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Applying constraints to chemical equilibrium calculations through the use of virtual elements

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ABSTRACT

Through the judicious use of "virtual elements" that have zero atomic mass but that are included in the materials balances, it is possible to apply a variety of constraints to chemical equilibrium calculations without the necessity of writing dedicated software for each individual application. Several examples are presented, including the suppression of decomposition of metastable molecules and ions or redox reactions in aqueous solutions, the suppression of internal equilibria in molten salts and ceramics, the calculation of the surface tension of solutions, following the course of reactions with time, paraequilibrium calculations and limiting the extent of a reaction.

1. Introduction

Chemical equilibrium calculations are most often performed by Gibbs energy minimization under constraints of constant temperature, pressure and elemental materials balances. Additional constraints may be required for particular applications. In many cases, these additional constraints can be applied simply through the judicious use of "virtual elements" as will be shown in the present article by means of examples. For a general discussion of applying constraints to chemical equilibrium calculations, see Pajarre *et al* [1] and Koukkari [2].

All calculations have been performed with the FactSage 8.2 package of software and optimized thermochemical databases [3].

The software has been programmed to recognize the "chemical symbols" Qa, Qb, Qc, … …..,Qz as representing "virtual elements" with atomic masses equal to zero. In the following examples, the virtual elements as well as the real elements are included in the materials balances.

2. Example calculations

2.1. Heating in a crucible that partially dissolves in its contents

In this example, 95 g of PbO are placed in an Al_2O_3 crucible at 25°C and heated to 1200°C. The crucible weighs 100 g. We wish to calculate the heat required for this process (assuming no heat losses) if only 5.0 g of Al_2O_3 dissolve in the molten PbO. We assume that it is known in advance that the liquid PbO does not become saturated in Al_2O_3.

The calculation is performed by associating the virtual element Qa with the Al_2O_3 which does not dissolve, as shown in Table 1. The properties of solid alpha Al_2O_3(Qa) have been set equal to those of solid alpha Al_2O_3. Data were taken from the FactSage 8.2 FToxid database. Since the change in enthalpy in heating from 25°C to 1200 °C is to be calculated, the input specifies the initial conditions (pure PbO and Al_2O_3 solids at 25°C) as well as the number of moles of each element (The parentheses around the virtual elements in Table 1 and elsewhere are included only for the sake of clarity.).

The calculated output is shown in Table 1. At equilibrium at 1200°C there are 95 g of pure solid alumina (the remaining undissolved crucible) and 100 g of a molten oxide solution containing 5 g of Al_2O_3 and 95 g of PbO. The calculated enthalpy change for the process is calculated to be 1.7953(10^5) Joules as shown in Table 1. Note that an equivalent result could have been obtained if the virtual element was connected to the 5 g of Al_2O_3 that dissolve in the liquid phase.

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Table 1
Calculation of the enthalpy required to heat 95 g PbO in a 100 g Al_2O_3 crucible from 25 °C to 1200 °C when only 5.0 g of Al_2O_3dissolve in the molten oxide.

Input (at 25°C)

95 g PbO solid (litharge)
95 g Al2O3(Qa) solid (alpha)
5 g Al2O3 solid (alpha)

Output (Equilibrium at 1200°C)

100.00 gram Slag liquid
5.0000 wt.% Al2O3
+ 95.000 wt.% PbO

+ 95.00 gram Al2O3(Qa) Corundum (alpha)

DELTA H (J)	DELTA G (J)	DELTA S (J/K)
1.795338E+05	-2.461584E+05	2.266964E+02

2.2. Applying kinetic constraints to internal reactions in molten salt solutions

In this example, a mixture consisting of 1.0 mol each of $NaNO_3$, $NaNO_2$, $NaClO_4$ and NaCl is equilibrated in the presence of 100 mol of air at 1.0 bar pressure.

In Table 2a is shown the input and calculated equilibrium state for unconstrained equilibrium at 550°C. Since, in this example, only the final equilibrium conditions will be calculated, the input serves only to set the number of moles of each element. The following reaction occurs within the molten salt solution, with nearly complete consumption of $NaClO_4$.

Table 2a
Calculation of equilibrium between a molten salt solution and air at 550 °C with no constraints.

