Joule Inversion Temperatures for Some Simple Real Gases

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Abstract: In the present work we calculate inversion temperatures T_i, for some simple real gases (He, Ne, Ar, Kr and H_2) in the case of a Joule expansion; that is, a free adiabatic expansion. These calculations are made by means of an intermolecular potential of the Lennard-Jones type (12, 6), slightly modified by using a Jagla linear ramp in the repulsive part of the potential. For the Helium we find a T_i in agreement with both previous calculations published by other authors and with experimental results. For Ne and Ar our results are also within the interval of values previously reported, and for Kr we also obtain a very high inversion temperature as some other authors. However, for H_2 we find a T_i approximately twice to big than its estimated experimental value. This last calculation is corrected if we use a short ranged Lennard-Jones potential of the type (24, 12), obtaining a result in good agreement with the recognized experimental value.

INTRODUCTION

It is well known that all real gases undergoing a throttling process (the so-called Joule-Kelvin expansion) have an inversion temperature, T_i ; that is, a temperature at which the process changes from a heating to a cooling process. This temperature depends upon the particular gas and upon both the initial and final pressures [1]. On the other hand, only in some few references [2-4], the problem of an inversion temperature associated to the so-called Joule expansion (free adiabatic expansion) for real gases is discussed. In fact, Goussard and Roulet [2] asserted that there exists an inversion temperature, T_i, for all real gases undergoing an adiabatic free expansion. If T_0 is the initial temperature, then for $T_0 < T_i$, the gas is cooler after a free expansion and for $T_0 > T_i$, the gas is warmer. According to Goussard and Roulet [2], all real gases which can be described by intermolecular potentials $u(r)$ which diverge with small values for r at least like r^{-3}, necessarily have an inversion temperature. For example, for the Lennard-Jones model $u(r) \sim r^{-12}$ for $r \to 0$, and they used this potential to calculate T_i for helium and hydrogen [2]. Their result for the helium case is excellent according to experimental variations of the second virial coefficient $B(T)$ measured by Holborn and Otto [5] and also given in [1]. However, for the hydrogen case they calculated T_i twice to big than its estimated experimental value [1, 5]. Boschi-Filho and Buthers [3] studied the Joule inversion temperature for several simple real gases at high temperatures based on the $B(T)$ behavior and they suggested that most of simple real gases have an inversion temperature corresponding to the maximum value of $B(T)$ in a range of temperatures so high that few experimental data are available. Recently, Parsafar, *et al*. [4] proposed a method to

modify hard-core potentials to predict real fluid properties at low densities, including the inversion temperature. In the present article we discuss the problem of the Joule inversion temperature by means of a Lennard-Jones potential slightly modified in its repulsive and positive part according to the so-called Jagla potential [6]. This potential allows to obtain analytical expressions for the second virial coefficient and for its first derivative dB/dT, necessary to calculate the Joule inversion temperature. With this potential we calculate T_i for He, Ne, Ar, Kr and H_2.

Our results for He, Ne and Ar are in agreement with [2] and [3] respectively, and for Kr we obtain a very high inversion temperature as in [3]. For the hydrogen case we also obtain a T_i value twice to big the recognized experimental value reported in [1]. However, we recuperate a correct result by using a Lennard-Jones potential with exponents (24, 12). The article is organized as follows: In section 2 we present the Lennard-Jones modified model for the intermolecular potential. In section 3 we use experimental data to fit our approximated model to calculate T_i. In section 4, we calculate T_i for hydrogen by using a (24, 12) Lennard-Jones potential. Finally we present our concluding remarks.

THE MODIFIED LENNARD-JONES POTENTIAL

The temperature change for a gas undergoing an adiabatic free expansion can be calculated by means of the so-called Joule coefficient,

$$J = \left(\frac{\partial T}{\partial V}\right)_E = -\left(\frac{\partial T}{\partial E}\right)_V \left(\frac{\partial E}{\partial V}\right)_T = -\frac{1}{C_V}\left(\frac{\partial E}{\partial V}\right)_T \qquad (1)$$

being T the absolute temperature, V the volume, E the internal energy and C_V the heat capacity at constant volume. Since C_V is always positive, the sign of the temperature variation along the expansion is determined by the sign of $(\partial E/\partial V)_T$. The coefficient J can also be calculated knowing C_V and the gas state equation [2],

