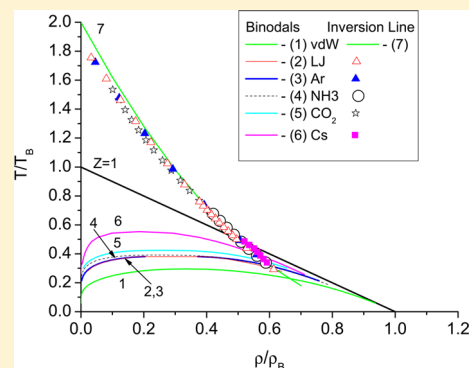


The Similarity Law for the Joule–Thomson Inversion Line

E. M. Apfelbaum* and V. S. Vorob'ev

Joint Institute for High Temperatures, Russian Academy of Science, Izhorskaya 13, Building 2, Moscow 125412, Russia

ABSTRACT: We show that the expression for the Joule–Thomson inversion temperature following from the van der Waals equation and recorded in a form reduced to the Boyle values has a universal character and can be applied to many real substances and model systems.



INTRODUCTION

The throttling or Joule–Thomson process is of the highest technical importance. So it has been investigated for more than a century.^{1,2} It is a fundamental aspect of thermal machines such as refrigerators, air conditioners, heat pumps, and liquefiers. Furthermore, throttling is a fundamentally irreversible process. In thermodynamics, the Joule–Thomson effect describes the temperature change of a gas or liquid when it is forced through a valve or porous plug while kept insulated so that no heat is exchanged with the environment. At room temperature, all gases except hydrogen, helium, and neon are cooled upon expansion by the Joule–Thomson process. Besides, all real gases have an inversion point at which the cooling replaces heating. The temperature of this point, the Joule–Thomson inversion temperature (JTIT), depends on the kind of gas, its pressure before and after expansion, and the density. Undoubtedly, it is interesting to determine some general relations for the Joule–Thomson process, such as the similarity laws^{3–5} which are valid both for various substances and model systems.

Earlier, we constructed the similarity laws for the so-called Zeno-line.^{4–7} It was shown that the equation for binodals at the density–temperature plane can be constructed using the critical-point coordinates and the Zeno-line parameters only. So in the present paper we suggest the equation for JTIT expressed via the Zeno-line parameters, analogous to the one previously derived for binodals.

The Expression for the JTIT Line Following from the van der Waals Equation. We start from the van der Waals equation (VDW). We should note that it is a very simple model. Its simplification can result in many errors such as, for instance, incorrect behavior near the critical point. But in some cases these errors appear to compensate each other. As a result the VDW equation has amazing features associated with the fact that some of its consequences are valid for a great number of various model and real systems described by completely

different equations of state. This was the case for the similarity laws such as the corresponding state principle or the law of rectilinear diameter.^{1,2} So, keeping the general limitations for VDW in mind, we will show below that the expressions for the JTIT line and value of the thermal expansion coefficient along this line, following from the VDW equation, nevertheless are valid for a very wide spectrum of substances and model systems.

The Joule–Thomson coefficient (JT) is determined as

$$\mu = \left(\frac{\partial T}{\partial P} \right)_H = \frac{V}{C_p} (\alpha T - 1) \quad (1)$$

where T , P , H are the temperature, pressure and enthalpy respectively; V is the gas volume, C_p is the heat capacity at constant pressure, α is the coefficient of thermal expansion. The set of points at the density–temperature plane, where the JT becomes zero, forms the inversion line. Evidently, this line can be found from the condition

$$\alpha T = 1 \quad (2)$$

The volumetric expansion coefficient α is determined as

$$\alpha = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_p \quad (3)$$

Here ρ is the particle density. It should be noted, that eq 2 corresponds to the enthalpy minimum at constant temperature, that is, $(\partial H / \partial P)_T = 0$. This fact follows from the thermodynamic relation $dH = C_p dT + V(1 - \alpha T) dP$. It also can be obtained if the chain rule is applied to eq 1.

