

# On the Differential and Integral Inversion States of the Joule-Thomson Effect and their Interrelation

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## ABSTRACT

The differential inversion curve is the loci of thermodynamic states of the vanishing Joule-Thomson coefficient. The integral inversion curve is the loci of states of vanishing integral isothermal Joule-Thomson effect. The present study examines the behavior of some thermodynamic functions along both inversion curves and explores the interrelation between the two curves. Closed form expressions are derived through the van der Waals equation of state and these are confronted with the real gas data.

## NOMENCLATURE

$c_p$	Isobaric specific heat capacity, $J \cdot mol^{-1} \cdot K^{-1}$
$c_v$	Isochoric specific heat capacity, $J \cdot mol^{-1} \cdot K^{-1}$
$h$	Enthalpy, J/mol
$h^R$	Residual enthalpy at common pressure and temperature, J/mol
$\Delta h^T$	The integral isothermal Joule-Thomson effect, J/mol
$P$	Inversion pressure, Pa
$R$	Universal constant of gases, $8.314 J \cdot mol^{-1} \cdot K^{-1}$
$T$	Inversion temperature, K
$T^{MAX}$	Maximum inversion temperature, K
$s$	Entropy, $J \cdot mol^{-1} \cdot K^{-1}$
$s^r$	Residual entropy at common density and temperature, $J \cdot mol^{-1} \cdot K^{-1}$
$v$	Specific volume, $m^3/mol$
$Z$	Compressibility, $P/(R \cdot T \cdot \rho)$

## Greek notation

$\rho$	Density of an inversion state, $mol/m^3$
$\Theta$	Reduced temperature, $T/T_C$ , K
$\bar{\Theta}$	Normalized inversion temperature, $T/T^{MAX}$ , K
$\Pi$	Reduced inversion pressure, $P/P_C$
$\Phi$	Reduced density of an inversion state, $P/P_C$
$\mu$	Adiabatic Joule-Thomson coefficient, K/Pa

$\varphi$  Isothermal Joule-Thomson coefficient, J/Pa

### Subscripts/Superscript

$C$  Critical state  
 $DIC$  Differential inversion curve  
 $IIC$  Integral inversion curve

## INTRODUCTION

The inversion of the Joule-Thomson (J-T) effect was studied at the very early stage (1898) through the van der Waals equation of state

$$P = \frac{RT}{v-b} - \frac{a}{v^2} \quad (1)$$

by Witkowski<sup>1</sup>, Berthelot<sup>2</sup>, Olszewski<sup>2</sup>, and van der Waals himself.<sup>4</sup> The molecular attractive and repulsion coefficients,  $a$  and  $b$ , characterize each particular gas. The locus of the differential inversion states is defined by the vanishing of the Joule-Thomson coefficient

$$\mu \equiv \left( \frac{\partial T}{\partial P} \right)_h = 0 \quad \text{or} \quad \varphi \equiv \left( \frac{\partial h}{\partial P} \right)_T = -\mu \cdot c_p = 0 \quad (2)$$

The states of vanishing integral isothermal J-T effect are the integral inversion state

$$\Delta h_T \equiv h(T, P=0) - h(T, P) = 0 \quad (3)$$

Figure 1 displays for nitrogen the differential inversion curve (DIC) and the integral inversion curve (IIC), both sharing the same maximum inversion temperature,  $T^{MAX}$ . Under an isenthalpic expansion, inside the DIC (the bounded zone marked by A, in Figure 1) temperature decreases whether the pressure drop is differential or integral (down to zero pressure). At the unbounded zone marked by C temperature increases under both, a differential and an integral pressure drop. In region B, temperature decreases as a result of an integral pressure drop but increases when it is differential.

The associated reduced value,  $\Theta^{MAX} = T^{MAX}/T_C$ , of a van der Waals gas is 27/4 while for most real gases (except the quantum gases) range from 4.5 to 5.2. In order to avoid this mismatch, the inversion temperatures are normalized by the particular  $\Theta^{MAX}$  (or  $T^{MAX}$ ) of each gas

$$\bar{\Theta} = \Theta/\Theta^{MAX} = T/T^{MAX} \leq 1 \quad (4)$$

For the purpose of this study, it replaces the traditional reduced temperature,  $\Theta$ . The van der Waals predictions are expressed in such a normalized form and compared to real gas data. On a similar ground tried Hendricks et al.<sup>5</sup> to verify the van der Waals prediction that the maximum inversion temperature is twice the Boyle temperature defined by

$$\left( \frac{\partial Z}{\partial P} \right)_T = 0 \quad @ P \rightarrow 0 \quad (5)$$