Input (moles)

1.0 NaNO3
1.0 NaNO2
1.0 NaClO4
1.0 NaCl
79.0 N_2
21.0 O_2

Output (Equilibrium at 550°C)

101.52 mol gas
0.77820 N2
+ 0.22179 O2

+ 3.2040 mol Salt (liquid)
0.37578 NaCl
+ 0.61438 NaNO3
+ 9.8458E-03 NaNO2
+ 1.5255E-20 NaClO4

+ 0.79597 mol NaCl Solid

$$4\ NaNO_2 + NaClO_4 = 4\ NaNO_3 + NaCl \quad (1)$$

Furthermore, reaction with the gas phase takes place.

In reality it has been observed that, due to kinetic constraints, reaction (1) does not occur, nor does the salt react with the air. In Table 2b are shown the input and calculated equilibrium conditions for a constrained equilibrium calculation in which the number of moles of $NaNO_3$, $NaNO_2$, $NaClO_4$ and NaCl remain constant. The thermodynamic properties of the solid species $NaNO_3$(Qa), $NaNO_2$(Qb), …. have been set equal to those of the same species without the virtual elements. That is, the properties of solid $NaNO_3$(Qa) are the same as those of $NaNO_3$ solid; the properties of solid $NaNO_2$(Qb) are the same as those of solid $NaNO_2$, etc. For convenience, this equivalence is set by default by the FactSage software, but users may override this option by creating private databases containing any desired properties for species containing virtual elements, including species not explicitly entered at input.

Before performing the calculation, the end-members of the molten salt solution and of all solid salt solutions in the FactSage 8.2 FTsalt database were changed from $NaNO_3$, $NaNO_2$, $NaClO_4$ and NaCl to $NaNO_3$(Qa), $NaNO_2$(Qb), $NaClO_4$(Qc) and NaCl(Qd), with no change in the thermodynamic properties of the end-members nor in the Gibbs energy of mixing of the solutions. Since materials balances are respected for the virtual elements as well as for the real elements, the number of moles of Qa, Qb, Qc and Qd in the output are necessarily equal to the number of moles at input. At 550°C is can be seen that reaction (1) has been prevented within the salt solution as has any reaction with the air. At 200°C solid phases precipitate, but the total number of moles of all

Table 2b
Calculation as in Table 2a but with constraints prohibiting internal reaction within the molten salt solution and reaction with the air.

Input (moles)

1.0 NaNO3(Qa)
1.0 NaNO2(Qb)
1.0 NaClO4(Qc)
1.0 NaCl(Qc)
79.0 N_2
21.0 O_2

Output (Equilibrium at 550°C)

100.00 mol gas
0.79000 N2
+ 0.21000 O2

+ 4.00 mol Salt (liquid)
0.25000 NaCl(Qd)
+ 0.25000 NaNO3(Qa)
+ 0.25000 NaNO2(Qb)
+ 0.25000 NaClO4(Qc)

Output (Equilibrium at 200°C)

100.00 mol gas
0.79000 N2
+ 0.21000 O2

+ 2.5692 mol Salt (liquid)
2.5836E-02 NaCl(Qd)
+ 0.38922 NaNO3(Qa)
+ 0.38922 NaNO2(Qb)
+ 0.19572 NaClO4(Qc)

+ 0.93362 mol NaCl(Qd) Solid

+ 0.49715 mol NaClO4(Qc) Solid (alpha)

ions remain constant. For example, the total number of moles of ClO_4^-, which is equal to the total number of moles of Qc, is 2.5692(0.19572) + 0.49715 = 1.00 mol as was entered at input.

A calculated isothermal phase diagram at 200°C for the $NaNO_3$–$NaNO_2$–$NaClO_4$–NaCl system with constrained equilibrium is shown in Fig. 1. The diagram is calculated at a constant mole fraction X_{NaCl} = 0.25. The axes of the diagram are the molar ratios $NaNO_3/(NaNO_3 + NaNO_2 + NaClO_4)$, $NaNO_2/(NaNO_3 + NaNO_2 + NaClO_4)$ and $NaClO_4/(NaNO_3 + NaNO_2 + NaClO_4)$. The limited solubility of $NaNO_3$ in solid NaCl and $NaNO_2$ and of $NaNO_2$ in solid ht($NaNO_3$) are taken into account in the calculation.

