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The effect of the spinodal curve condition on J – T inversion curves for van der Waals real gas

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This paper examines a consequence of spinodal curve condition on the Joule – Thomson inversion curves, for van der Waals real gas. To this end, we consider the differential form of Joule – Thomson coefficient, and concentrate on the parametrical algebraic equation of the corresponding family of curves in a P – V Cartesian frame of reference. The aim of this work is not the prediction of Joule – Thomson inversion curves for the van der Waals Eos, but to derive inequality relations amongst the variables T, V and the parameters which appear in this constitutive law. Here, we should clarify beforehand that all proposed expressions concern only the intersection points between the set of inversion curves and the isothermal spinodal lines, which are drawn in the same P – V frame of reference.

Key words: JT inversion curves, spinodal curve condition, van der Waals Eos, P – V frame of reference.

INTRODUCTION

The Joule – Thomson inversion curve, is defined as the locus of thermodynamic states in which the temperature of a gas, (identical or real), remains invariant with respect to isenthalpic expansion. However, to carry out a direct measurement of the inversion curves is a very difficult experimental process and may yield unreliable conclusions (Colazo et al., 1992). At near – inversion conditions, the vanishing of Joule – Thomson coefficient implies that even very large pressure changes will result in small temperature differences and therefore extremely accurate measurements of temperature are necessary for the reliable determination of inversion pressures (Colazo et al., 1992; Smith, 1982).

The Joule – Thomson coefficient depends on the volume, specific heat capacity, temperature, and thermal

expansion coefficient of the gas and generally arises from the following expression (Smith, 1982; Caldin, 1958).

$$\mu_{JT} = \frac{V}{C_p} (aT - 1) \quad (1)$$

Where a denotes the thermal expansion coefficient of the gas and is given by the following relationship

$$a = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \quad (2)$$

Besides, the enthalpy depends on the specific heat

capacity, as well as the temperature and pressure of the gas before expansion. For all real gases, μ_{JT} is equal to zero at some point called the inversion point. If the gas temperature is below its inversion point temperature, the coefficient μ_{JT} is positive and if the gas temperature is above its inversion point temperature, it is negative. Also, the variation of pressure is always negative when a gas expands. Thus, the following two firm conclusions are drawn (Caldin, 1958; McGlashan, 1979).

- i) If the gas temperature is below its inversion temperature the coefficient μ_{JT} is positive and since the change of P is always negative it follows that the gas must cool since the change of T must be negative.
- ii) If the gas temperature is above its inversion temperature the coefficient μ is negative and since the change of P is always negative the gas heats because the change of T must be positive.

Depending on state conditions, the Joule – Thomson coefficient may be positive or negative. Positive values imply a cooling of the gas as it passes through an adiabatic throttle. The curve connecting all state points where μ_{JT} is zero is the Joule –Thomson inversion curve. Evidently, this is an alternative equivalent definition of a $J - T$ curve.

Francis and Luckhurst (1963) investigated the Joule – Thomson coefficient and claimed that the law of "corresponding states" fits the isothermal Joule – Thomson coefficient but not the adiabatic one, because of the specific heat. They also claimed that the law of corresponding states conforms not only to pure gases but also to their mixtures. Meanwhile, it has been admitted that the prediction of the Joule – Thomson inversion curve constitutes a very reliable test of an equation of state (Colazo et al., 1992; McGlashan, 1979). The prediction of adiabatic Joule –Thomson coefficient for the type of inert gases, on the basis of numerous intermolecular potentials has been carried out by Nain and Aziz (Nain and Aziz, 1976). Up to date, the Joule – Thomson inversion curves for several types of real gases have been evaluated either numerically or by means of molecular simulation methods. In particular, an amount of valuable molecular simulation analyses was presented by Haghighi et al. (2003, 2004); Matin and Haghighi (2000); Colina and Muller (1999); Colina et al. (2002); Chasin et al. (1999); Colina and Muller (1997) and Vrabec et al. (2005), whereas prominent numerical techniques were performed by Dilay and Heidemann (1986) and Kioupis and Maginn (2002). After all, we should elucidate that the objective of the present investigation is not to optimize the simulative calculation of this coefficient in accordance with van der Waals constitutive law, but to obtain some further qualitative information in regards to the independent variables T , V and the parameters which

participate in the aforementioned Eos.

