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# Development of an Equation of State for the Representation of Solid-Liquid, Solid-Vapor, and Liquid-Vapor Equilibria of Substances of Interest for the Air Distillation Process

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## Introduction

Cryogenic distillation of air is the most highly developed separation technology for the industrial production of N<sub>2</sub> and O<sub>2</sub>. The conventional scheme of a double column apparatus presents one column under the other one and a reboiler-condenser in between. The two columns are known as the medium-pressure column and the low pressure column, respectively.

Air contains undesirable contaminants that, upon cooling, become solids and foul the heat transfer surfaces, impeding the heat exchange and increasing the pressure drops through the air distillation process. H<sub>2</sub>O and CO<sub>2</sub> must be removed as their freezing points are above the temperatures required for air liquefaction and they will freeze out in the heat exchanger and block the equipment. Furthermore, air distillation plants are generally installed on industrial sites and this contributes to air contamination by different types of pollutants, like N<sub>2</sub>O and light hydrocarbons.

In order to avoid these common problems in the industrial cryogenic processes involving separation of gas mixtures into their components, the accurate knowledge of thermodynamic properties like solid-liquid, liquid-vapor and solid-vapor equilibria is of a great importance.

In this work, we present the Solid-Liquid-Vapor Peng-Robinson Equation of State (SLV PR EoS) used for representing phase equilibria of pure compounds and binary mixtures of interest in the cryogenic air distillation process.

## Method

The SLV PR EoS has been obtained starting from the Yokozeki EoS [1] in which the Peng-Robinson's attractive term has been considered. The proposed EoS, used for representing phase equilibria of some pure compounds (N<sub>2</sub>, O<sub>2</sub>, Ar, Kr, Xe, Ne, CO<sub>2</sub>, N<sub>2</sub>O, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>8</sub> and C<sub>3</sub>H<sub>6</sub>) and binary mixtures, is defined as follow :

$$P = \frac{RT}{v - c} \left( \frac{v - d}{v - b} \right) - \frac{a}{v^2 + 2bv - b^2}$$

*P*: pressure *T*: temperature *R*: gas constant *v*: volume  
*a, d*: parameters *b*: liquid covolume *c*: solid covolume

## Results Pure Compounds

For each pure compound, a pressure-temperature range has been fixed; each range extends from a minimum to a maximum, located on the SVE and the SLE branches, respectively. These values are indicated in Table 1 for N<sub>2</sub>, O<sub>2</sub>, Ar, CO<sub>2</sub>, CH<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub>. The VLE branch is instead studied between the triple and the critical points for all the pure compounds. For the hydrocarbons, except methane, the lower limits correspond to the triple point coordinates.

| Compound                      | SVE      |           | SLE      |            |
|-------------------------------|----------|-----------|----------|------------|
|                               | Tmin / K | Pmin / Pa | Tmax / K | Pmax / MPa |
| N <sub>2</sub>                | 40       | 11        | 130      | 400        |
| O <sub>2</sub>                | 48       | 12        | 160      | 1500       |
| Ar                            | 50       | 37        | 160      | 380        |
| CO <sub>2</sub>               | 125      | 11        | 310      | 610        |
| CH <sub>4</sub>               | 60       | 16        | 200      | 600        |
| C <sub>2</sub> H <sub>6</sub> | 90.37    | 1.1       | 340      | 4100       |

Table 1: P-T ranges for the pure compounds studied.

The quantitative comparison of the phase equilibrium values obtained with the SLV PR EoS and those from auxiliary equations [2] has been evaluated with reference to the common statistical indexes: AAD%, Bias% and MAD%. Table 2 represents these errors obtained calculating the equilibrium temperature at fixed pressure, for the same compounds reported in Table 1.

| Compound                      | VLE   |        |      | SVE   |       |      | SLE   |       |      |
|-------------------------------|-------|--------|------|-------|-------|------|-------|-------|------|
|                               | AAAD% | BIAS%  | MAD% | AAAD% | BIAS% | MAD% | AAAD% | BIAS% | MAD% |
| N <sub>2</sub>                | 0.12  | -0.1   | 0.31 | 0.05  | 0.02  | 0.1  | 0.47  | 0.03  | 0.91 |
| O <sub>2</sub>                | 0.41  | -0.37  | 0.81 | 0.26  | 0.24  | 0.38 | 1.08  | -0.79 | 2.56 |
| Ar                            | 0.20  | -0.18  | 0.29 | 0.13  | 0.04  | 0.29 | 0.46  | -0.33 | 1.62 |
| CO <sub>2</sub>               | 0.43  | -0.28  | 0.82 | 0.16  | 0.04  | 0.29 | 0.44  | -0.21 | 1.49 |
| CH <sub>4</sub>               | 0.05  | -0.01  | 0.1  | 0.06  | -0.06 | 0.22 | 0.08  | 0.03  | 1.25 |
| C <sub>2</sub> H <sub>6</sub> | 0.12  | -0.004 | 0.22 |       |       |      | 0.49  | 0.47  | 0.95 |

Table 2: Summary of the statistical errors in calculating SVE, SLE, and VLE with the SLV PR EoS.