2.3. Following the course of a reaction

In this example, 1.0 mol of an initially equimolar Zn–Mg solution is placed in a 50 L container with 1.5 mol Ar at 1500 K. The compositions of the liquid and gaseous phases are followed as evaporation occurs by assuming gas/liquid equilibrium and by constraining the amount of remaining liquid as the reaction progresses.

The input and some outputs are shown in Table 3. Due to the higher vapor pressure of Zn, the vapor phase is enriched in Zn at the early stages of the evaporation process. Data were taken from the FactSage 8.2 FTlite database with the end-members of the liquid re-defined as Mg(Qa) and Zn(Qa). By selecting the number of moles of Qa at input, the amount of remaining liquid can be constrained.

2.4. Avoid decomposition of metastable molecules at room temperature

Under the assumption of Gibbs energy minimization acetic acid CH_3COOH decomposes at room temperature and 1 bar atm to water and graphite. However, everyone who has eaten a salad with oil and vinegar knows that vinegar does not decompose spontaneously even though it consists primarily of water and 3 to 9% acetic acid. Therefore, it is obvious that the acetic acid molecule does not decompose within months due to kinetic limitations.

Traditionally, in Gibbs energy minimization software species that are not observed due to kinetic limitations are simply removed from the equilibrium calculation. It is shown in Fig. 2 that in the case of vinegar

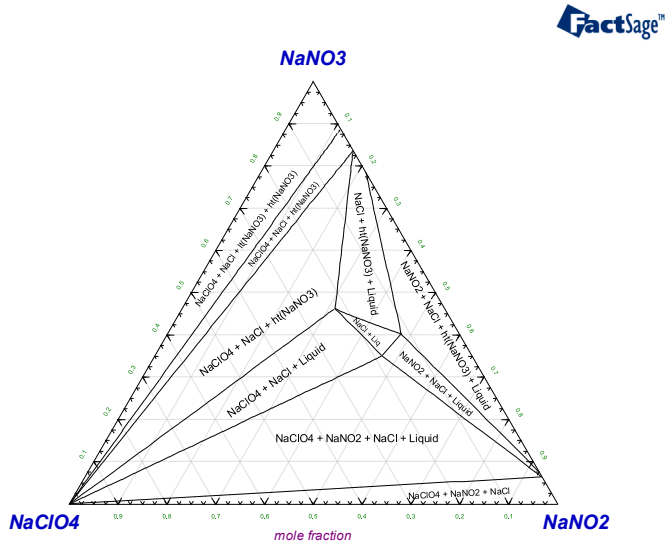

Fig. 1. Calculated phase diagram at 200°C of the $NaNO_3$–$NaNO_2$–$NaClO_4$–NaCl system at a constant mole fraction X_{NaCl} = 0.25 with constrained equilibrium as described in Section 2.2. Axes are the molar ratios $NaNO_3/(NaNO_3 + NaNO_2 + NaClO_4)$, $NaNO_2/(NaNO_3 + NaNO_2 + NaClO_4)$ and $NaClO_4/(NaNO_3 + NaNO_2 + NaClO_4)$.

(for simplicity: 95% H_2O and 5% CH_3COOH), besides graphite (case 2) also CO_2 and CH_4 need to be removed, both in the gas phase (case 3) and in the aqueous phase (case 4). However, this process makes it impossible to describe the interaction between e.g. carbonic acid and acetic acid.

Instead of excluding all species but the acetic acid and its residue ion, a virtual element Qa can be associated to the latter, forming $CH_3COOHQa$ (aqueous and gas phase species) and CH_3COOQa[-], which have identical Gibbs energies as the original acetic acid. Thus, by inputting an equal molar amount of CH_3COOH and Qa in the system, the acetic acid can only dissociate or evaporate. The output is shown in Table 4a. Note that also the equilibrium partial pressure of acetic acid in the gas phase is obtained.

This can then also be used to model an easy kitchen experiment: When adding 20 g of acetic acid and one package of standard baking powder (15 g, from which 4.8 g are $NaHCO_3$) to 100 g of water, one can easily note gas formation and absence of the smell characteristic for acetic acid. This corresponds well with the results for an equilibrium calculation as shown in Table 4a where the dissociation of acetic acid is constrained: There is formation of a gas phase and compared to the pure acetic acid shown in Table 4b, the partial pressure of CH3COOH in the gas phase is three orders of magnitude lower, leading to the absence of the characteristic smell of acetic acid. It should be noted that this approach is significantly easier to implement than an approach based on constraining reaction equations (See e.g. Alberty [4].).

