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The Joule-Thomson Coefficient—A Molecular Interpretation

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A discussion of the Joule-Thomson coefficient is presented in terms of its molecular interpretation. Certain aspects of the actual process are then explained in terms of these results. It is also shown how one may use the experimental data to study molecular interactions in gases.

INTRODUCTION

In 1915, in a paper¹ entitled "Note on the Value of Joule-Thomson Observations for Computing Steam Tables," H. N. Davis made the observation that

... it is often supposed that Joule-Thomson or throttling experiments are of value chiefly in evaluating the thermodynamic or Kelvin temperature, and in discussions of molecular attractions.

Davis then went on to elaborate a practical aspect of the Joule-Thomson process.

In this writer's opinion, what was exoteric in 1915 is the esoteric today. Most thermodynamic texts discuss the Joule-Thomson process in terms of a purely thermodynamic analysis (which usually consists of showing the process to be isenthalpic) and an application of the process to the liquefaction of gases. Statistical thermodynamics books (those that mention the process at all) usually limit the discussion to showing that the sign of the Joule-Thomson coefficient depends qualitatively on the magnitude of the second-virial coefficient.

It is the purpose of this note to offer a simple but quantitative molecular interpretation of the

Joule-Thomson coefficient and to indicate how one may use the process to study intermolecular interactions in the gas phase.

There are two Joule-Thomson coefficients which are simply related²: the usual isenthalpic coefficient μ defined in Eq. (1),

$$\mu = \lim_{P_2 \rightarrow P_1} (T_2 - T_1) / (P_2 - P_1) = (\partial T / \partial P)_H, \quad (1)$$

and the less common isothermal Joule-Thomson coefficient ϕ defined in Eq. (2),

$$\phi = \lim_{P_2 \rightarrow P_1} [H(P_2) - H(P_1)] / (P_2 - P_1) = (\partial H / \partial P)_T. \quad (2)$$

From the expression $dH = C_p dT + (\partial H / \partial P)_T dP$, it follows that

$$\phi = -\mu C_p. \quad (3)$$

In the isenthalpic experiment, a gas at a constant pressure P_1 and temperature T_1 is expanded through a throttling plug against a lower constant pressure P_2 . By fixing the initial conditions P_1 and T_1 and varying the final pressure, an isenthalpic line is generated, the slope of which is the Joule-Thomson coefficient at some specific temperature and pressure. The curve ABC in Fig. 1 is the inversion line and corresponds to the condition that $\mu = 0$ at the point it crosses each isenthalp.

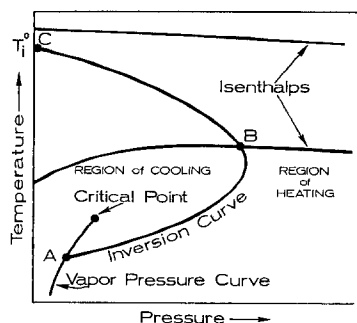


FIG. 1. Schematic of the Joule-Thomson expansion process. The zero-pressure inversion temperature T_i^0 is defined by point C.

It will be noted that the inversion curve intercepts the temperature axis at $P=0$ on the upper branch and the vapor pressure curve on the lower branch.

From Fig. 1 it is seen that the occurrence of cooling or warming will depend on the final and initial states of the expansion process. If both the final and initial states are inside of the inversion envelope, cooling results. Conversely, heating occurs when the coordinates of the process are defined entirely external to the inversion envelope. In particular, heating will always result for any expansion in which the final temperature is above the zero pressure value of the inversion temperature T_i^0 , (point C, Fig. 1).

The quantity ϕ is measured by performing the usual isenthalpic expansion and then either adding or removing heat from the throttled gas until $T_2=T_1$. Thus, from the adiabatic case where $H(P_1, T_1)=H(P_2, T_2)$, one may, by measuring the quantity $q=H(P_2, T_1)-H(P_2, T_2)$, which is the heat required to restore the gas to the initial temperature at constant pressure, obtain the ratio $[H(P_2)-H(P_1)]/(P_2-P_1)$, which is ϕ in the limit of zero pressure drop.