ANALYSIS

It is known from the literature, McGlashan (1979) and Adkins (1968) that the thermodynamical behavior of any van der Waals gas is described by the following Eos

$$\left(P + \frac{n^2 a}{V^2} \right) (V - nb) = nRT \tag{3}$$

The coefficients a, b are related with the coordinates of the critical point (P_0, V_0, T_0) , which characterizes any van der Waals gas, as follows:

$$V_0 = 3b; 27b^2 P_0 = a; 27bRT_0 = 8a \tag{3a,b,c}$$

Next, by focusing on one mole of the gas, we can write out Equation (3) in the following form:

$$\left(P + \frac{a}{V^2} \right) (V - b) = RT \tag{4}$$

Here, one may also remark that after the necessary algebraic manipulation the following equivalent third degree polynomial equation arises (McGlashan, 1979; Adkins, 1968)

$$V^3 - \left(b + \frac{RT}{P} \right) V^2 + \frac{a}{P} V - \frac{a}{P} b = 0 \tag{5}$$

Obviously, the above equation cannot be equivalently written in the explicit form

$$V = V(T, P) \tag{6}$$

In continuing, let us return at Equation (3) and solve it for T to find

$$T = \frac{1}{R} \left(P + \frac{a}{V^2} \right) (V - b) \tag{7}$$

Next, by differentiating the latter equation with respect to V we obtain

$$\left(\frac{\partial T}{\partial V} \right)_P = \frac{1}{R} \left(-\frac{2a}{V^3} (V - b) + P + \frac{a}{b^2} \right) \Leftrightarrow$$

$$\left(\frac{\partial T}{\partial V} \right)_P = \frac{1}{R} \left(P + \frac{2ab}{V^3} - \frac{a}{V^2} \right) \Leftrightarrow$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P + \frac{2ab}{V^3} - \frac{a}{V^2}} \Leftrightarrow$$

$$\frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{PV + \frac{2ab}{V^2} - \frac{a}{V}} \quad (8)$$

Thus, it is evident that the thermal expansion coefficient α for a van der Waals gas is given as

$$\alpha = \frac{R}{PV + \frac{2ab}{V^2} - \frac{a}{V}} \quad (9)$$

Hence, the Joule – Thomson coefficient for a van der Waals gas can be estimated as follows

$$\mu_{JT} = \frac{V}{C_p} \left(\frac{RT}{PV + \frac{2ab}{V^2} - \frac{a}{V}} - 1 \right) \Leftrightarrow$$

$$\mu_{JT} = \frac{V}{C_p} \left(\frac{RT - PV - \frac{2ab}{V^2} + \frac{a}{V}}{PV + \frac{2ab}{V^2} - \frac{a}{V}} \right) \quad (10)$$

Meanwhile, since $RT = PV - Pb + \frac{a}{V} - \frac{ab}{V^2}$ Equation (10) yields

$$\mu_{JT} = \frac{1}{C_p} \left(\frac{2aV^2 - PbV^3 - 3abV}{PV^3 - aV + 2ab} \right) \quad (11)$$

Thus, the parametric algebraic equation of the inversion curves is given as

$$PbV^3 - 2aV^2 + 3abV = 0 \quad (12a)$$

Since the variable of volume cannot be zero, it implies

$$PbV^2 - 2aV + 3ab = 0 \quad (12b)$$

On the other hand, it is known from Equilibrium Thermodynamics (Adkins, 1968) that the spinodal points of an arbitrary isothermal curve in a $P - V$ frame of reference are conveyed mathematically by the following expression:

$$\frac{\partial P}{\partial V} = -\frac{RT}{(V-b)^2} + \frac{2a}{V^3} = 0 \quad (13)$$

Here, we illustrate that the critical points described by Equations (3a,b,c) also verify the above equation, even if the system of Equations (3a,b,c) is not equivalent to Equation (13). Thus we infer

$$\frac{2a}{(V-b)^2} \left(\frac{(V-b)^2}{V^3} - \frac{RT}{2a} \right) = 0 \Leftrightarrow$$

$$(V-b)^2 = \frac{RT}{2a} V^3 \Leftrightarrow$$

$$(V-b)^2 = \frac{\left(PV - Pb + \frac{a}{V} - \frac{ab}{V^2} \right)}{2a} V^3 \Leftrightarrow$$

$$2aV^2 + 2ab^2 - 4abV = PV^4 - PbV^3 + aV^2 - abV \Leftrightarrow$$

$$PV^4 - PbV^3 - aV^2 + 3abV - 2ab^2 = 0 \quad (14)$$

Hence, if one centers his/her investigation on the intersection points of the inversion curves with the isothermal spinodal lines, which evidently constitute the loci of the isothermal spinodal points, the pressure P can be considered as a parameter.