2.5. Prohibiting redox reactions in aqueous solutions

In aqueous solutions, redox reactions among oxidation states of elements (as, for example, among SO_4^{2-}, S^{2-}, and SO_3^{2-} ions) are often kinetically hindered. An equilibrium calculation constrained only by elemental materials balances will always permit such reactions. In order to prohibit redox reactions so that, for instance, the number of SO_4^{2-} ions in the input to the calculation is equal to the number of SO_4^{2-} ions in the output, virtual elements can be employed to provide the required constraints.

This example considers an equilibrium between an aqueous solution and solid salts with such constraints applied.

The input to the calculation is shown in Table 5. Data were taken from the FactSage 8.2 FactPS database. Since, in this example, only the final equilibrium conditions will be calculated, the input serves only to set the number of moles of each element. The thermodynamic properties of the species K_2SO_4(Qa), K_2S(Qb), …… $SO_4(Qa)^{2-}$,…… have been set equal to those of the same species without the virtual elements. That is, the properties of solid K_2SO_4(Qa) are the same as those of K_2SO_4 solid; the properties of aqueous $SO_4(Qa)^{2-}$ are the same as those of SO_4^{2-} etc. For convenience, this equivalence is set by default by the FactSage software, but users may override this option by creating private databases containing any desired properties for species containing virtual elements, including species not explicitly entered at input.

The corresponding calculated output for equilibrium at 25°C is shown in Table 5. Since materials balances are respected for the virtual elements as well as for the real elements, the number of moles of Qa, Qb and Qc in the output are necessarily equal to the number of moles at input. For example, since K_2SO_3(Qc) solid and $SO_3(Qc)^{2-}$ were the only selected output species containing Qc, the total number of moles of SO_3^{2-} at equilibrium is equal to 7.0 which is the number of moles at input. That is:

$$6.9596 + (100/55.508)(0.022444) = 7.0 \quad (2)$$

(The FactSage output in Table 5 lists the molalities (moles per kg of H_2O) of the solutes, and 55.508 mol of H_2O has a mass of 1 kg) Similarly, the number of moles of SO_4^{2-} and S^{2-} remain unchanged.

That is, the redox reaction

$$4\ SO_3^{2-} = 3\ SO_4^{2-} + S^{2-} \quad (3)$$

Table 3
Following the course of evaporation of an initially equimolar Zn + Mg solution at 1500 K in a 50 L container.

Input
0.5 mol Zn, 0.5 mol Mg, 1.5 mol Ar, variable amount of Qa

Outputs

Qa = 1.0 (All Mg and Zn in liquid)

1.5000	mol gas	
	1.0000	Ar
+ 1.0000	mol liquid	
	0.50000	Mg(Qa)
	+ 0.50000	Zn(Qa)

Qa = 0.9 (Zn passes into gas more readily than Mg. Gas contains more Zn than Mg. Liquid contains less Zn than Mg)

1.6000	mol gas	
	0.93750	Ar
	+ 4.7860E-02	Zn
	+ 1.4640E-02	Mg
	+ 2.6402E-07	Mg2
+ 0.90000	mol liquid	
	0.52953	Mg(Qa)
	+ 0.47047	Zn (Qa)

Qa =0.1 (Zn/Mg ratio in gas now close to 1.0)

2.3999	mol gas	
	0.62504	Ar
	+ 0.19778	Zn
	+ 0.17713	Mg
	+ 5.7969E-05	Mg2
+ 0.10000	mol liquid	
	0.74642	Mg(Qa)
	+ 0.25358	Zn(Qa)

Qa = 0.0 (All liquid has evaporated. Gas is now equimolar in Zn and Mg)

