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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 N₂ and O₂. 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. H₂O and CO₂ 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 N₂O 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 (N₂, O₂, Ar, Kr, Xe, Ne, CO₂, N₂O, CH₄, C₂H₆, C₂H₄, C₃H₈ and C₃H₆) 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 N₂, O₂, Ar, CO₂, CH₄, and C₂H₆. 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 ₂	40	11	130	400
O ₂	48	12	160	1500
Ar	50	37	160	380
CO ₂	125	11	310	610
CH ₄	60	16	200	600
C ₂ H ₆	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 ₂	0.12	-0.1	0.31	0.05	0.02	0.1	0.47	0.03	0.91
O ₂	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 ₂	0.43	-0.28	0.82	0.16	0.04	0.29	0.44	-0.21	1.49
CH ₄	0.05	-0.01	0.1	0.06	-0.06	0.22	0.08	0.03	1.25
C ₂ H ₆	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 CH₄ + CO₂ Mixture

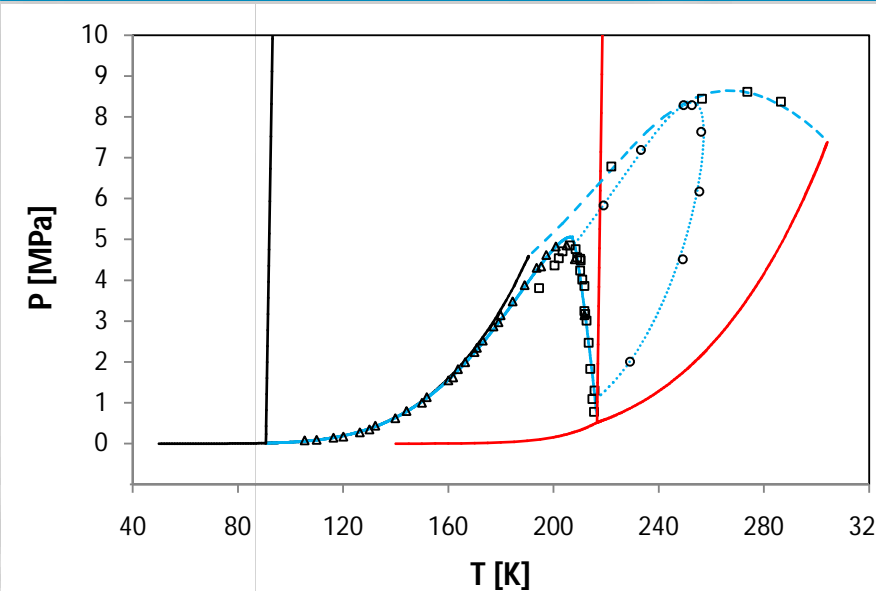


Figure 1: P-T equilibrium behavior. Calculated values: — CH₄; — CO₂; — S₂S₁V triple line; — critical line; — VL phase envelope xCH₄=0.524. Data: □ Donnelly and Katz [3]; △ Davis et al. [4]; ○ Esper et al. [5].