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$$J = \frac{1}{C_V}\left[P - T\left(\frac{\partial P}{\partial T}\right)_V\right] \tag{2}$$

with P the gas pressure. Writing the virial expansion as

$$PV = nRT\left(1 + \frac{nB}{V} + \frac{n^2 C}{V^2} + \frac{n^3 D}{V^3} + \cdots\right) \tag{3}$$

which expresses the deviation of P from that of an ideal classical gas, it is easy to show, that in the thermodynamic limit $V \to \infty$ [3], the Joule coefficient can be expressed as

$$J = -\frac{n^2 RT^2}{C_V V^2}\left(\frac{dB}{dT}\right) \tag{4}$$

being $B=B(T)$ the second virial coefficient and n the molar number. If an inversion temperature T_i exists then,

$$\left(\frac{dB}{dT}\right)_{T_i} = 0 \tag{5}$$

Boschi-Filho and Buthers [3] showed that some state equations such as Van der Waals, Berthelot, Dieterici, Redlich-Kwong and Beattie-Bridgeman have not an inversion temperature. This fact according to Goussard and Roulet [2] occurs because for real gases the existence of an inversion temperature comes directly from the fact that there is a high but not infinite repulsive part in $u(r)$. On the other hand, for a hard sphere repulsive part, $u(r) = \infty$ for $r < \sigma$ and therefore $(\partial E/\partial V)_T$ is always positive in their Eq. (6), [2]. This is clearly the case for a Van der Waals gas, which always cools in a Joule expansion [2].

As is well known [7], the second virial coefficient can be written as

$$B = 2\pi N_A \int_0^\infty \left(1 - e^{-u/kT}\right) r^2 dr \tag{6}$$

where $u(r)$ is the intermolecular potential, k the Boltzmann's constant, N_A the Avogadro's number, and r is the distance between a pair of molecules. In the present article we use the Lennard-Jones (LJ) potential, that is,

$$u(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6\right] \tag{7}$$

being ε the well depth and σ the point where $u(r) = 0$. We slightly modify the LJ-potential following the procedure of Jagla [6], which is depicted in Fig. (**1**), and is given by:

$$u(r) = \begin{cases} +\infty & \text{if} \quad 0 \le r \le \lambda \\ \alpha(r-\sigma) & \text{if} \quad \lambda \le r \le \sigma \\ 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6\right] & \text{if} \quad \sigma \le r \le +\infty \end{cases} \tag{8}$$

where:

$$\alpha = \left(\frac{4\varepsilon}{\lambda - \sigma}\right)\left[\left(\frac{\sigma}{\lambda}\right)^{12} - \left(\frac{\sigma}{\lambda}\right)^6\right] \tag{9}$$
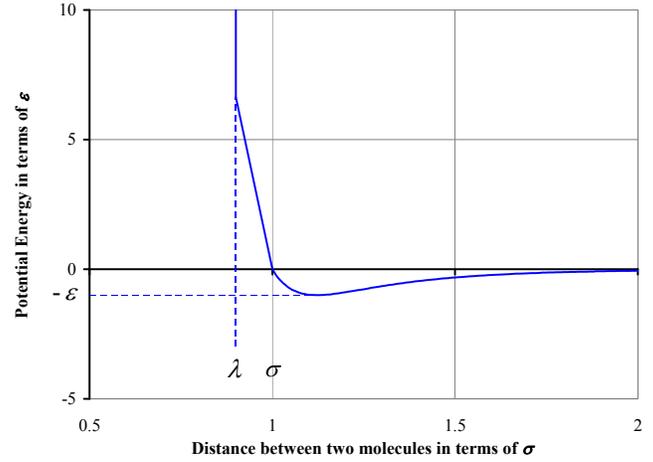

Fig. (1). The modified LJ-potential. The function is composed by three parts. The first part is in the interval corresponding to $0 < r < \lambda$ where the function is $+\infty$. The second part is formed by a ramp with negative slope for $\lambda < r < \sigma$. Finally, the third part is the LJ-potential in the interval corresponding to $\sigma < r < +\infty$.

