

MODELLING CHEMICALLY REACTING PROCESSES INVOLVING MULTIPLE PHASES

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SYNOPSIS

An algorithm for calculating combined phase and chemical equilibria is used in combination with a number of models for the non-ideality of fluid mixtures. The resulting package can be used interactively to study a process or can be incorporated into a simulation program. Three examples are presented: the reaction of methanol and isobutene to form methyl tertiary butyl ether (MTBE); the reaction of solid nickel with carbon monoxide to form nickel carbonyl in the presence of other liquids and gases; the effect of composition on the equilibrium concentration of elemental oxygen in molten steel alloys.

INTRODUCTION

The possible presence of more than one phase in a chemically reacting process is of considerable significance when modelling the process. The equilibrium concentrations of the products can have a marked effect on the extent to which the reactants are in contact with or are separated from one another. The number and nature of the phases at equilibrium may also change depending on the conditions.

In order to study reactive processes, the authors have developed a new algorithm for calculating combined phase and chemical equilibria (1) involving solids, liquids and gases. The algorithm is designed so that it can be conveniently used as part of an interactive program which allows the user to perform repeated equilibrium calculations under varying conditions or else it can be built into a larger simulation program.

The algorithm is also designed to be used with different physical property models and sources of data. The algorithm starts by calling for the chemical formulae of all the components that are present in the system or which the user considers may form. No reaction scheme is needed as this is not thermodynamically necessary to calculate the equilibrium; all possible reactions can be deduced implicitly by the program from the chemical formulae. Next the algorithm calls for the Gibbs energy of formation of each component in the ideal gas state at the temperature specified, which requires that the program is linked to a suitable physical property data base. Finally at each iteration the algorithm calls for the fugacity coefficients of each component in each fluid phase that is present. Ideal fluid phases can easily be modelled by setting all fugacity coefficients to unity. By linking the algorithm to standard phase equilibrium software, it is possible to model a reactive process that also involves vapour-liquid phase equilibria using normal industry methods for modelling the thermodynamics of fluid mixtures.

MTBE PRODUCTION

The production of methyl tertiary-butyl ether (MTBE) from methanol and isobutene is a process involving phase and chemical equilibrium. To model the process, we took the thermochemical properties of methanol, isobutene and MTBE for calculating the Gibbs energy of formation from

the DIPPR compilation (2). As MTBE and methanol are highly polar compounds, it is not sufficient to assume that the liquid phase is ideal. We therefore used the UNIFAC method to estimate the fugacity coefficients of the liquid mixture. The vapour phase was assumed to be ideal. Figure 1 shows the equilibrium yield of MTBE from an equimolar mixture of methanol and isobutene predicted by the model as a function of temperature for isobars at 1, 5 and 10 bar. The algorithm incorporates a phase stability analysis procedure which enables it automatically to detect which phases are present under different conditions.

The results show that when the system is all liquid, the yield of MTBE is essentially unaffected by pressure and falls slightly with temperature. As the temperature rises, a reactive bubble point is found at which point yield drops rapidly until the system becomes all vapour when yield drops more slowly with rising temperature. The program clearly shows that optimum yield is obtained at the all-liquid line. Lowering the temperature theoretically increases yield but will make it increasingly difficult to attain equilibrium. The best compromise position is clearly the bubble point which combines good yield and high temperature. The pressure must be just high enough to position the bubble point at a temperature that is high enough to give the required rate of reaction.

Reactive distillation is used to increase yield beyond the equilibrium value. A liquid mixture was taken with the composition corresponding to the bubble point at 50°C. The pressure was reduced below the bubble point and the mole fraction of MTBE in the remaining liquid calculated. As the pressure drops, column 1 of Table 1 shows that the MTBE yield also decreases. This is because the ratio of isobutene and methanol is no longer equimolar in both phases, i.e. the feed ratio is less favourable for the production of MTBE because the isobutene and methanol have been partially separated. On the other hand, column 2 shows the result of flashing the same mixture with no chemical reaction taking place. As MTBE is the least volatile component, the resulting liquid has an even higher MTBE concentration. Effective separation therefore depends as much on preventing reactions from occurring during the distillation process as promoting them in the liquid phase around the catalyst.

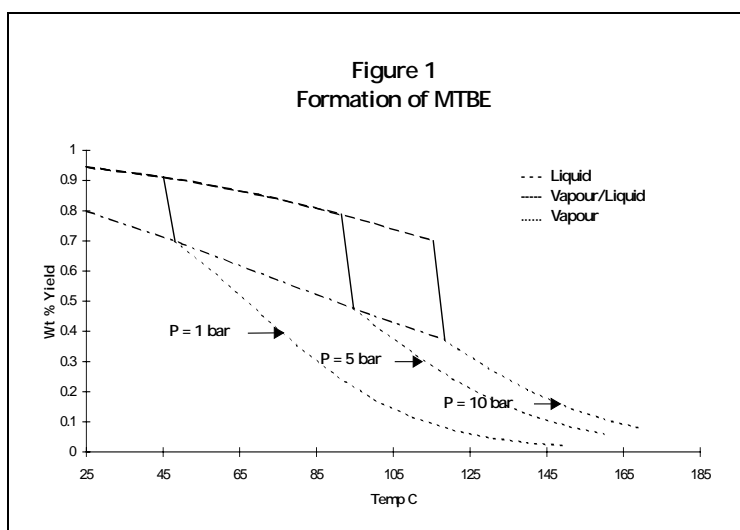


Table 1
Vapour-liquid equilibria: MTBE yield at 50 °C in liquid

At Chemical Equilibrium wt %	No Chemical Equilibrium wt %	Pressure bar
94.9	94.9	1.7079 (bubble pt)
94.9	95.5	1.15
94.5	96.1	1.10