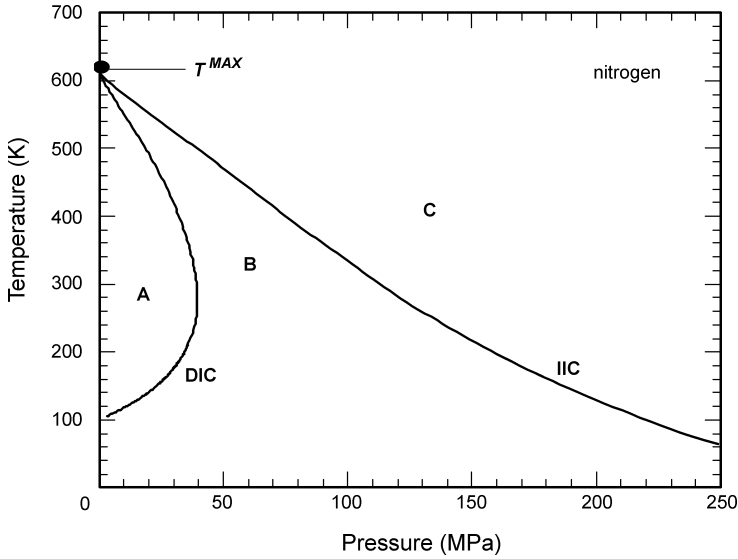
As well, Holleran<sup>6</sup> examined the van der Waals prediction that the compressibility along the DIC gets the unity value at a temperature which is half of the Boyle temperature.

While the DIC was intensively explored since the discovery of this effect, the IIC was studied less significantly.<sup>7,8</sup> Furthermore, the interrelation between the two inversion curves was not studied at all. The inversion curves of the quantum gases deserve a special attention and were discussed elsewhere.<sup>8,9</sup>

## THE DENSITY

Along the DIC of the van der Waals gas,

$$\bar{\Theta} = \left( 1 - \frac{\Phi}{3} \right)^2 \quad \text{or} \quad \Phi = 3 \left( 1 - \bar{\Theta}^{1/2} \right) \quad (6)$$



**Figure 1.** The differential (DIC) and integral (IIC) inversion curves of nitrogen divide the thermodynamic plane into the three regions: **A** ( $\mu > 0, \Delta h_T > 0$ ), **B** ( $\mu < 0, \Delta h_T > 0$ ), and **C** ( $\mu < 0, \Delta h_T < 0$ ).

and along the IIC

$$\bar{\Theta} = 1 - \frac{\Phi}{3} \quad \text{or} \quad \Phi = 3(1 - \bar{\Theta}) \quad (7)$$

This linear prediction of density dependence on temperature is confronted in Figure 2 with real gas data. As one may observe, the relation is linear indeed although the slope is somewhat smaller than of the van der Waals gas. At  $\bar{\Theta} = 1$  the slope of the DIC is larger than of the IIC (see Figure 1) when expressed in the coordinates of  $(\bar{\Theta}, \Phi)$  or  $(\bar{\Theta}, \Pi)$

$$\left( \frac{d\bar{\Theta}}{d\Phi} \right)_{DIC} = 2 \cdot \left( \frac{d\bar{\Theta}}{d\Phi} \right)_{IIC} = -\frac{2}{3} \quad @ \quad \bar{\Theta} = 1 \quad (8)$$

$$\left( \frac{d\bar{\Theta}}{d\Pi} \right)_{DIC} = 2 \cdot \left( \frac{d\bar{\Theta}}{d\Pi} \right)_{IIC} = -\frac{1}{27} \quad @ \quad \bar{\Theta} = 1 \quad (9)$$

However, in the plane of  $(\Phi, \Pi)$  they share the same slope

$$\left( \frac{d\Phi}{d\Pi} \right)_{DIC} = \left( \frac{d\Phi}{d\Pi} \right)_{IIC} = -\frac{1}{18} \quad @ \quad \bar{\Theta} = 1 \quad (10)$$