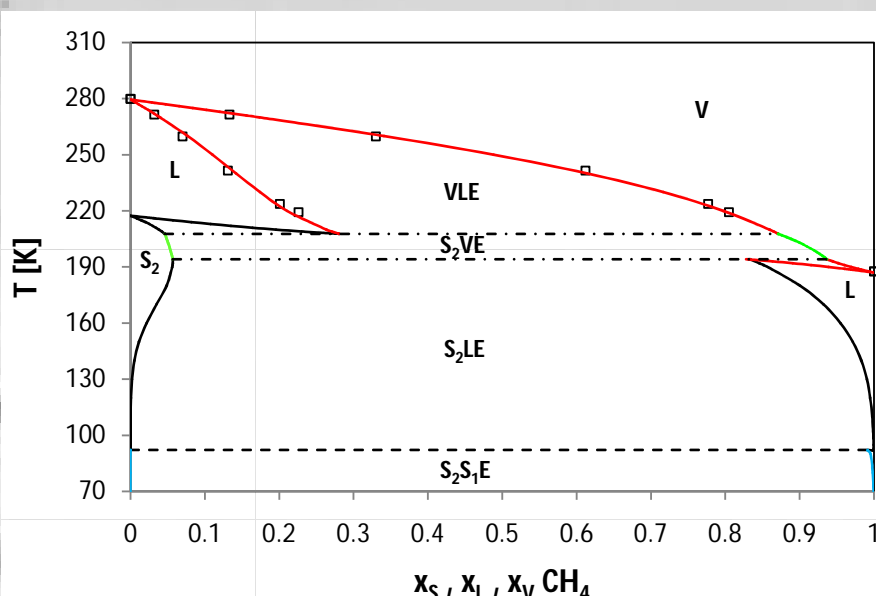


Figure 2: T-x equilibrium behavior. Calculated values: — S₂S₁L; — S₂S₁V; — S₂S₁V; — VLE; — critical line. Data [3]: 4.14 MPa (□); — S₂S₁V triple point; — S₂S₁L triple point.

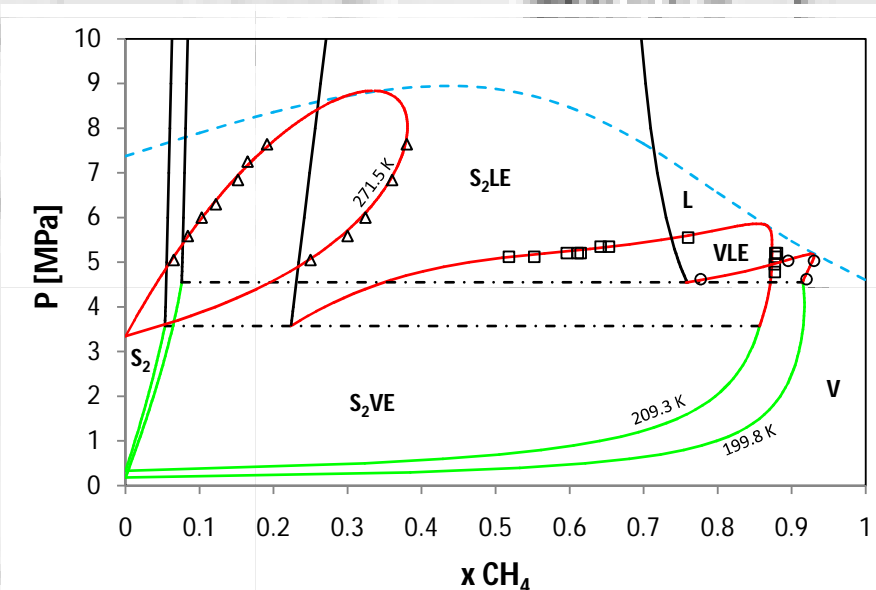


Figure 3: P-x equilibrium behavior. Calculated values: — S₂S₁L; — S₂S₁V; — VLE; — critical line. Data [3]: 271.5 K (△); 209.3 K (□); 199.8 K (○); — S₂S₁V triple point.