## Results CH<sub>4</sub> + CO<sub>2</sub> Mixture

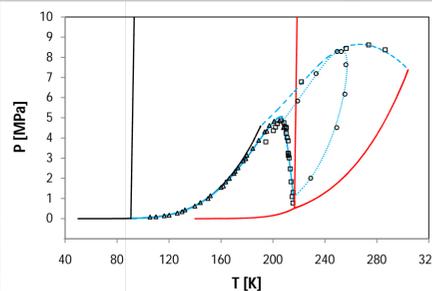


Figure 1: P-T equilibrium behavior. Calculated values: — CH<sub>4</sub>; — CO<sub>2</sub>; — S<sub>2</sub>S<sub>1</sub>V triple line; — critical line; — VL phase envelope xCH<sub>4</sub>=0.524. Data: □ Donnelly and Katz [3]; △ Davis et al. [4]; ○ Esper et al. [5].

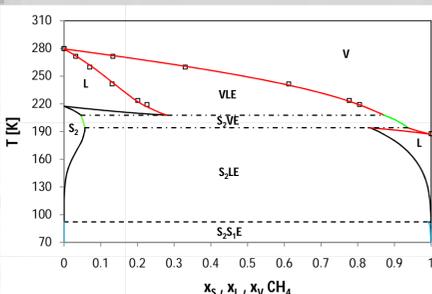


Figure 2: T-x equilibrium behavior. Calculated values: — S<sub>2</sub>S<sub>1</sub>L; — S<sub>2</sub>S<sub>1</sub>V; — S<sub>2</sub>S<sub>1</sub>V; — VLE; — critical line. Data [3]: 4.14 MPa (□); — S<sub>2</sub>S<sub>1</sub>V triple point; — S<sub>2</sub>S<sub>1</sub>L triple point.

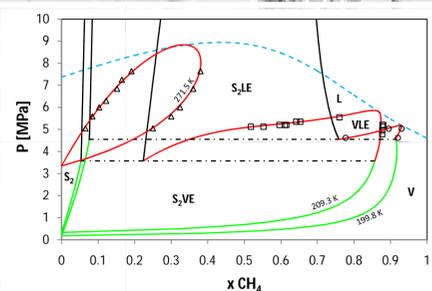


Figure 3: P-x equilibrium behavior. Calculated values: — S<sub>2</sub>S<sub>1</sub>L; — S<sub>2</sub>S<sub>1</sub>V; — VLE; — critical line. Data [3]: 271.5 K (△); 209.3 K (□); 199.8 K (○); — S<sub>2</sub>S<sub>1</sub>V triple point.

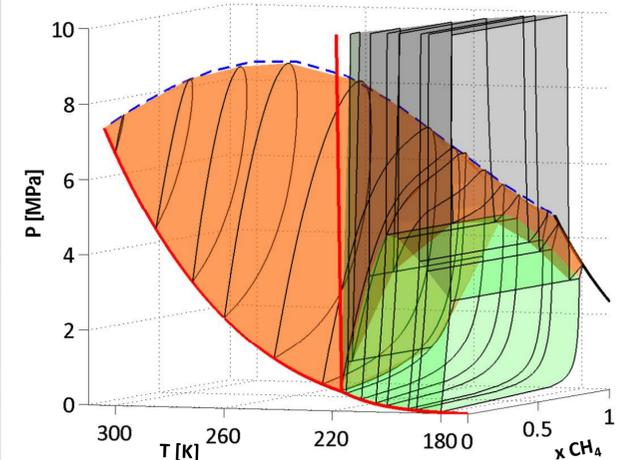


Figure 4: P-T-x equilibrium behavior. Calculated values: — VLE CH<sub>4</sub>; — CO<sub>2</sub>; — critical line. P-x cross sections: ■ VLE; ■ SLE; ■ SVE.

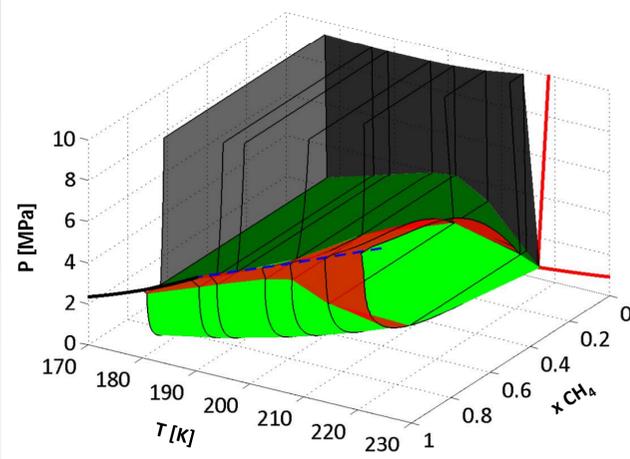


Figure 5: P-T-x equilibrium behavior. Calculated values: — VLE CH<sub>4</sub>; — CO<sub>2</sub>; — critical line. P-x cross sections: ■ VLE; ■ SLE; ■ SVE.