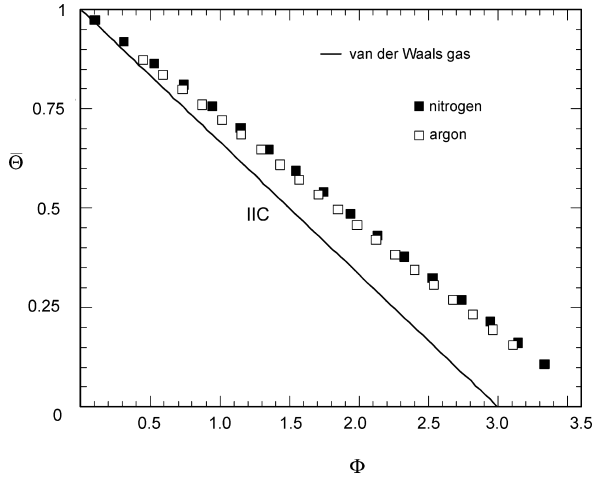
The relation between the normalized differential and integral inversion temperatures at the same reduced density is

$$\bar{\Theta}_{DIC}(\Phi) = \bar{\Theta}_{IIC}^2(\Phi) \quad (11)$$

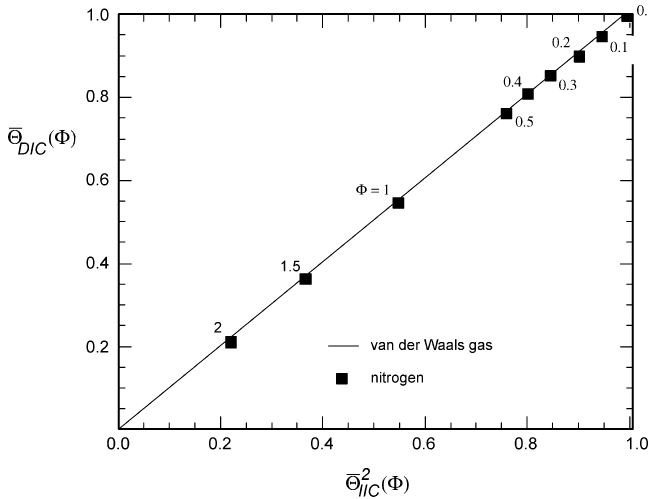
As displayed in Figure 3, this prediction holds quite nice for real gases. The densities along the DIC and the IIC at the same normalized temperature are interrelated through

$$\Phi_{IIC}(\bar{\Theta}) = \Phi_{DIC}(\bar{\Theta}) \cdot \left[ 2 - \frac{1}{3} \Phi_{DIC}(\bar{\Theta}) \right] \quad (12)$$

The reduced density,  $\Phi$ , along the DIC increases from 0 to 2 as the temperatures becomes lower. It passes through the value of 1 at the state of peaking inversion pressure. Along the IIC, the reduced



**Figure 2.** The relation between the normalized inversion temperature and the reduced density along the integral inversion curve versus van der Waals' prediction.



**Figure 3.** The interrelation of the differential and integral inversion temperatures sharing the same density.

changes from 0 to 3.

**THE COMPRESSIBILITY**

Along the DIC of the the van der Waals gas

$$Z = \frac{1}{2} \left( \frac{3}{\Theta^{1/2}} - \frac{1}{\Theta} \right) \tag{13}$$

Z is continuous function along the DIC and peaks at the inversion state of highest differential inversion pressure ( $\Theta = 3$  or  $\Theta = 4/9$ ). The highest Z value along the DIC is 9/8. The Z dependence on pressure,  $\Pi$ , is formulated by the double expression, one for each wing

$$Z = \frac{9 \cdot \Pi / 8}{\left[ 3 \pm \sqrt{9 - \Pi} \right] \cdot \left[ \frac{15}{4} - \frac{\Pi}{12} \mp \sqrt{9 - \Pi} \right]} \tag{14}$$

It is discontinuous at the same state of highest  $Z$  where the two wings match.

Along the IIC of a van der Waals gas can be defined as

$$Z = \frac{1}{2} \left( \frac{1}{\bar{\Theta}} + 1 \right) \quad (15)$$

In this case  $Z > 1$ , continuous and monotonically increasing as the temperature decreases. Figure 4 displays the van der Waals prediction versus nitrogen and argon real gas data.