For this potential we propose the following approximations: for the interval $0 < r < \lambda$, the term $1 - e^{-\beta u}$ inside the integral of Eq. (6) can be approximated by

$$1 - e^{-\beta u} \approx 1 \tag{10}$$

being $\beta = 1/kT$. For the interval $\lambda < r < \sigma$ the term $1 - e^{-\beta u}$ is maintained as it is. And finally, in the interval $\sigma < r < +\infty$, for the case $|\beta u| \ll 1$, we take:

$$1 - e^{-\beta u} \approx \beta u \tag{11}$$

By using these approximations, Eq. (6) can be written as,

$$B(T) = 2\pi N_A \int_0^\lambda r^2 dr + 2\pi N_A \int_\lambda^\sigma \left(1 - e^{-\beta u}\right) r^2 dr$$
$$+ 2\pi N_A \int_\sigma^{+\infty} \beta u r^2 dr \tag{12}$$

which leads to

$$B = \frac{2}{3}\pi N_A \sigma^3 - \frac{16\pi\varepsilon N_A \sigma^3}{9kT} + \frac{2\pi N_A kT}{\alpha}\left[\sigma^2 - \lambda^2 e^{\alpha\beta(\sigma-\lambda)}\right]$$
$$+ \frac{4\pi N_A k^2 T^2}{\alpha^2}\left[\sigma - \lambda e^{\alpha\beta(\sigma-\lambda)}\right] + \frac{4\pi N_A k^3 T^3}{\alpha^3}\left[1 - e^{\alpha\beta(\sigma-\lambda)}\right] \tag{13}$$

The first derivative of $B(T)$ is immediately obtained,

$$\frac{dB}{dT} = \frac{16\pi\varepsilon N_A \sigma^3}{9kT^2} + \frac{2\pi N_A k}{\alpha}\left[\sigma^2 - \lambda^2 e^{\alpha\beta(\sigma-\lambda)}\right]$$
$$+ \frac{8\pi N_A k^2 T}{\alpha^2}\left[\sigma - \lambda e^{\alpha\beta(\sigma-\lambda)}\right] + \frac{12\pi N_A k^3 T^2}{\alpha^3}\left[1 - e^{\alpha\beta(\sigma-\lambda)}\right]$$
$$+ \frac{2\pi N_A kT}{\alpha}\left[\frac{\alpha(\sigma-\lambda)\lambda^2 e^{\alpha\beta(\sigma-\lambda)}}{kT^2}\right]$$
$$+ \frac{4\pi N_A k^2 T^2}{\alpha^2}\left[\frac{\alpha(\sigma-\lambda)\lambda e^{\alpha\beta(\sigma-\lambda)}}{kT^2}\right]$$

$$+ \frac{4\pi N_A k^3 T^3}{\alpha^3} \left[\frac{\alpha(\sigma-\lambda)e^{\alpha\beta(\sigma-\lambda)}}{kT^2} \right] \qquad (14)$$

In the following section we shall use these algebraic results to obtain the Joule inversion temperatures for several simple real gases. We will plot $B(T)$ and $f(T) = (T^2/2\pi) \times (dB/dT)$ against T for several gases (He, Ne, Ar, Kr and H_2).

JOULE INVERSION TEMPERATURES

In this section we shall use Eqs. (13) and (14) to calculate the Joule inversion temperature for several simple real gases (He, Ne, Ar, Kr, and H_2).

A) Helium

For this gas we take experimental data for $B(T)$ reported by White *et al.* [8] for obtaining λ, σ and ε in Eq. (13) as fitting parameters. In Fig. (**2**) we see the experimental points of $B(T)$ and the fitted curve given by Eq. (13). The resulting values of the parameters are $\lambda = 2.002807 \times 10^{-10}$ m, $\sigma = 2.477172 \times 10^{-10}$ m, and $\varepsilon = 1.260382 \times 10^{-22}$ J, which means $\varepsilon/k = 9.1289$ K. From quantum mechanics calculations, Poling *et al.* [9] give for the helium $\varepsilon/k = 10.22$ K. In Fig. (**3**) we depict $f(T) = (T^2/2\pi) \times (dB/dT)$ against T according to Eq. (14). The inversion temperature is given by the point where $dB/dT=0$ and it corresponds to $T_i \approx 177$ K. Goussard and Roulet [2] for a LJ-potential, obtained an inversion temperature given by $T_i \approx 25\varepsilon/k$, which for He gives $T_i \approx 200$ K (See Figs. **2** and **3**).