We calculate this coefficient according to the van der Waals equation (VDW)

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$$P = \frac{\rho T}{1 - \rho b} - a\rho^2 \quad (4)$$

Let us introduce the Boyle units: $\rho_B = 1/b$; $T_B = a/b$; $P_B = a/b^2$ (see ref 6). Then one can introduce the reduced pressure, density, and temperature: $P' = P/P_B$; $\rho' = \rho/\rho_B$; $T' = T/T_B$. In these reduced units eq 4 can be transformed as

$$P' = \frac{\rho' T'}{1 - \rho'} - (\rho')^2 \quad (5)$$

Let us also write the equation for the line (Zeno line (ZL)) along which the factor compressibility is equal to unity. The equation of this line is

$$\rho/\rho_B + T/T_B = 1 \quad (6)$$

We should note that ZL is described by eq 6 not only for VDW, but for many other models and real substances. In this case the Boyle parameters ρ_B , T_B can be calculated whether by means of virial coefficient or by means of extrapolation of ZL to the zero density and zero temperature (see refs 6–8, 11).

Using eqs 3 and 5 we obtain

$$\alpha T' = \frac{1 - \rho'}{1 - \frac{2\rho'(1-\rho')^2}{T'}} \quad (7)$$

From eqs 7 and 2 it follows that temperature along the Joule-Thomson inversion line in ordinary units is

$$T = 2T_B(1 - \rho/\rho_B)^2 \quad (8)$$

The same equation describes also the minimal enthalpy line at constant temperature.⁸ The temperature at the Zeno line from eq 6 is $T'_{\text{Zeno}} = 1 - \rho'$. Then it follows from eq 8 that for VDW equation at a given density $T'_{\text{JTIT}} = 2(T'_{\text{Zeno}})^2$.

RESULTS AND DISCUSSION

In Figure 1 we have presented the phase diagram and JTIT in the reduced units for several substances and models.

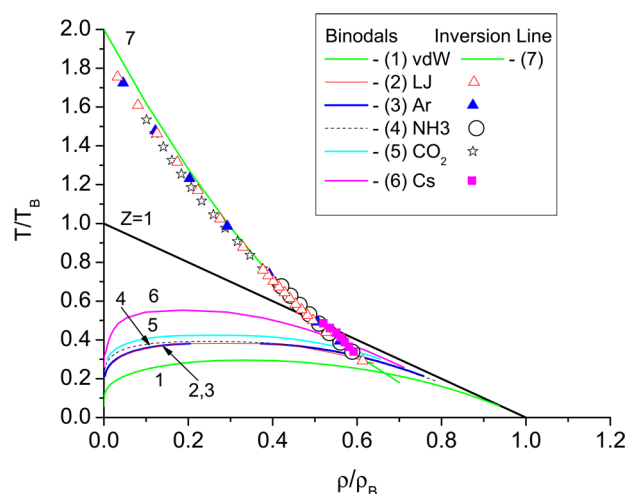


Figure 1. Phase diagram density–temperature in reduced (Boyle) units. The lines 1–6 are the binodals for the VDW equation, Lennard-Jones model, Ar, NH₃, CO₂, and Cs, respectively. Line Z = 1 is the Zeno line, according to eq 6. Line 7 is the JTIT according to eq 8. The symbols describe the inversion lines for the same models and substances.

Lines 1–6 are the binodals, the line Z = 1 is the Zeno-line (according to eq 6); the line 7 corresponds to eq 8 and gives the JTIT in the reduced units according to the VDW equation. The symbols correspond to the minimum enthalpy line as mentioned above. For Ar and Lennard-Jones system they were taken from ref 8. Besides, we calculated the JTIT line and binodal for cesium using experimental data of ref 9. To construct the inversion lines and binodals for NH₃ and CO₂ we have used the NIST database.¹⁰ One can see that the calculated points are grouped near line 7. So we can talk about a certain universality of this line. We have also checked some other substances, like hydrocarbons and diatomic molecules O₂, N₂, and F₂. Their inversion lines are also located near line 7. We do not show lines for these substances here to avoid the figure overloading. Besides, we should note that at smaller densities the inversion lines of real substances show a slight deviation from the line 7. This difference is related to the fact that the equation for the true enthalpy minimum line (or inversion line) includes not the T_B parameter but T_H (see ref 8.). The Boyle temperature T_B is defined by the usual condition⁴ $B_2(T = T_B) = 0$, where $B_2(T)$ is the second virial coefficient. The expansion of the enthalpy into the series of density powers gives⁸

$$H/(NT) = 5/2 + \left(B_2(T) - T \frac{\partial B_2}{\partial T} \right) \rho + \dots \quad (9)$$