## THE ENTROPY

The residual entropy while referred to the ideal gas (IG) at the same density and temperature

$$s^r = s(\rho, T) - s^{IG}(\rho, T) \quad (16)$$

For the van der Waals gas

$$s^r = R \cdot \ln(1 - \rho \cdot b) \quad (17)$$

Along the DIC and the IIC

$$s_{DIC}^r(\rho, T) = \frac{1}{2} \ln \bar{\Theta} \quad (18)$$

$$s_{IIC}^r(\rho, T) = \ln \bar{\Theta} \quad (19)$$

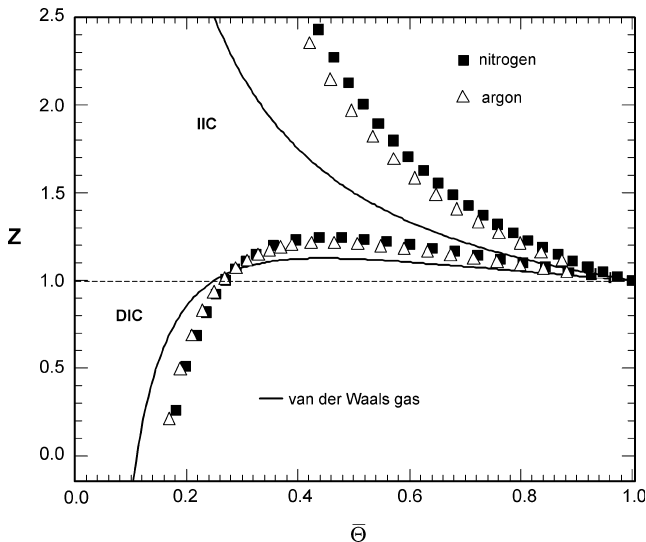
The predictive power of each of these expressions alone is limited. However, the interrelation of  $s^r$  along the two inversion curves at the same normalized temperature, namely,

$$s_{IIC}^r(\bar{\Theta}) = 2 \cdot s_{DIC}^r(\bar{\Theta}) \quad (20)$$

accurately predicts the real behavior of gases accurately as one may observe in Figure 5. At the same temperature, the residual entropy of the IIC is twice that of the DIC.

## THE JOULE-THOMSON EFFECT

The integral isothermal J-T effect is actually the residual enthalpy,  $h^R$ , while referred to the



**Figure 4.** The van der Waals prediction of compressibility along the differential (DIC) and integral (IIC) inversion curves versus nitrogen and argon real gas data.

ideal gas (IG) at the same pressure and temperature.

$$h^R \equiv h(T, P) - h^{IG}(T, P) = -[h(T, P = 0) - h(T, P)] \equiv -\Delta h_T \tag{21}$$

That is because  $h(T, P = 0)$  may be replaced by  $h^{IG}(T, P)$ . Through the van der Waals equation of state, it is

$$h^R = -a\rho + \frac{P}{\rho} - RT \tag{22}$$

and along the DIC

$$\left(\frac{\Delta h_T}{RT^{MAX}}\right)^{1/2} = 1 - \bar{\Theta}^{1/2} = \frac{\Phi}{3} \tag{23}$$

Figure 6 displays a reasonable match with real data of nitrogen and argon. One should pay attention to the simplicity and accuracy of this expression, gained by the employment of  $T^{MAX}$ . The  $\Delta h_T$  may be interpreted as the specific cooling capacity of a Joule-Thomson cryocooler. It is a simple and accurate (normalized) temperature dependence of  $\Delta h_T$ .

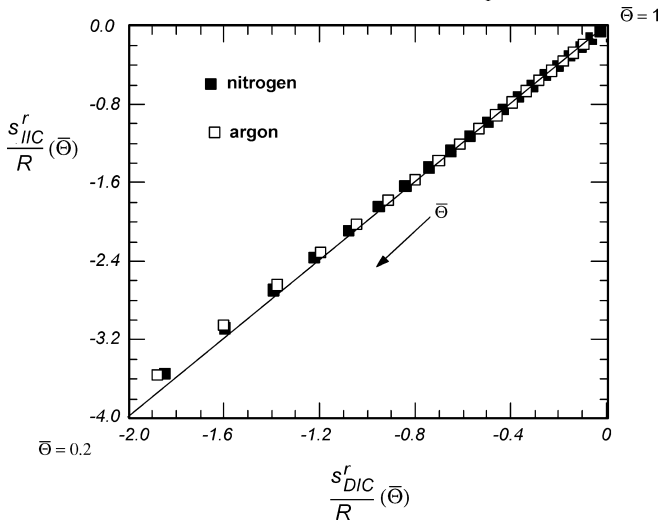


Figure 5. Interrelation of residual entropy along the differential and integral inversion curves.