2.4998	mol gas	
	0.60006	Ar
	+ 0.20002	Zn
	+ 0.19986	Mg
	+ 7.6879E-05	Mg2

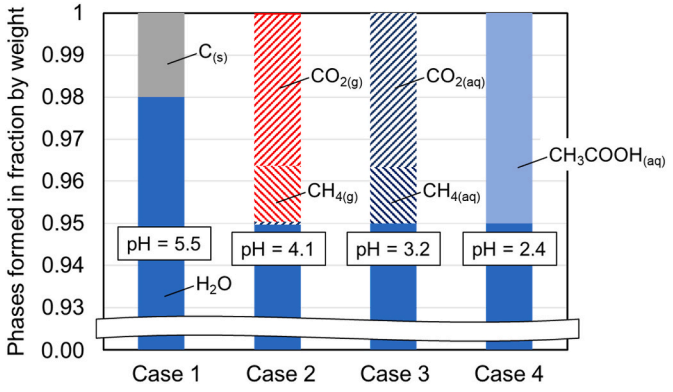

Fig. 2. Calculated phase formation for 95 wt% H_2O + 5 wt% CH_3COOH at 25 °C. Case 1: Full equilibrium. Case 2: Formation of C(s) is suppressed. Case 3: Formation of C(s) and gas phase is suppressed. Case 4: Only dissociation of CH_3COOH and H_2O into CH_3COO[-], H[+] and OH[-] is considered in equilibrium calculation. The pH value of the aqueous solution is indicated.

has been prohibited. If this same calculation is performed without the inclusion of virtual elements, then at equilibrium reaction (3) proceeds nearly to completion.

2.6. Suppressing internal equilibria within a spinel phase

In this calculation, 1 mol of $FeAl_2O_4$ spinel is cooled rapidly from 1473 K to 298.15 K in a calorimeter. We wish to calculate the heat evolved, given that the equilibrium cation distribution

$$(Fe^{2+}) + [Al^{3+}] = [Fe^{2+}] + (Al^{3+}) \quad (4)$$

between tetrahedral and octahedral lattice sites at 1473 K is retained metastably at 298.15 K (where round parentheses and square parentheses indicate ions on tetrahedral and octahedral sites respectively.)

Table 6a shows the calculated equilibrium cation distribution at 1473 K. The end-members of the solution (from the FactSage 8.2 FToxid database) are $(Fe)[Fe]_2O_4^{2-}$, $(Fe)[Al]_2O_4$ $(Al)[Al]_2O_4^{+}$ and $(Al)[Fe]_2O_4^{-}$ as shown in the table. The calculated "degree of inversion", defined as the concentration of (Al^{3+}) ions on tetrahedral sites, is 0.265. The enthalpy at 1473 K is-1.75790(10^6) J/mol.

Table 6a also shows the calculation of the equilibrium cation distribution at 298.15 K. The degree of inversion is essentially zero and the

Table 4a
Calculation of dissociation of acetic acid in an aqueous solution by the inclusion of a virtual element Qa to suppress the decomposition of CH3COOH.

Input (at 25°C)

95 g H2O
5 g $CH_3COOHQa$

Output (Equilibrium at 25°C, 1 bar)

0	mol gas_ideal	
	(3.1E-02 bar	H2O
	+ 4.0E-03 bar	CH3COOHQa)
+ 100.00	gram aqueous	
	+ 0.87 molal	CH3COOHQa
	+ 4E-3 molal	CH3COOQa[-]
	+ 4E-3 molal	H[+]
	+ 2E-12 molal	OH[-]

pH = 2.4

Table 4b
Calculation of neutralization of acetic acid by baking powder (here abbreviated by: NaHCO3).

Input (at 25°C)

```
100.0 g H2O
20.0 g acetic acid (19 g H2O  +  1 g CH3COOHQa)
 4.8 g NaHCO3
```

Output (Equilibrium at 25°C, 1 bar)

```
   0.013    mol  gas_ideal
        ( 0.97 bar    CO2
         + 3E-2 bar H2O
         + 2E-6 bar CH3COOHQa)

+ 124.23   gram  aqueous
        ( 2.2E-1 molal HCO[-]
          3.6E-1 molal Na[+]
          1.4E-1 molal CH3COOQa[-]
          1.2E-1 molal NaHCO3
          4.5E-4 molal CH3COOHQa
          1.6E-7 molal OH[-]
          6.0E-8 molal H[+])
pH = 7.2
```

Table 5
An equilibrium calculation involving an aqueous solution with constraints prohibiting redox reactions.