THEORETICAL EXPRESSION FOR μ

It is a standard thermodynamic result that

$$\mu = \left(\frac{\partial T}{\partial P}\right)_H = \frac{T(\partial V/\partial T)_{P-V}}{C_p} \quad (4)$$

Furthermore, the most general way to represent a real gas is with the virial equation of state³

$$PV = A + BP + CP^2 + DP^3 + \dots, \quad (5)$$

where $A = NRT$ and the coefficients B, C , etc., are functions of the temperature but not pressure. As written here, B is the usual second virial coefficient. Substitution of Eq. (5) into Eq. (4) gives

$$\mu = \frac{[(B'T - B) + (C'T - C)P + (D'T - D)P^2 + \dots]}{C_p}, \quad (6)$$

where the primes denote differentiation with respect to temperature. In order to keep the argument simple, we limit the discussion to the zero pressure case. Then from Eq. (6),

$$\lim_{P \rightarrow 0} \mu \rightarrow \mu^0 = (B'T - B)/C_p^0, \quad (7)$$

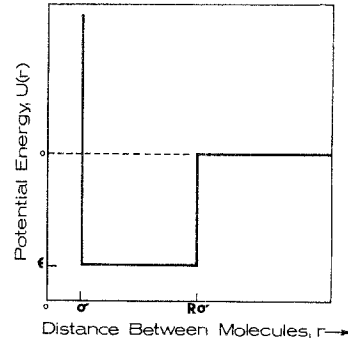


FIG. 2. Schematic of the square-well potential.

which is the limiting slope of an isenthalp at zero pressure and is a property characteristic of a gas at a specific temperature; C_p^0 is the value of C_p at zero pressure. It is interesting to note that even in the limit of zero pressure where gas behavior is essentially ideal, the coefficient μ^0 is still a function of an imperfection parameter. A general and lucid discussion of this fact is presented in Vol. II of Kestin's series on thermodynamics.⁵ In addition we see that, since the inversion curve is defined by both temperature and pressure coordinates, a theoretical inversion curve necessitates the use of the higher virial coefficients.

In order to relate μ^0 to the molecular properties of the gas it will be necessary to use one of the more elegant results of statistical mechanics. The second virial coefficient B , derivable from the theory of imperfect gases in terms of the "cluster integrals," may be written

$$B = 2\pi N \int_0^\infty r^2 \left[1 - \exp\left(\frac{-U(r)}{kT}\right) \right] dr \quad (8)$$

for spherically symmetric molecules, where $U(r)$ is the interaction potential for a molecular pair.

In order to evaluate B and hence μ^0 , it is necessary to define a specific potential function.

The potential function $U(r)$, chosen for the purposes of illustration and tractability, is the square well, defined in Eq. (9) and Fig. 2:

$$\begin{aligned} U(r) &= \infty & \text{for } r < \sigma \\ &= -\epsilon & \text{for } \sigma < r < R\sigma \\ &= 0 & \text{for } r > R\sigma. \end{aligned} \quad (9)$$

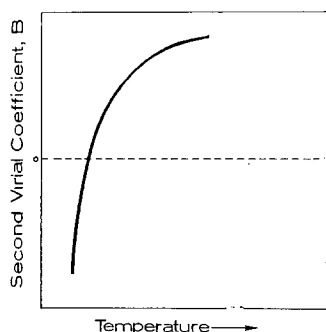


FIG. 3. Typical plot of the second virial coefficient against temperature.

Here ϵ is the depth of the potential well, r is the "effective" center-to-center distance between molecules in the gas phase and R is a scale constant. In spite of its simplicity, the square well with its three adjustable parameters is often a useful function for complex molecules. In order actually to use this function to obtain numerical results, one must know (usually indirectly from experiment) the potential parameters R , σ , and ϵ for a specific gas.