B) Neon

In this case we took $B(T)$ experimental data from Prausnitz *et al.* [7] and Dymond and Smith [10]. In Fig. (**4**), we depict the fitted curve, Eq. (13), to experimental data obtaining the following values for the parameters $\lambda = 2.027787 \times 10^{-10}$ m, $\sigma = 2.571497 \times 10^{-10}$ m, and $\varepsilon = 6.311761 \times 10^{-22}$ J, which give $\varepsilon/k = 45.7158$ K. From viscosity data, Poling *et al.* [9] report for Neon $\varepsilon/k = 32.8$ K. In Fig. (**5**) we obtain an inversion temperature of $T_i \approx 867$ K, which is within the T_i-interval given by ref. [3], for Neon 870 ± 390 K.

C) Argon

In this case we take experimental second virial data given by Fender and Halsey [11] (see Fig. **6**). The resulting fitted parameters according with Eq. (13) are $\lambda = 3.145084 \times 10^{-10}$ m, $\sigma = 4.74678 \times 10^{-10}$ m, and $\varepsilon = 1.231451 \times 10^{-21}$ J, which give $\varepsilon/k = 89.1935$ K. From viscosity data, Poling *et al.* [9] find $\varepsilon/k = 93.3$ K. In Fig. (**7**) we have $f(T)$ versus T, and we obtain $T_i \approx 3448$ K which is within the T_i-interval reported by Boschi-Filho and Buthers [3] for Argon, $T_i \approx 3800 \pm 1800$ K.

D) Krypton

For this gas we use $B(T)$ experimental data also given by Fender and Halsey [11] (see Fig. **8**). The resulting fitted parameters by using Eq. (13) are $\lambda = 3.631624 \times 10^{-10}$ m, $\sigma = 6.153939 \times 10^{-10}$ m, and $\varepsilon = 1.276291 \times 10^{-21}$ J, which give $\varepsilon/k = 92.4413$ K. From viscosity data, Poling *et al.* [9]

obtain $\varepsilon/k = 178.9$ K. In Fig. (**9**) we see that T_i for krypton seemingly has a very high value, $T_i \approx 6481$ K. Boschi-Filho and Buthers [3] assert that at least for the temperature range 0-4000 K this gas does not show a maximum in its second virial coefficient. However, for $T_i > 4000$ K we find a possible inversion temperature.

E) Hydrogen

In the hydrogen case we found an inversion temperature by taking $B(T)$ experimental data from Prausnitz *et al.* [7] and Dymond and Smith [10]. By means of Eqs. (13) and (14) we obtained $T_i \approx 922$ K. The fitted parameters are $\lambda = 2.368190 \times 10^{-10}$ m, $\sigma = 2.861934 \times 10^{-10}$ m, and $\varepsilon = 5.513926 \times 10^{-22}$ J, which give $\varepsilon/k = 39.9372$ K. On the other hand, from viscosity data, Poling *et al.* [9] report $\varepsilon/k = 59.7$ K (See Figs. **10** and **11**).
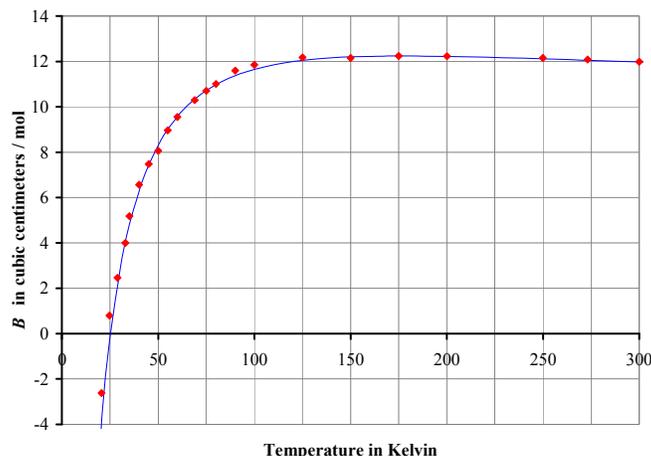