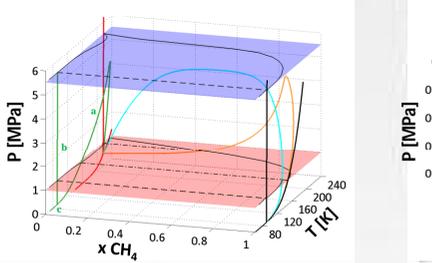


Figure 6: P-T-x equilibrium behavior. Pure compounds: — CH<sub>4</sub>; — CO<sub>2</sub>. Triple lines: S<sub>2</sub>S<sub>1</sub>L (—ax<sub>2</sub>; —x<sub>1</sub>); S<sub>2</sub>S<sub>1</sub>L (—bx<sub>2</sub>); S<sub>2</sub>S<sub>1</sub>V (—cx<sub>2</sub>). T-x cross sections: □ 5.5 MPa; ■ 1 MPa. Triple points: — S<sub>2</sub>S<sub>1</sub>L; — S<sub>2</sub>S<sub>1</sub>V.

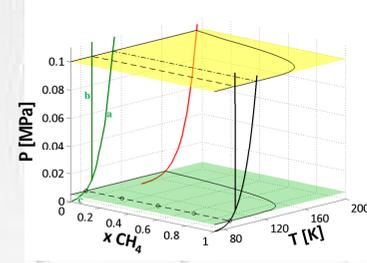


Figure 7: P-T-x equilibrium behavior. Pure compounds: — CH<sub>4</sub>; — SVE CO<sub>2</sub>. Triple lines: S<sub>2</sub>S<sub>1</sub>L (—ax<sub>2</sub>); S<sub>2</sub>S<sub>1</sub>L (—bx<sub>2</sub>); S<sub>2</sub>S<sub>1</sub>V (—cx<sub>2</sub>). T-x cross sections: □ 0.1 MPa; ■ 0.005 MPa. Triple points: — S<sub>2</sub>S<sub>1</sub>L; — S<sub>2</sub>S<sub>1</sub>V; — S<sub>2</sub>S<sub>1</sub>V.

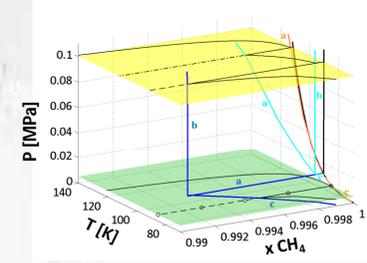


Figure 8: P-T-x equilibrium behavior. Pure compound: — CH<sub>4</sub>. Triple lines: S<sub>2</sub>S<sub>1</sub>L (—ax<sub>1</sub>; —ax<sub>2</sub>); S<sub>2</sub>S<sub>1</sub>L (—bx<sub>1</sub>; —bx<sub>2</sub>); S<sub>2</sub>S<sub>1</sub>V (—cx<sub>1</sub>); S<sub>2</sub>S<sub>1</sub>V (—cx<sub>2</sub>). T-x cross sections: □ 0.1 MPa; ■ 0.005 MPa. Triple points: — S<sub>2</sub>S<sub>1</sub>L; — S<sub>2</sub>S<sub>1</sub>V; — S<sub>2</sub>S<sub>1</sub>V.

## Conclusion and Perspectives

The SLV PR EoS allows a good representation of the SLE, SVE, and VLE in a wide range of temperature and pressure for different compounds of interest in the cryogenic air distillation processes. The intention of the authors is to extend the study to other pure compounds and to reduce the number of the parameters included in the SLV PR EoS for an industrial application of this equation.

The EoS proposed can be extended to mixtures, and allows evaluating their thermodynamic behavior in the cryogenic field. This should be an important aid for designing and optimizing industrial cryogenic processes; knowing at which conditions in a mixture the solid-fluid equilibria appears (where fluid means either the liquid or the vapor phases) represents an opportunity of great interest, because it could be used for improving the cryogenic processes and for avoiding some drawbacks as solidification of the impurities. The phase diagrams, as Px and Tx cross sections at cryogenic conditions, can give important information for evaluating new air separation techniques, exploiting the capability of the SLV PR EoS in representing phase equilibrium values in which also the solid phase is involved.

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