One weakness of this model is the use of UNIFAC which is a general predictive method for vapour-liquid equilibria, but not particularly accurate. Better results can be obtained using a model such as NRTL or UNIQUAC for the fugacity coefficients and regressing their binary interaction parameters to experimental vapour-liquid equilibrium data. By combining our chemical equilibrium algorithm with a non-linear regression program, it is possible directly to regress reactive vapour-liquid equilibrium experimental data to give the best possible model for the process.

NICKEL CARBONYL FORMATION.

Nickel can react with carbon monoxide to form nickel carbonyl. This can be a problem with nickel catalysts when carbon monoxide is present, as the nickel can be taken up into the reacting mixture and deposited further on in the process. To illustrate how this can be modelled, we took 1 mole of hydrogen, 1 mole carbon monoxide and 1 mole of a mixture of hydrocarbons ranging from butane to undecane. We assumed that the hydrogen and hydrocarbons would not react and set the program accordingly. Solid nickel was assumed to be present in excess under all conditions. Nickel carbonyl was allowed to form. The fugacity coefficients were calculated for both liquid and gas phases with the API variant of the Redlich-Kwong-Soave equation, which incorporates a special correlation for hydrogen.

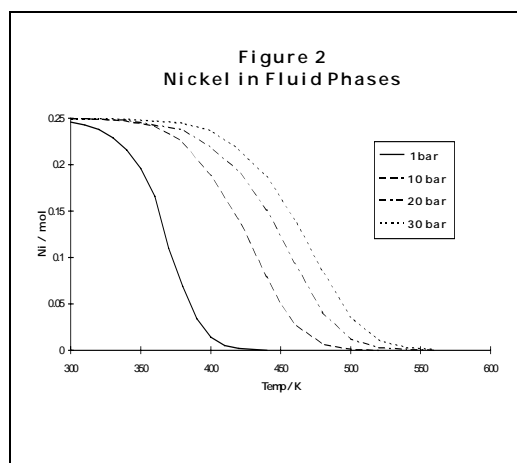
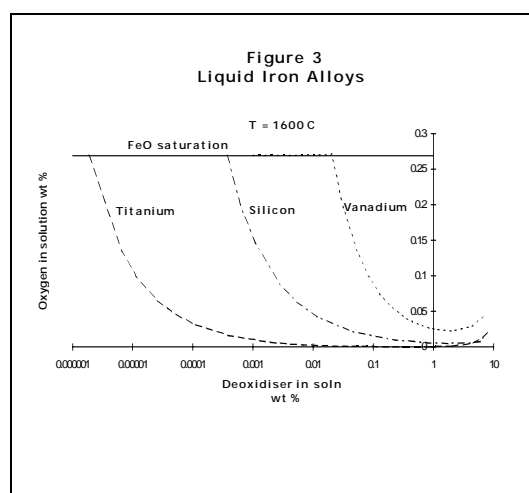


Figure 2 shows the amount of nickel that is taken into the fluid phases as a function of temperature for a number of isobars. Unlike the MTBE process, the phase behaviour of the fluid does not have a marked influence on the shape of the isobars. For a given fluid, the amount of nickel taken up can easily be calculated as a function of pressure and temperature.

MOLTEN STEEL ALLOYS

The flexibility of the chemical equilibrium algorithm is shown by its application to molten steel alloys. Important physical properties such as surface tension of molten alloys are controlled by the concentration of impurities such as elemental oxygen or sulphur. These in turn are buffered by the presence of metal oxides or sulphides in the melt. As there is only one fluid phase, liquid steel, the Gibbs energy of formation for each component was calculated using the liquid phase as the standard reference phase. The non-ideality of iron alloys was therefore represented by calculating the activity coefficients rather than the fugacity coefficients. The algorithm was linked with a different physical property software package in which the activity coefficients for iron melts as set out in (3) were calculated. The algorithm needs to establish which of the many possible oxides will form under given conditions.



As an illustration, Figure 3 shows the predicted concentration of elemental oxygen in molten iron at 1600degC as a function of admixtures of deoxidisers vanadium, silicon and titanium. At low concentrations the oxygen content is buffered by the presence of FeO. As the concentration rises, oxides of titanium, silicon or vanadium form in preference. As the concentration of the deoxidiser rises, the oxygen concentration changes in a complex way that reflects both the thermodynamic properties of the oxides formed and the influence of the presence of deoxidiser on the activity of oxygen.

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