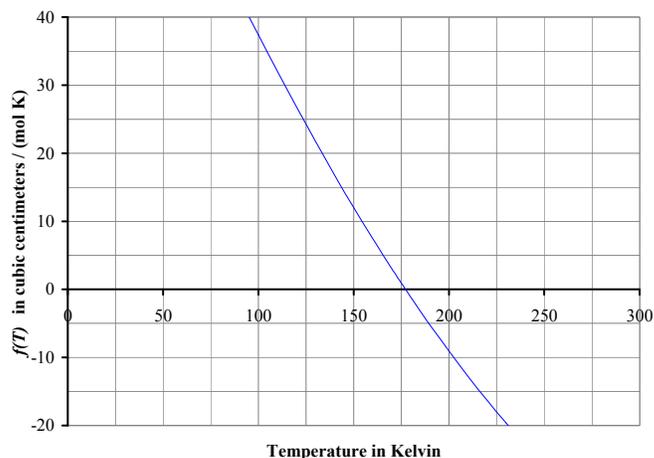**Fig. (2).** Fitted curve for $B(T)$ Helium data.

Fig. (3). $f(T)$ versus T for Helium, resulting $T_i \approx 177$ K.

(24, 12) LENNARD-JONES POTENTIAL

According to Callen [1], the experimental Joule inversion temperature for hydrogen is $T_i \approx 400$ K. By means of a LJ-potential, Goussard and Roulet [2] calculated $T_i \approx 800$ K. However, if one uses the algebraic expression for $B(T)$ given by Holborn and Otto [3, 5] the resulting T_i is 474 K, no so far the accepted experimental value $T_i \approx 400$ K. In section 3, we

found that by means of a LJ-potential modified by using a Jagla type ramp the Joule inversion temperature for H_2 is $T_i \approx 922$ K. However, if we use a Lennard-Jones potential with exponents (12, 6), $B(T)$ can be calculated as an infinite power series [3, 12].
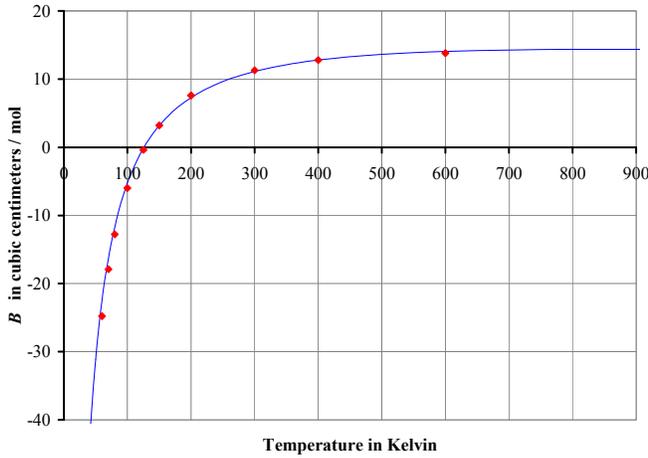

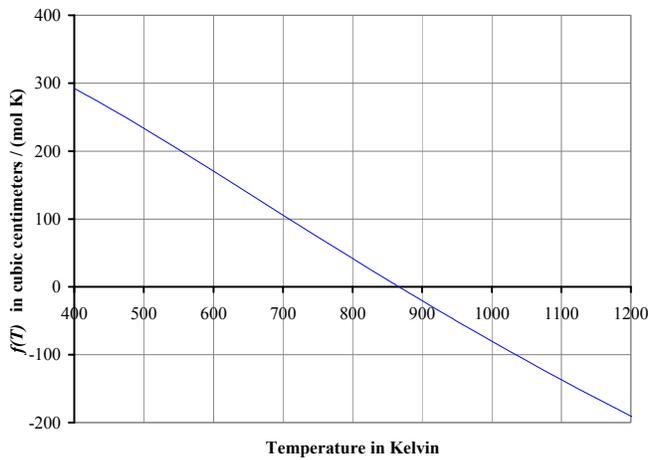**Fig. (4).** Fitted curve for *B(T)* Neon data.