Substitution of Eq. (9) into Eq. (8) leads, together with Eq. (7), and after a series of simple integrations, to the expression for μ^0 in terms of the molecular parameters:

$$\mu^0 C_p^0 = \left\{ \frac{2\pi N \sigma^3 (R^3 - 1)}{3} \left[\frac{\epsilon}{KT} \exp\left(\frac{\epsilon}{KT}\right) + \exp\left(\frac{\epsilon}{KT}\right) - 1 \right] \right\} - \frac{2\pi N \sigma^3}{3}. \quad (10)$$

The term in braces arises from the integrations from σ to $R\sigma$ and represents the attractive energy contributions to μ^0 . The last term is the repulsive energy corresponding to the region 0 to σ . From

TABLE I. Comparison between theoretical and experimental zero pressure inversion temperatures (in degrees Kelvin).

	T_i^0 (exptl) ^a	T_i^0 (theor)
CO ₂	1500	1308
N ₂	621	634
A	723	791

^a J. G. Kirkwood and I. Oppenheim, *Chemical Thermodynamics* (McGraw-Hill, New York, 1961), p. 83.

Eq. (10) it is seen that at sufficiently high temperatures, in particular, temperatures above T_i^0 , the repulsive energy term will predominate leading to a negative value for $\mu^0 = (\partial T / \partial P)_H$ since σ and C_p^0 are positive. This implies that the gas will warm on expansion since the pressure change is always negative. At temperatures below T_i^0 , the major effect is from attractive forces with the result that μ^0 will be positive and the gas will cool on expansion.

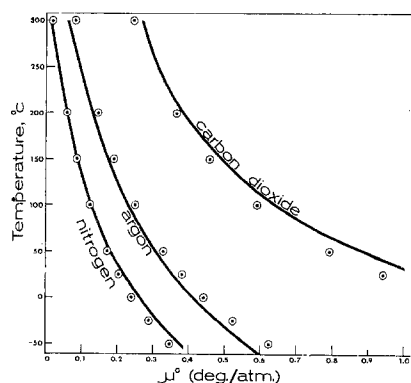


FIG. 4. Plot of μ^0 vs T for N₂, A, and CO₂. The encircled points represent the theoretical values for μ^0 based on Eq. (10). The solid lines are the experimental results. References are as follows: N- μ^0 vs T and C_p (at 1 atm) from J. R. Roebuck and H. Osterberg [Phys. Rev. **48**, 450 (1935)]; A- μ^0 vs T from J. R. Roebuck and H. Osterberg [Phys. Rev. **46**, 785 (1934)]; C_p^0 was taken as 4.968 cal/mole·deg; CO₂- μ^0 vs T from J. R. Roebuck *et al.* [J. Amer. Chem. Soc. **64**, 400 (1942)], C_p^0 from K. K. Kelley [U. S. Bur. Mines Bull. **584** (1960)]. The μ^0 values from these references were obtained, when necessary, by extrapolation of the tabulated μ -vs- P data to zero pressure. See J. R. Roebuck and H. Osterberg [J. Chem. Phys. **8**, 627 (1940)] for pressure corrections to the data tabulated in the first three references.

A somewhat more qualitative argument, based on Eq. (7), for the sign of μ^0 can also be given. Figure 3 is a typical plot of the second virial coefficient B as a function of temperature. At low temperatures TB' will be large relative to B so μ^0 will be positive implying cooling. Conversely, at high temperatures, TB' will be small, B will predominate and μ^0 will be negative with the result that heating occurs on expansion.

In order to examine the validity of the square well potential, μ^0 was calculated numerically from Eq. (10) for N₂, A, and CO₂. The results are shown in Fig. 4 with the appropriate references listed in

the legend. The constants R , σ , and ϵ , based on second virial coefficient data, are from Ref. 5. In addition one may calculate the maximum inversion temperature T_i^0 by setting Eq. (10) equal to zero. Table I lists the results of this calculation for CO_2 , N_2 , and A.