So at $\rho \rightarrow 0$ the enthalpy minimum is achieved at $T = T_H$ defined by the condition:⁸

$$B_2(T_H) = T_H \left(\frac{\partial B_2}{\partial T} \right)_{T=T_H} \quad (10)$$

T_H is also the temperature where the inversion line intersects the temperature axis. For VDW $T_H = 2a/b = 2T_B$ exactly. But for other systems this equality is valid only approximately: $2T_B \approx T_H$. One can see in Figure 1 that T_H is slightly below $2T_B$ for the substances under investigation. There is no strict proof for this fact for any arbitrary substance, but for the model system (with known potentials) we can check it directly using eqs 9 and 10. For instance, for the Lennard-Jones (LJ) system⁸ $T_B = 3.418$, while $T_H = 6.431 = 1.88T_B$. For the system of particles interacting via Square Well potential the value $B_2(T)$ is known analytically⁷ as well as T_B and T_H . All these values are dependent on the width of the well λ . It is easily to show that T_H is always a little smaller than $2T_B$ for finite λ . They are equal only when $\lambda \rightarrow +\infty$. For multicenter LJ molecules¹³ $T_H = 1.875T_B$. Thus, the inexactness in relation $2T_B \approx T_H$ gives rise to the discussed small deviation of real inversion lines from that one given by eq 8.

As we have mentioned above the presentation of all investigated substances in Figure 1 would overload the figure. But it is possible to consider the line JTIT for real substances $T_{\text{real}}(\rho)$. Then we can compare it with $T_{\text{model}}(\rho)$ from eq 8 and find the maximum error in the available range of densities, that is,

$$\varepsilon = \max_{\rho} |1 - T_{\text{real}}(\rho)/T_{\text{model}}(\rho)|$$

The real JTIT $T_{\text{real}}(\rho)$ can be obtained from NIST database,¹⁰ where, as a rule, the density range spreads from $\rho \rightarrow 0$ to the intersection with the binodal (see Figure 1). The value ε (in percentage) is presented in Figure 2.

The symbol “C–H” at the X-axis means the group of hydrocarbons, which includes CH₄, C₂H₆, C₂H₄, C₃H₈, C₆H₁₄,

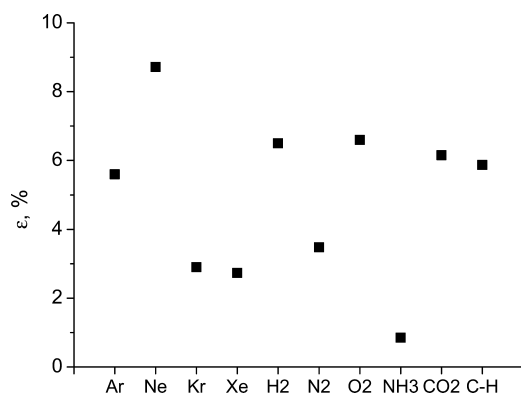


Figure 2. Maximum error of eq 8 for various substances in comparison with real JTIT (see text).

R13, R22, R32. The maximum error for all these substances is 5.87%. Among the other materials, neon has the maximum error 8.72%. We should note that helium and water completely disagree with eq 8. The error for them is $\sim 50\%$. It is not surprising, as water does not satisfy any known similarity laws. This is also often the case for so-called quantum liquids like helium, hydrogen, and neon. But for eq 8 the quantum corrections are evidently necessary for helium and partially for neon. For hydrogen the error is smaller.

It is also interesting to find the values of the coefficient of thermal expansion along the JTIT line. Dimensionless values of this coefficient as a function of reduced density are shown in Figure 3.