Input (moles)

```
100 H2O   2.0 K2SO4(Qa)   0.0 SO4(Qa)[2-]
                          0.0 HSO4(Qa)[-]
          3.0 K2S(Qb)     0.0 S(Qb)[2-]
          7.0 K2SO3(Qc)   0.0 SO3(Qc)[2-]
```

Output (Equilibrium at 25°C)

```
 109.13    mol   aqueous
       55.508          H2O
      + 3.3783         K[+]
      + 1.6653         S(Qb)[2-]
      + 2.2444-02      SO3(Qc)[2-]
      + 1.4671E-03     SO4(Qa)[2-]

 + 6.9596    mol   K2SO3(Qc) Solid

 + 1.9974    mol   K2SO4(Qa) Solid (alpha)
```

enthalpy is -1.97892(10^6) J/mol.

Table 6b shows a calculation at 298.15 K in which the degree of inversion is constrained to be equal to its equilibrium value at 1473 K. The degree of inversion, the concentration of (Al^{3+}), is equal to the sum of the concentrations of the $(Al)[Al]_2O_4^+$ and $(Al)[Fe]_2O_4^-$ end members. By adding the virtual element Qa to the formulae of these two end-members in the database (with no change in their thermodynamic properties) and by setting Qa = 0.265 in the input as shown, the degree of inversion is constrained as desired. The enthalpy of the metastable solution is-1.96299(10^6) J/mol.

The actual heat evolved during rapid non-equilibrium cooling can now be calculated as(-1.96299 + 1.75790)(10^6)) = -2.05090(10^5) J/mol, which may be compared to (-1.97892 + 1.75790)(10^6)) = -2.21020 (10^5) J/mol which is the heat effect that would be observed were equilibrium maintained during quenching.

Table 6a
Calculation of the equilibrium cation distribution between tetrahedral and octahedral lattice sites in 1 mol of FeAl2O4 spinel at 1473 K and at 298.15 K.

INPUT (moles)
1.0 FeAl2O4

OUTPUT (Equilibrium cation distribution at 1473 K)

```
1.0000    mol   Spinel
          9.7426E-02    Fe3O4[2-]      = (Fe)[Fe]2O4 [2-]
        + 0.63741       Fe1Al2O4       = (Fe)[Al]2O4
        + 0.23001       Al3O4[1+]      = (Al)[Al]2O4 [+]
        + 3.5156E-02    Al1Fe2O4[1-]   = (Al)[Fe]2O4 [-]

        Site fractions of sublattice constituents:
        Fe[2+]T          0.73484    Stoichiometry = 1
        Al[3+]T          0.26516  (High temp. degree of inversion = 0.265)
        ------------------------------------------------------------
        Fe[2+]O          0.13250    Stoichiometry = 2
        Al[3+]O          0.86742
  ************************************
     H                  G                  S
    (J)                (J)               (J/K)
 ************************************
 -1.75790E+06   -2.31351E+06   3.77192E+02
```

OUTPUT (Equilibrium cation distribution at 298.15 K)

```
1.0000    mol   Spinel
          2.7177E-06    Fe3O4[2-]      = (Fe)[Fe]2O4 [2-]
        + 0.99999       Fe1Al2O4       = (Fe)[Al]2O4
        + 5.4353E-06    Al3O4[1+]      = (Al)[Al]2O4 [+]
        + 1.4771E-11    Al1Fe2O4[1-]   = (Al)[Fe]2O4 [-]

        Site fraction of sublattice constituents:
        Fe[2+]T          0.99999    Stoichiometry = 1
        Al[3+]T          5.4353E-06  (Degree of inversion = 0.00)
        ------------------------------------------------------------
        Fe[2+]O          2.7177E-06    Stoichiometry = 2
        Al[3+]O          1.0000
  ************************************
     H                  G                  S
    (J)                (J)               (J/K)
 ************************************
 -1.97892E+06   -2.00727E+06   9.51007E+01
```

2.7. Paraequilibrium calculations

In certain solid systems, some elements diffuse much faster than others. Hence, if an initially homogeneous single-phase system at high temperature is quenched rapidly and then held at a lower temperature, a temporary paraequilibrium state may result in which the rapidly diffusing elements have reached equilibrium, but the more slowly diffusing elements have remained essentially immobile. The best known, and most industrially important, example occurs when homogeneous austenite is quenched and annealed. Interstitial elements such as C and N are much more mobile than the metallic elements. For a detailed description of paraequilibrium constraints, see Pajarre et al. [1] and Pelton et al. [5].