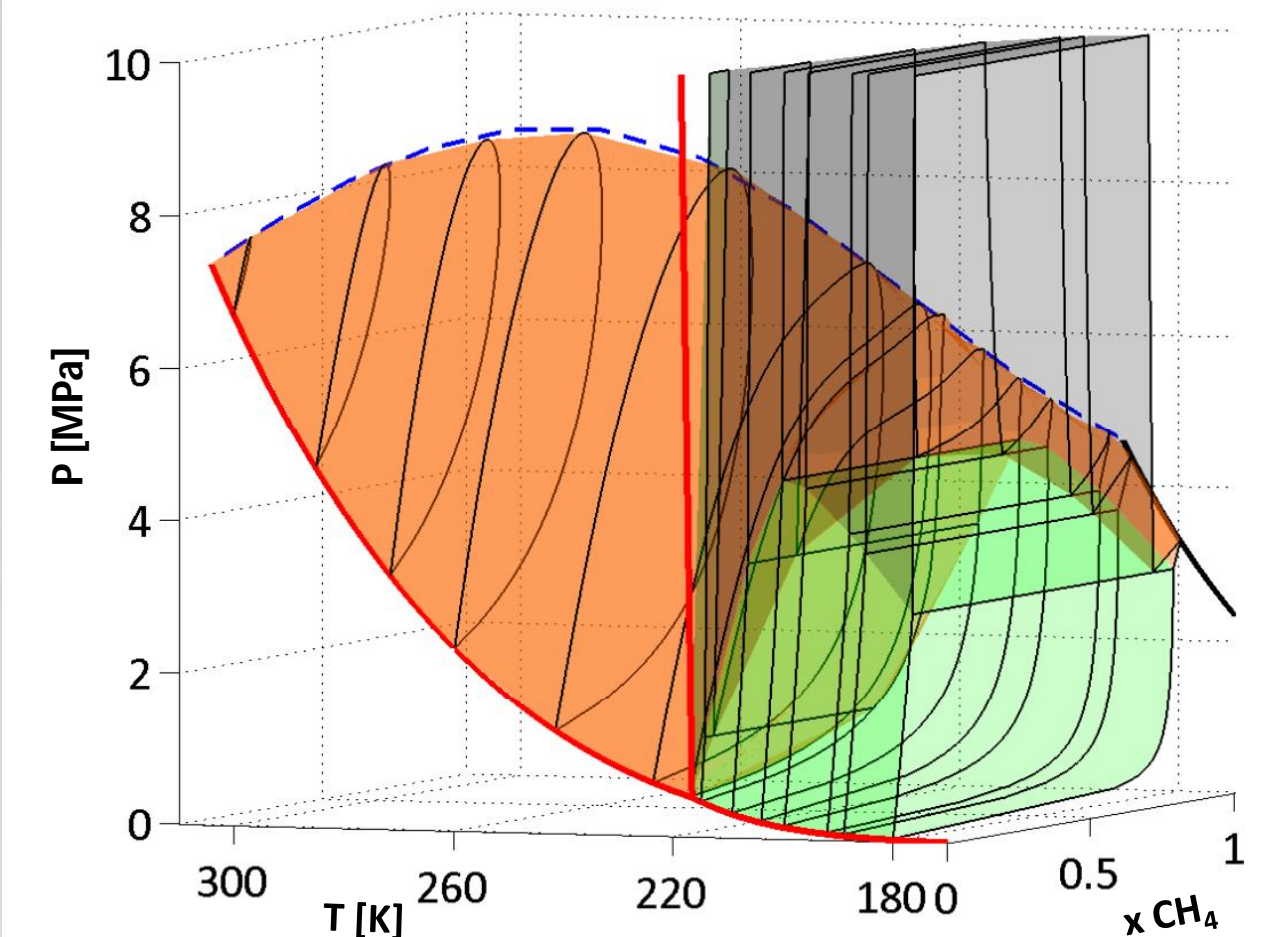


Figure 4: P-T-x equilibrium behavior. Calculated values: — VLE CH₄; — CO₂; — critical line. P-x cross sections: ■ VLE; ■ SLE; ■ SVE.