Apparently, the same consideration concerns the intersection points of the inversion curves with the family of curves motivated by Equation (14). This implies that Equation (12b) can be encountered as a single – valued polynomial equation of second order with roots r_1, r_2 such that

$$r_1 + r_2 = \frac{2a}{Pb} \quad (15a)$$

$$r_1 \cdot r_2 = \frac{3a}{P} \quad (15b)$$

In addition, by considering the pressure P as a parameter, the third degree polynomial on the left member of Equation (12a) substantially reduces to a single – valued continuous real function in the form,

$$f(V) = PbV^3 - 2aV^2 + 3abV, \quad \text{with roots } (r_1, r_2, r_3) = (r_1, r_2, 0)$$

Also,

$$f'(V) = 3PbV^2 - 4aV + 3ab \quad \text{and}$$

$$f''(V) = 6PbV - 4a$$

In the sequel, let us assume without violating the generality of our mathematical formalism, that the

polynomial function $f(V)$ has three distinct real roots. Then, as it is known from single – valued Calculus (Nikolsky, 1977) the following statement holds

$$\frac{r_1}{f'(r_1)} + \frac{r_2}{f'(r_2)} + \frac{r_3}{f'(r_3)} = 0 \tag{16}$$

Since the root r_3 vanishes, Equation (16) yields

$$\begin{aligned} \frac{r_1}{f'(r_1)} + \frac{r_2}{f'(r_2)} &= 0 \Leftrightarrow \\ \frac{r_1}{f'(r_1)} &= -\frac{r_2}{f'(r_2)} \Leftrightarrow \frac{r_1}{r_2} = \frac{f'(r_1)}{(-f'(r_2))} \Rightarrow \frac{r_1 - r_2}{r_1 + r_2} = \frac{f'(r_1) + f'(r_2)}{f'(r_1) - f'(r_2)} \Leftrightarrow \\ r_1 - r_2 &= (r_1 + r_2) \frac{f'(r_1) + f'(r_2)}{f'(r_1) - f'(r_2)} \Leftrightarrow \\ r_1 - r_2 &= \frac{3Pb(r_1^2 + r_2^2) - 4a(r_1 + r_2) + 6ab}{3Pb(r_1^2 - r_2^2) - 4a(r_1 - r_2)} \cdot \frac{2a}{Pb} \Leftrightarrow \\ r_1 - r_2 &= \frac{3Pb(r_1 + r_2)^2 - 6Pbr_1r_2 - 4a(r_1 + r_2) + 6ab}{3Pb(r_1^2 - r_2^2) - 4a(r_1 - r_2)} \cdot \frac{2a}{Pb} \Leftrightarrow \\ (r_1 - r_2)^2 &= \frac{3Pb(r_1 + r_2)^2 - 6Pbr_1r_2 - 4a(r_1 + r_2) + 6ab}{3Pb(r_1 + r_2) - 4a} \cdot \frac{2a}{Pb} \Leftrightarrow \\ (r_1 - r_2)^2 &= \frac{3Pb\left(\frac{2a}{Pb}\right)^2 - 6Pb\left(\frac{3a}{P}\right) - 4a\left(\frac{2a}{Pb}\right) + 6ab}{3Pb\left(\frac{2a}{Pb}\right) - 4a} \cdot \frac{2a}{Pb} \Leftrightarrow \\ (r_1 - r_2)^2 &= \frac{12a^2}{P^2b^2} - \frac{18a}{P} - \frac{8a^2}{P^2b^2} + \frac{6a}{P} \tag{17} \end{aligned}$$

At this point, one may observe that since $r_1 \neq r_2$ the following inequality emerges

$$\begin{aligned} \frac{12a^2}{P^2b^2} - \frac{18a}{P} - \frac{8a^2}{P^2b^2} + \frac{6a}{P} &> 0 \Leftrightarrow \\ \frac{2a^2}{P^2b^2} - \frac{6a}{P} &> 0 \Leftrightarrow \\ \frac{a^2}{P^2b^2} - \frac{3a}{P} &> 0 \tag{18} \end{aligned}$$

Here, we should denote the above inequality concerns the algebraic rates of all the involved quantities, since the term $(r_1 - r_2)$ is not a dimensionless quantity.