In this example, an Fe(0.96)Cr(0.04)C(0.01) alloy (compositions shown are molar) is rapidly cooled from the homogeneous γ-austenite (fcc) range to 700°C where a metastable state is reached with the molar Cr/Fe ratio equal to 4/96 in all phases, while C is assumed to diffuse between the phases, attaining paraequilibrium. The calculation is shown in Table 7. Zero moles of the virtual elements Qa, Qb and Qc are entered. Data are taken from the FactSage 8.2 FSstel database. The formulae for the end-members of the fcc, bcc and cementite phases were modified as shown to associate, in each phase, 96 mol of a virtual element with every mole of Cr and -4 mol of the same virtual element with every mole of Fe.

Table 6b
Calculation of the equilibrium cation distribution between tetrahedral and octahedral lattice sites in 1 mol of FeAl2O4 spinel at 1473 K and at 298.15 K when the degree of inversion is constrained to be 0.265.

INPUT (moles)

1.0 FeAl2O4
0.265 Qa

OUTPUT (at 298.15 K with degree of inversion constrained to be 0.265)

```
1.0000    mol  Spinel
        9.7387E-02   Fe3O4[2-]          = (Fe)[Fe]2O4 [2-]
      + 0.63761      Fe1Al2O4           = (Fe)[Al]2O4
      + 0.22989      Al3O4(Qa)[1+]      = (Al)[Al]2O4 [+]
      + 3.5112E-02   Al1Fe2O4(Qa)[1-]   = (Al)[Fe]2O4 [-]

      Site fractions of sublattice constituents:
      Fe[2+]T          0.73500   Stoichiometry = 1
      Al[3+]T          0.26500   (Degree of inversion = 0.265)
      ------------------------------------------------------------
      Fe[2+]O          0.13250   Stoichiometry = 2
      Al[3+]O          0.86750

  ************************************
    H              G              S
   (J)            (J)           (J/K)
 ************************************
 -1.96299E+06   -1.99642E+06   1.12130E+02
```

Table 7
A paraequilibrium calculation in which an Fe(0.96)Cr(0.4)C(0.001) alloy is rapidly cooled from the homogeneous austenite range to 700 °C. The Cr/Fe ratio remains equal to 4/96 in every phase.

INPUT (moles)

0.04 Cr
0.96 Fe
0.01 C
0.00 Qa
0.00 Qb
0.00 Qc

OUTPUT (at paraequilibrium at 700°C)

```
0.74795    mol   BCC A2
         1.4400E-05     CrC3(Qb96)
       + 3.9986E-02     Cr(Qb96)
       + 3.4560E-04     FeC3(Qb-4)
       + 0.95965        Fe(Qb-4)

 + 0.25205    mol   FCC A1
         3.8541E-02     Cr(Qa96)
       + 0.92499        Fe(Qa-4)
       + 1.4588E-03     CrC(Qa96)
       + 3.5011E-02     FeC(Qa-4)

 + 0.00       mol   Cementite
         4.0000E-02     Cr3C1(Qc96)
       + 0.96000        Fe3C1(Qc-4)
```

Since the number of moles of the virtual elements are all zero, the Cr/Fe molar ratio is thereby constrained to be equal to 4/96 in every phase.

2.8. Calculating the surface tension of a solution

According to Butler [6], the surface of a solution may be considered as a separate phase consisting of a monolayer of atoms. For a solution with components M − N, Pajarre et al. [7] proposed treating the surface phase as a solution M(Qa)-N(Qa) containing the virtual element Qa (See also Kang [8] and Koukkari [1]). The Gibbs energy difference between M and M(Qa) is the molar surface energy $A(M)\sigma(M)$ (J/mol), where $A(M)$ is the molar surface area (m^2/mol) and $\sigma(M)$ is the surface tension of pure M (N/m). $A(M)$ can be calculated from lattice parameters, and $\sigma(M)$ is determined experimentally. It can be shown [7] that the surface energy $A\sigma$ of the binary solution is equal to the chemical potential of Qa (where the molar surface area A of the solution is estimated as varying linearly with the surface mole fractions between the molar surface areas of pure M and N.) It may be noted that this situation is formally analogous to an equilibrium between a solution M − N and a very small amount of an oxide solution MO-NO.