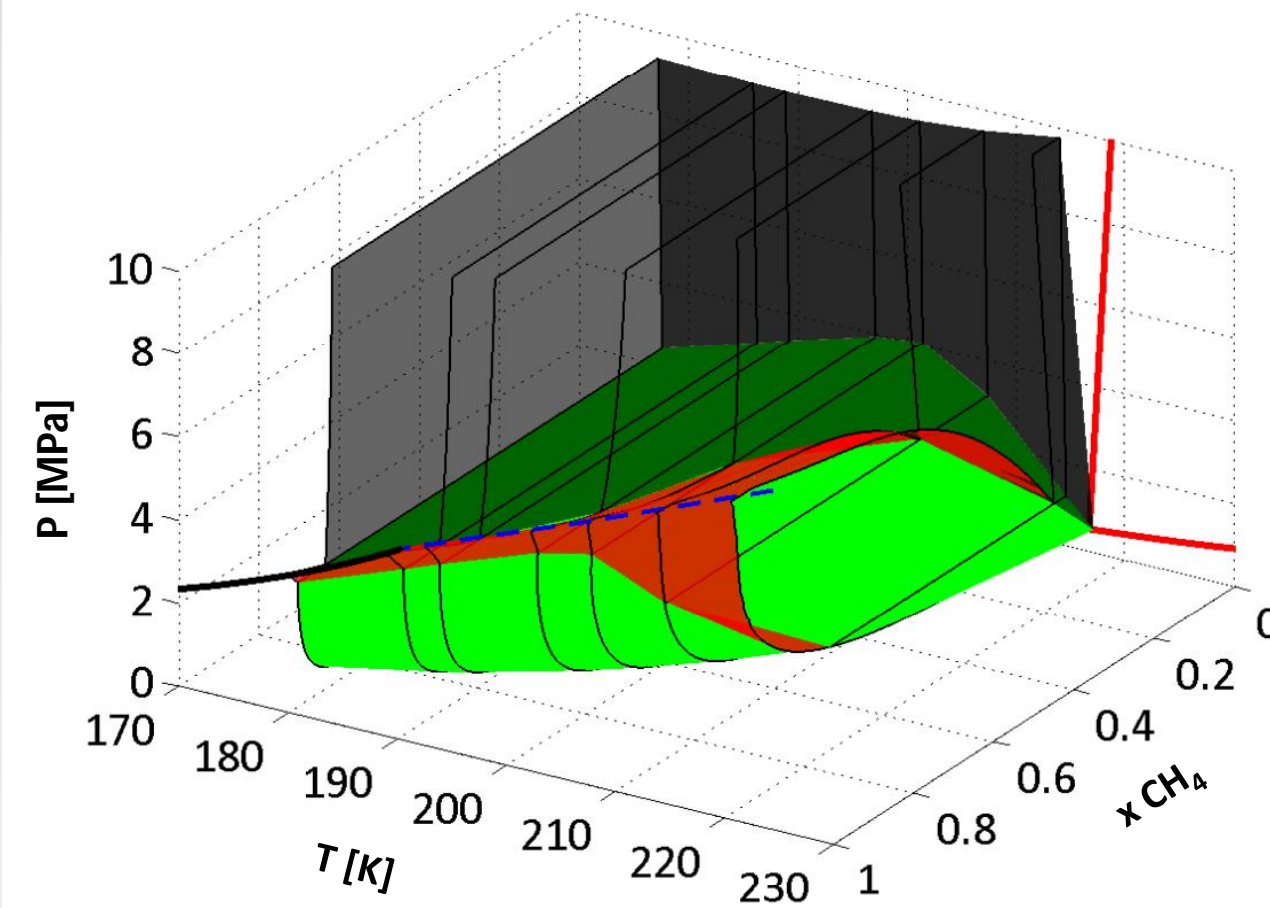


Figure 5: P-T-x equilibrium behavior. Calculated values: — VLE CH₄; — CO₂; — critical line. P-x cross sections: ■ VLE; ■ SLE; ■ SVE.

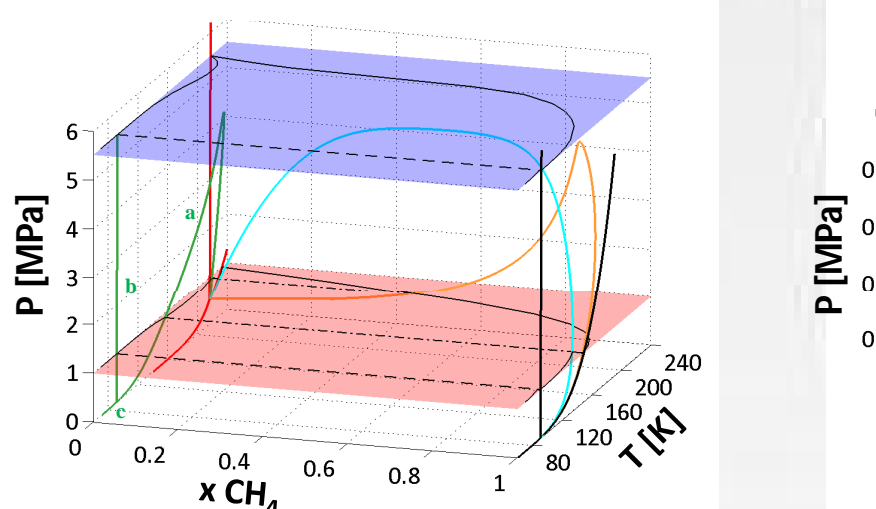


Figure 6: P-T-x equilibrium behavior. Pure compounds: — CH₄; — CO₂. Triple lines: S₂S₁L (—ax₂); S₂S₁V (—bx₂); S₂S₁V (—cx₂). T-x cross sections: □ 5.5 MPa; ■ 1 MPa. Triple points: — S₂S₁L; — S₂S₁V.