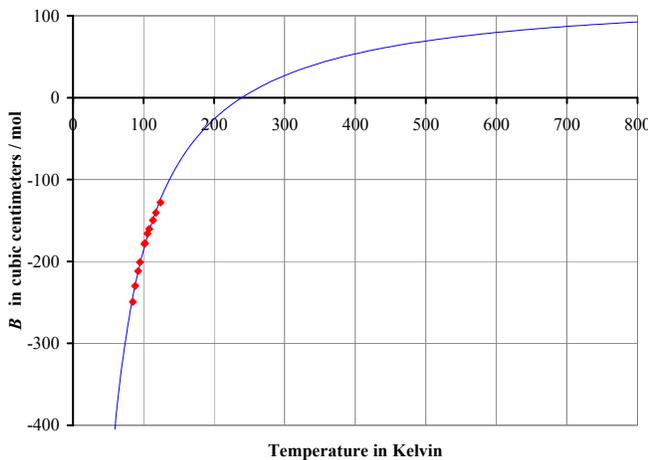**Fig. (5).** *f(T)* versus *T* for Neon, resulting $T_i \approx 867$ K.

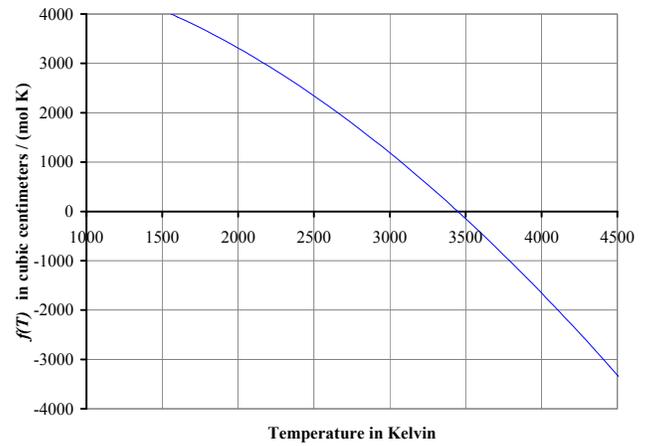**Fig. (6).** Fitted curve for *B(T)* Argon data.

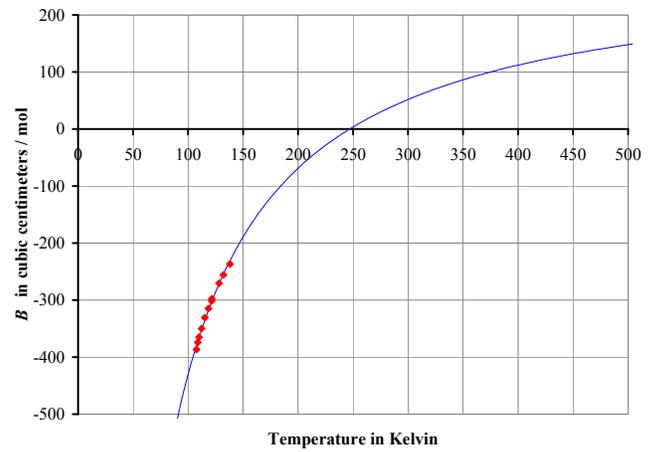**Fig. (7).** *f(T)* versus *T* for Argon, resulting $T_i \approx 3448$ K.

Fig. (8). Fitted curve for *B(T)* Krypton data.
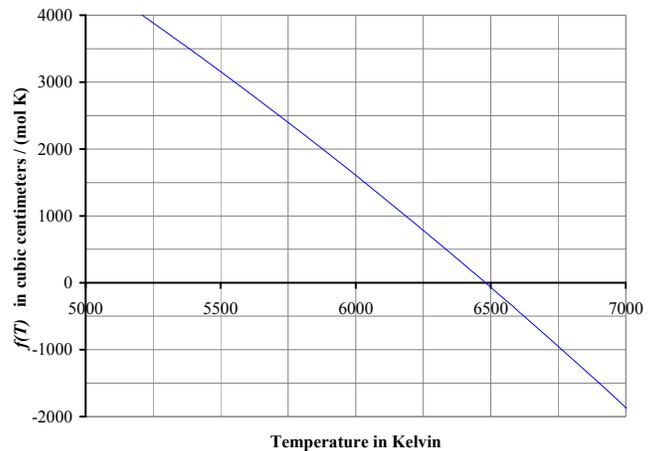