In the present example, the surface tension of a liquid Ag–Pb solution containing 30 mol% Pb at 1000 K is calculated. A user-defined database has been created. The database contains a file for the bulk Ag–Pb solution in which the molar Gibbs energies g^o_{Ag} and g^o_{Pb} of the pure liquid end-members are taken from the FactSage 8.2 FactPS database and with the excess molar Gibbs energy at 1000 K as given by Koukkari [2]:

$$g^{E(bulk)} = X_{Ag}X_{Pb}\,(6741.7–1464.8\,X_{Ag}X_{Pb} - 1978\,X^2_{Ag}X^2_{Pb})\ \text{J/mol} \quad (5)$$

where X_{Ag} and X_{Pb} are the mole fractions in the solution. The database also contains a file for the surface phase with end-members Ag(Qa) and Pb(Qa). At 1000 K, for pure Ag, $A(Ag) = 47{,}329\ m^2$/mol [1] and $\sigma(Ag) = 0.916$ N/m [2]. Hence, $A(Ag)\ \sigma(Ag) = 43{,}353$ J/mol. The Gibbs energy of the Ag(Qa) end-member is then set at 1000 K as

$$g^o_{Ag(Qa)} = g^o_{Ag} + 43{,}353\ \text{J/mol} \quad (6)$$

Similarly, $A(Pb) = 70,\ 215\ m^2$/mol and $\sigma(Pb) = 0.388$ N/m [2]. Hence

$$g^o_{Pb(Qa)} = g^o_{Pb} + (70{,}215)(0.388)\ \text{J/mol} \quad (7)$$

Finally, as proposed by Tanaka et al. [9], the excess Gibbs energy of the surface solution is estimated as

$$g^{E(surface)} = 0.83\ g^{E(bulk)} \quad (8)$$

due to the reduced coordination number of surface atoms.

Finally, the database contains a file for "pure Qa". In the calculation this "phase" is selected as a "dormant" phase. That is, the FactSage software will set its equilibrium amount equal to zero but will calculate its chemical potential.

The calculation is shown in Table 8. The calculated composition of the surface phase is 13.854 mol% Ag and 86.146 mol% Pb. Only a very small amount of the virtual element Qa = 0.0001 mol is included so that the amount of the surface phase is negligibly small. As long as Qa is very small the result will be independent of Qa since the formation of the surface phase will leave the composition of the bulk phase virtually unchanged. The calculated compositions of the bulk and surface phases at 1000 K are shown in Table 8 as well as the calculated chemical activity of Qa. The surface energy of the solution is equal to the chemical potential of Qa:

$$A\ \sigma = \mu(Qa) = RT\ln a(Qa) = 8.315\ (1000)\ \ln\ (53.978)\ \text{J/mol} \quad (9)$$

It is further assumed that the area A varies linearly with the surface mole fractions of the components:

$$A = 0.13854\ (47329) + 0.86146\ (70215)\ m^2\text{/mol} \quad (10)$$

Therefore, from eqs 9 and 10 the surface tension of the solutions

Table 8
Calculation of the surface tension of a Pb(0.3)Ag(0.7) alloy at 1000 K.

INPUT (moles)
0.3 Pb
0.7 Ag
0.0001 Qa
and Qa is selected as a dormant "phase"

OUTPUT (at 1000 K)

0.99990 mol bulk solution
0.7000 Ag
+ 0.3000 Pb
(bulk phase composition)

+ 1.0000E-04 mol surface solution
0.13854 Ag(Qa)
+ 0.86146 Pb(Qa)
(surface phase composition. Amount is negligibly small)

+ 0.00 mol Qa
(1000 K, a = 53.978) **(activity of Qa)**

containing 30 mol% Pb is $\sigma = 0.495$ N/m.

3. Conclusions

Through the judicious use of "virtual elements" that have zero atomic mass but that are included in the materials balances, it is possible to apply a variety of constraints to equilibrium calculations without the necessity of writing dedicated software for each individual application. The concept has been demonstrated through several examples. Many more diverse applications can be envisaged. The FactSage 8.1 and higher software [3] permits the inclusion of virtual elements. Here, virtual elements can not only be associated with pure compound species but also with solution phase end-members on-the-fly and when using a write-protected database.

A more detailed presentation of the FactSage input/output for the examples in this paper are available at https://www.crct.polymtl.ca/fact/factsage/EquASage.pdf, and the thermodynamic data for the compounds can be found at https://www.crct.polymtl.ca/compweb.php.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data were used for the research described in the article.

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