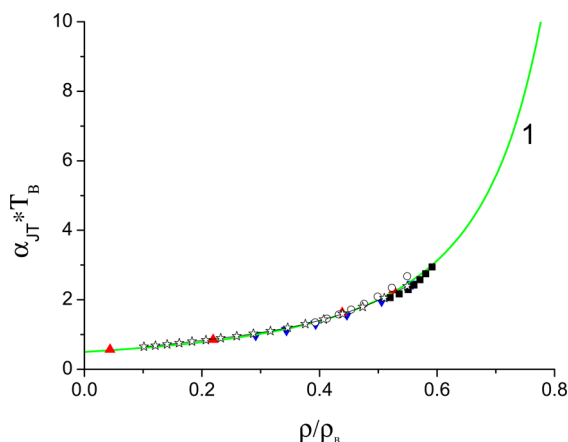


Figure 3. Values of dimensionless thermal expansion coefficient along the JTIT line versus density. Line 1 is calculated according to eq 8. Symbols are the same as in Figure 1.

Now let us draw attention to an interesting consequence of eq 8. Let us find the point of intersection of the JTIT line and the Zeno line. Obviously, that the Joule-Thomson inversion temperature corresponding to the intersection of the JTIT with ZL equals $T_B/2$ at the value of density $\rho_B/2$. It is interesting to see whether this finding is of a general nature or it is valid only for the VDW.

At first let us consider the model system of particles interacting via the Lennard-Jones potential (LJ). (This is the main test model for all thermodynamic studies). For LJ $0.5T_B = 1.709$ and $0.5\rho_B = 0.57$. In our previous study,⁸ we have used the integral equation (IE) technique to calculate VEC. These data and eq 2 give the density at the inversion line at $0.5T_B$ as

0.565. The error is less than 1% and corresponds to the general accuracy of the IE approach. So we claim that for LJ the intersection point is located at $0.5\rho_B$. Now let us consider real substances.

Earlier we have tested some similarity relationships for a wide range of substances (see Table 1 in ref 11.). Here we have used the same substances to find the intersection point of the JTIT with ZL. To do it, we have fixed the temperature $T = T_B/2$ and along the corresponding isotherm found the density ρ_μ where $\mu = 0$ (i.e., $\rho_\mu = \rho(\mu = 0)$). We have used NIST database¹⁰ as in our previous studies. The results are presented in Table 1.

Table 1

substance	$0.5T_B$, K	$0.5\rho_B$, g/cm ³	ρ_μ
Ar	200	0.94	0.947
Ne	60	0.82	0.846
Kr	270	1.62	1.650
Xe	370	1.93	2.014
NH ₃	468	0.48	0.49
CO ₂	371	0.90	0.891
C ₂ H ₆	390	0.37	0.374
C ₂ H ₄	357	0.39	0.392
CH ₄	249	0.285	0.29
N ₂	114	0.55	0.56
O ₂	200.05	0.77	0.782
C ₃ H ₈	392	0.43	0.43
R13	382	1.065	1.054
R22	454	0.995	0.988
R32	412	0.87	0.878
H ₂ O	635	0.60	0.768
H ₂	50	0.047	0.053
He ⁴	10	0.085	0.112
Cs	2060	0.98	1.045

For all substances presented in Table 1 $\rho_\mu \approx 0.5\rho_B$ within a few percent. The notable difference is only for water, hydrogen, and helium (see corresponding lines in Table 1). It can be explained as follows. The water generally does not obey various similarity laws as we have mentioned above. So the present relation is not an exception. At the same time, the helium and hydrogen are the quantum liquids. Consequently different similarity relations have to be corrected in an appropriate way to account for this fact.^{11,12,14}

CONCLUSIONS

The use of the basic thermodynamic variables (density and temperature) reduced to the Boyle values proves to be very effective in building new similarity relations. Thermodynamic relations thusly obtained can be used for a wider class of substances, compared with the spectrum of substances satisfying, for example, the law of corresponding states. The validity of this approach is manifested, in particular, by the fact that the VDW equation and the equation for the Zeno line do not contain any numerical factors. In this paper, another interesting similarity relation for the Joule–Thomson inversion temperature is revealed. Our basis was the corresponding expressions for the VDW system. We have shown that if they are written via the above-mentioned reduced values, then these formulas can be valid for many real substances, quite different from VDW. The exclusions are for water and quantum liquids like helium and hydrogen.

AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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