Fig. (9). *f(T)* versus *T* for Krypton, resulting $T_i \approx 6481$ K.

$$B(T) = b_0 \sum_{j=0}^{\infty} b^{(j)} T^{* -\left(\frac{2j+1}{4}\right)} \tag{15}$$

being $T^* = kT / \varepsilon$ the reduced temperature, $b_0 = (2/3)\pi N_A \sigma^3$ is four times the volume of a molecule multiplied by N_A, and
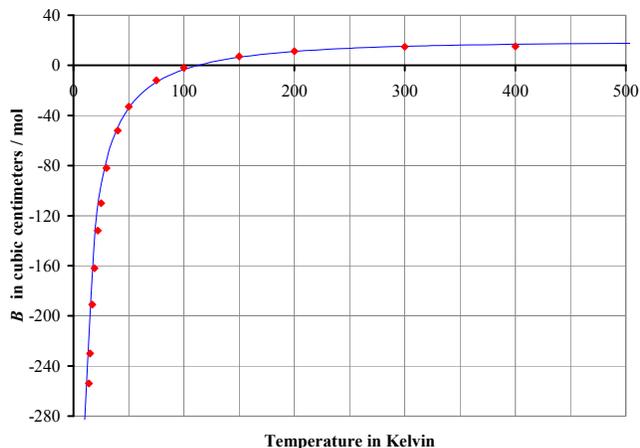
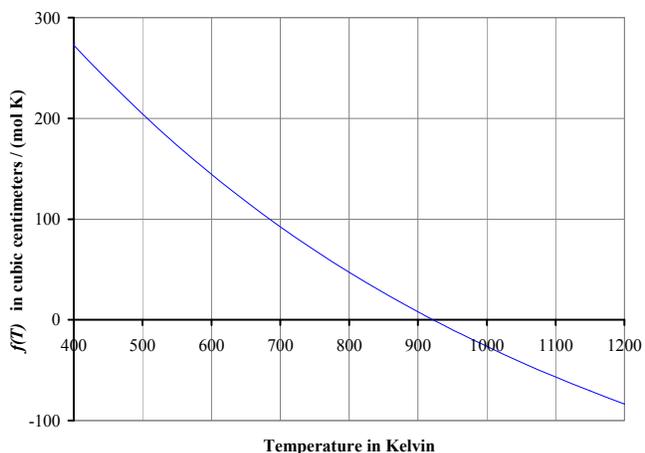**Fig. (10).** Fitted curve for *B(T)* Hydrogen data.

Fig. (11). *f(T)* versus *T* for Hydrogen, finding $T_i \approx 922$ K.

$$b^{(j)} = -\frac{2^{j+\frac{1}{2}}}{4\,j!}\Gamma\left(\frac{2j-1}{4}\right) \tag{16}$$

By means of $dB/dT = 0$ and taking $j = 5$ one finds [3]

$$T^* = \frac{kT_i}{\varepsilon} \approx 25.125 \tag{17}$$

which leads to $T_i \approx 930$ K for hydrogen; that is a value far from the recognized experimental value, $T_i \approx 400$ K. On the other hand, if we take the LJ-potential in the form [13],

$$u(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{2n} - \left(\frac{\sigma}{r}\right)^{n}\right] \tag{18}$$

in terms of the reduced temperature T^* for the second virial coefficient, we obtain,

$$B^*\left(T^*, 2n, n\right) = -\sum_{j=0}^{\infty}\frac{3}{2\,j!n}\Gamma\left(\frac{nj-3}{2n}\right)\left(\frac{4}{T^*}\right)^{(nj+3)/2n} \tag{19}$$

This expression, by means of $dB/dT = 0$ gives us the reduced inversion temperatures shown in Table **1**.