In this context, one may also infer that the algebraic rates

of the terms $\frac{a}{P}$ and $\frac{a}{Pb^2} - 3$ agree in sign. Moreover, after a combination of (18) with (3a), (3b) and (3a), (3c) respectively the next four inequalities read

$$\frac{9P_0^2}{P^2} - \frac{P_0}{P} > 0 \tag{19a}$$

$$\frac{3T_0^2}{P^2V_0^2} - \frac{T_0}{P} > 0 \tag{19b}$$

$$\frac{3V_0^2P_0^2}{P^2} - \frac{RT_0}{8P} > 0 \tag{19c}$$

$$\frac{9R^2T_0^2}{64P^2V_0^2} - \frac{V_0P_0}{P} > 0 \tag{19d}$$

Besides, as we have already mentioned, the pressure for one mole of a van der Waals gas is given as

$$P = \frac{RT}{V - b} - \frac{a}{3V^2} \tag{20}$$

Hence, (18) with the aid of (20) results in the following inequality

$$\begin{aligned} \frac{a^2 - 3ab^2\left(\frac{RT}{V - b} - \frac{a}{3V^2}\right)}{\left(\frac{RT}{V - b} - \frac{a}{3V^2}\right)^2} &> 0 \Rightarrow \\ a^2 - 3ab^2\left(\frac{RT}{V - b} - \frac{a}{3V^2}\right) &> 0 \Leftrightarrow \\ a^2 - \frac{V_0^2}{3}\left(\frac{RTa}{V - b} - \frac{a^2}{3V^2}\right) &> 0 \tag{21} \end{aligned}$$

In continuing, (21) can be combined with (3a,b) and (3a,c) respectively to yield the following two inequalities

$$3P_0^2 - \frac{RTP_0}{3V - V_0} + \frac{V_0^2P_0^2}{3V^2} > 0 \tag{22a}$$

$$\frac{9}{8}T_0 - T\frac{V_0}{3V - V_0} + T_0\frac{V_0^2}{8V^2} > 0 \tag{22b}$$

Here, one may point out that (22a) and (22b) do not concern only the algebraic rates of the involved physical quantities since all terms in the left member of (22a) agree in dimension, fact that also happens to those appearing in the left member of (22b). We emphasize again that these inequalities concern the intersection points of the inversion curves with the family of curves motivated by Equation (14). Last but not least, it still may

be observed that inequalities (19a, b, c, d) and (22a, b) constitute a restriction for the circumstantial rates of the pressure P even if this independent variable has been considered as a parameter.

DISCUSSION

The application of inequalities (19a, b, c, d) and (22a, b) to $P-V-T$ thermodynamical systems, premises that the localization of the isothermal spinodal lines, where obviously the pressure P is considered as a parameter, has been made beforehand. Also, the fact that inequalities (22a, b) hold exclusively on a lattice created by the intersection between the isothermal spinodal lines and the family of inversion curves, indeed constitutes a constraint. Moreover, to derive inequalities (22a, b) we have a priori supposed that the third degree polynomial function, which arises from Equation (12a) after the consideration of P as a parameter, has three distinct real roots. This hypothesis implies automatically that the single – valued quadratic function which appears in the left member of Equation (14), has two distinct real roots and therefore its discriminant should be strictly positive, that is, $4a^2 - 12Pab^2 > 0$ or equivalently $a^2 > 3Pab^2$. The latter inequality, in combination with the group of Equations (3a, b, c) which concern any van der Waals gas, finally yields: $\frac{P}{P_0} < 9$. Actually, the above inequality

is a necessary condition which should be satisfied indispensably, even if the pressure has been considered here as a parameter. Thus, a shortcoming of inequalities (22a, b) is that the range of their validity depends on the maximum value of the ratio $\frac{P}{P_0}$.

CONCLUSIONS

In this work, the author obtained some additional qualitative information about the locus of Joule – Thomson inversion curves for the van der Waals real gas, with the concurrent consideration of the spinodal curve condition.

The goal of this investigation was not a contribution to the prediction of Joule – Thomson inversion curves but the obtaining of inequality relations amongst the variables T , V and the parameters which appear in van der Waals Eos. In this context, we concentrated our study on the intersection points between the set of the inversion curves and the isothermal spinodal lines which were both drawn in the same $P - V$ Cartesian frame of reference. Thereupon, the pressure P was considered as a parameter and in the sequel by means of some

fundamental statements of single – valued Calculus a group of inequalities was derived the validity of which concerns any grid being motivated by the possible inversion curves. Apparently, these aforementioned inequalities may hold whenever the nature of the original thermodynamical problem that we investigate enables us to assume this variable as a parameter or alternatively to consider it as a sequence of distinct rates.

Conflict of Interest

The authors have not declared any conflict of interest.

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