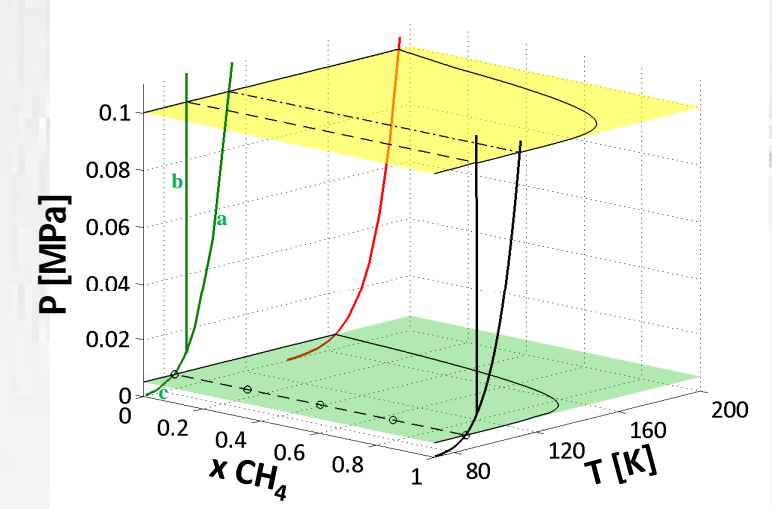


Figure 7: P-T-x equilibrium behavior. Pure compounds: — CH₄; — SVE CO₂. Triple lines: S₂S₁L (—ax₂); S₂S₁L (—bx₂); S₂S₁V (—cx₂). T-x cross sections: □ 0.1 MPa; ■ 0.005 MPa. Triple points: — S₂S₁L; — S₂S₁V; — S₂S₁V.

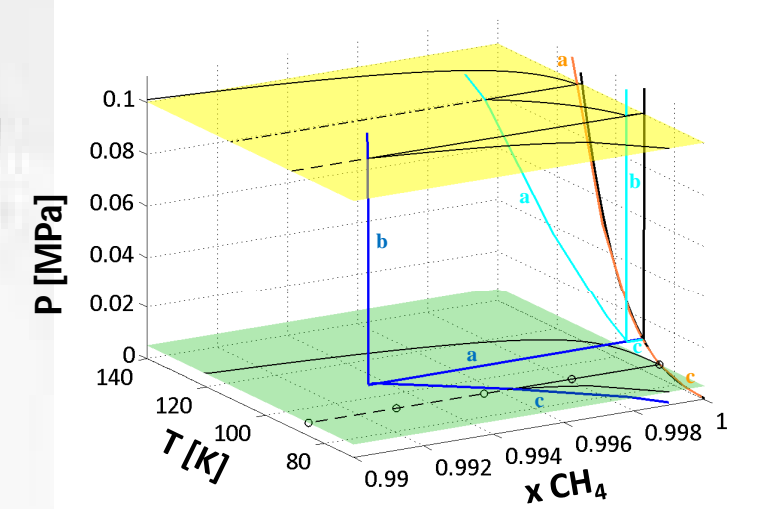


Figure 8: P-T-x equilibrium behavior. Pure compound: — CH₄. Triple lines: S₂S₁L (—ax₂); S₂S₁L (—bx₂); S₂S₁V (—cx₂). T-x cross sections: □ 0.1 MPa; ■ 0.005 MPa. Triple points: — S₂S₁L; — S₂S₁V; — S₂S₁V.

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.

References

- [1] Yokozeki A. 2003, Analytical Equation of State for Solid-Liquid-Vapour Phases, *International Journal of Thermophysics*, 24: 589-620.
- [2] Huber ML, McLinden MO, Lemmon EW. 2007, NIST Standard Reference Database 23, Reference Fluid Thermodynamic and Transport Properties-REFPROP, Version 8.0, National Institute of Standards and Technology, Standard Reference Data Program, Gaithersburg.
- [3] Donnelly HG, Katz DL. 1954, 46: 511-517.
- [4] Davis JA, Rodewals N, Kurata F. 1962, *AIChE Journal*, 8: 537.
- [5] Esper GJ, Bailey DM, Holste JC, Hall KR. 1989, *Fluid Phase Equilibria*, 49: 35-47.