase k	[-]

Greek Letters

	Description	**Units**
φ^{k}_{j}	Fugacity coefficient of component j in phase k	[-]
γ^{k}_{j}	Activity coefficient of component j in phase k	[-]
μ^{k}_{j}	Chemical potential of component j in phase k	[J/mol]

Acronyms

Description	
DTU	Danish Technical University
EOS	Equations of State
GS	Gas-Solid
NLP	Non-Linear programming
NRTL	Non Random Two Liquid
SRK	Soave-Redlich-Kwong Equation of State
UNIFAC	Universal Quasi Chemical Functional Activity Coefficients

VL	Vapour-Liquid
LL	Liquid-Liquid
VLL	Vapour-Liquid-Liquid

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