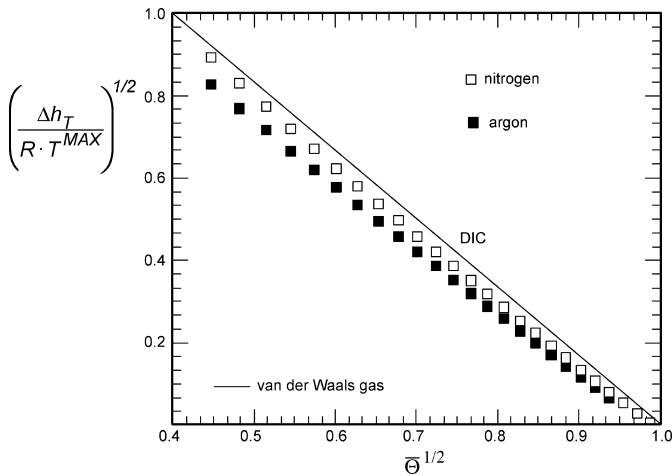


Figure 6. The integral isothermal Joule-Thomson effect along the differential inversion curve as function of the normalized temperature.

Along the IIC by the van der Waals equation of state, the differential isothermal J-T effect is

$$\varphi \cdot \rho_C = -\frac{(1-\bar{\Theta})/3}{1+(1-\bar{\Theta}) \cdot \bar{\Theta}} \tag{24}$$

It is negative and monotonically decreasing to its lowest value, which is -1/3.

**THE  $C_p - C_v$**

In general, by Maxwell relations

$$c_P - c_V = -\frac{T(\partial P/\partial T)_v^2}{(\partial P/\partial v)_T} \tag{25}$$

Along the DIC through the van der Waals equation of state

$$\frac{c_P - c_V}{R} = \frac{1}{\bar{\Theta}^{1/2}} \tag{26}$$

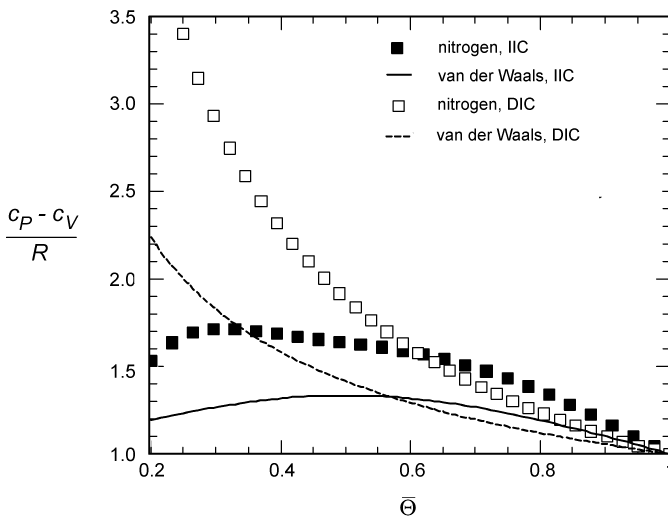
and along the IIC of a van der Waals gas

$$\frac{c_P - c_V}{R} = \frac{1}{\bar{\Theta}^2 - \bar{\Theta} + 1} \tag{27}$$

For an ideal gas, its value is unity. Along both inversion curves it is larger than 1. Along the IIC, it increases monotonically as the temperature decreases. However, along the DIC, it has a peaking behavior. The highest value for a van der Waals gas is 4/3 reached at  $\bar{\Theta} = 1/2$  which is the Boyle temperature. Figure 7 displays this prediction versus the real gas behavior.

**SUMMARY**

The van der Waals equation of state, combined with the temperature scaling by the maximum inversion temperature of each gas, exhibit a qualitative and a reasonable quantitative predictive power when applied to the study of the Joule-Thomson inversion states. At the same density, the normalized temperature of the DIC is the square of the normalized temperature of the IIC. The residual entropy by density and temperature of the IIC is twice than of the DIC, both at the same normalized temperatures.



**Figure 7.** The  $c_p - c_v$  along the differential (DIC) and integral (IIC) inversion curves versus nitrogen and argon real gas data.

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