Table 1. T_i^* **As Function of LJ-Potentials (2n, n)**

LJ(2n, n)	T_i^*
LJ(8, 4)	90
LJ(12, 6)	**25.15**
LJ(16, 8)	17
LJ(20, 10)	14
LJ(24, 12)	**12.47**
LJ(28, 14)	11
LJ(48, 24)	9.7
LJ(96, 48)	8.65

It is remarkable that for the exponents (24, 12) which corresponds to a very short ranged potential [14], $T_i^* = 12.47$. Thus by using $\varepsilon \approx 28\times10^{-4}$ eV for hydrogen [2, 15], we obtain a Joule inversion temperature of T_i (H$_2$) ≈ 400 K in agreement with the experimental value given by Callen [1]. In Fig. (**12**) we depict a comparison between the LJ-potential for both pairs of exponents (12, 6) and (24, 12).
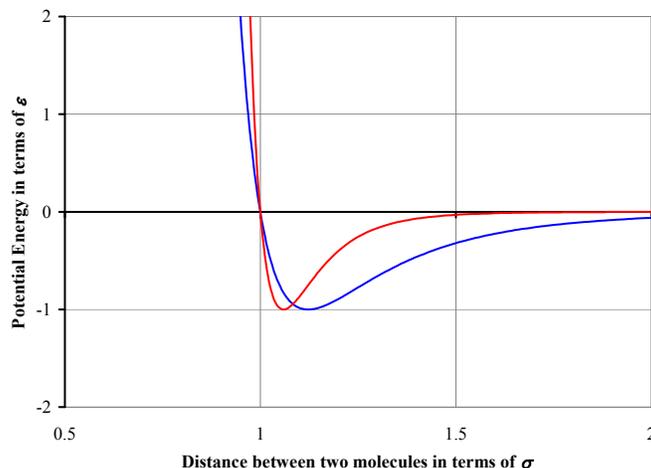

Fig. (12). LJ-potential (12, 6) is plotted by using a blue line. The red line shows the LJ-potential (24, 12), [14].

CONCLUDING REMARKS

Although the throttling Joule-Kelvin expansion is a process widely presented in thermodynamics textbooks, the so-called Joule expansion for real gases is scarcely discussed in the literature [2-4]. Goussard and Roulet [2] found that all real gases which can be described by an intermolecular potential $u(r)$ diverging for small values of r at least like r^{-3}, necessarily have an inversion temperature. These authors calculated T_i for He and H$_2$ by using a Lennard-Jones potential finding a good result for He and twice to big than its estimated experimental value for H$_2$. On the other hand, Boschi-Filho and Buthers [3] calculated T_i for several real gases at high temperatures by using $B(T)$ behavior and they concluded that most of simple real gases have T_i's in a range of temperatures so high that few experimental data are available.

In the present paper, we have calculated Joule inversion temperatures for some simple real gases by means of a

Table 2.   **Calculated Values for λ, σ and ε/k by Fitting the Experimental Data to Eq. (13). The Last Column Shows the ε/k Values Provided by Poling *et al.* [9]**

Gas	λ [$\times 10^{-10}$ m]	σ [$\times 10^{-10}$ m]	ε/k [K]	ε/k [K] by Poling *et al.* [9]
He	2.002807	2.477172	9.1289	10.22
Ne	2.027787	2.571497	45.7158	32.80
Ar	3.145084	4.746780	89.1935	93.30
Kr	3.631624	6.153939	92.4413	178.90
H$_2$	2.368190	2.861934	39.9372	59.70

Table 3.   **Joule Inversion Temperatures for Several Real Gases. The Second Column Shows Calculated T_i by Using Eq. (14). Also, the Calculated T_i's by Goussard and Roulet [2] and Those Calculated by Boshi-Filho and Buthers [3] are Shown in Third and Fourth Columns Respectively**

Gas	T_i [K] by Using eq. (14)	T_i [K] by [2]	T_i [K] by [3]
He	177	200	200 ± 50
Ne	867	-----	870 ± 390
Ar	3448	-----	3800 ± 1800
Kr	6481	-----	-----
H$_2$	922	800	660 ± 270

Lennard-Jones potential modified by a Jagla type ramp, obtaining T_i-results within a range similar to previous reported values [2, 3]. In Table **2** we present our obtained results for λ, σ and ε/k, according to experimental data and equation (13). In the same Table **2**, we show the values for ε/k provided by Poling *et al.* [9]. In Table **3** we show the Joule inversion temperatures obtained by using equation (14) and the results obtained by [2, 3]. However, for the case of hydrogen, we found that a Lennard-Jones potential with (24, 12) exponents is more suitable to calculate a T_i near its estimated experimental value of $T_i \approx 400$ K.

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