The results are perhaps surprisingly good in view of the crude nature of the square-well function. As discussed in the next section however, this merely reflects the insensitivity of μ^0 to a particular potential function, a fact that makes the reverse problem of calculating $U(r)$ from experimental Joule-Thomson data often ambiguous.

DETERMINATION OF POTENTIAL PARAMETERS

The potential function describing two-body interactions, while amenable in principle to determination from quantum mechanics, presents in reality a difficult task. A common alternative is to derive, on the basis of an assumed potential function with undetermined potential parameters, a theoretical expression for some measurable property of the system. This expression together with sufficient experimental data allows the evaluation of the potential parameters. In the case of gas phase interactions, the second virial, zero pressure Joule-Thomson, viscosity, and diffusion coefficients have been used for this purpose.

As an illustration of how the Joule-Thomson coefficient may be used to evaluate the square well potential function parameters, we chose some recent experimental data of Francis, McGlashan, and Wormald⁶ (FMW) in which ϕ for benzene was measured as a function of temperature and pressure.

The advantage of choosing ϕ over μ is that since ϕ is not a function of heat capacity, the entire effect results from changes in potential energy.

Seven values of ϕ vs P , spanning the temperature range from 343.05 to 403.42°K, were least squared in order to obtain the ϕ^0 (the zero-pressure isothermal Joule-Thomson coefficient) values and the standard errors. These data were then used to

TABLE II. Potential parameters for benzene.

R	1.646	0.77	0.80
σ (cm) $\times 10^8$	2.575	-4.7	-4.5
ϵ (ergs) $\times 10^{13}$	1.230	1.23	1.32

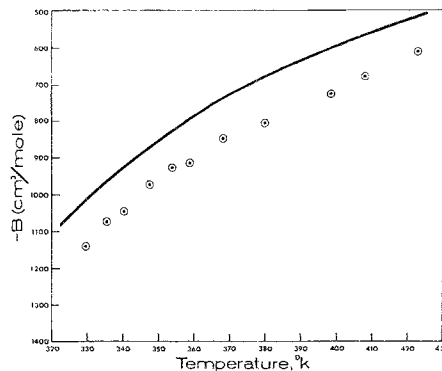


FIG. 5. Comparison between the calculated (solid line) and experimental (encircled points) second virial coefficient for benzene. The calculated line is from Eq. (11) and the experimental points from Ref. 6.

analyze Eq. (10) by computer [with Eq. (3)] to obtain the best fit values for R , σ , and ϵ . The results are listed in column 2 of Table II. The fit is quite good with an average discrepancy between the experimental and calculated ϕ^0 values of less than 0.5%.

As a test of these "best fit" values for R , σ , and ϵ , we have computed the theoretical second virial coefficient for benzene as a function of temperature. From the definition, Eq. (8), and use of the square well potential, Eq. (9), one obtains the result, on substitution of the "best fit" values for R , σ , and ϵ , that

$$B(\text{cm}^3/\text{mole}) = 96.0 - 74.5 \exp(890.7/T). \quad (11)$$

Comparison between Eq. (11) and the experimental second virial coefficient data of FMW is shown in Fig. 5. Although not shown on the graph, B becomes positive at about 3500°K.

FMW, in an analysis based on the required mutual consistency of experimental B , ϕ^0 , and calorimetric data, obtained a best fit relationship for B of the same form (square well) as Eq. (11):

$$B = -60.1 - 70.4 \exp(891.3/T). \quad (12)$$

From Eq. (12) we have calculated R , σ , and ϵ , the results of which are tabulated in column 3 of Table II. The negative value for σ is troublesome conceptually since it represents physically the collision diameter for two benzene molecules.

Summarizing the calculations, we have: (a) Equation (12), although physically unrealistic

since it seems unreasonable to expect B to be non-positive for all T (a fact noted by FMW), reproduces the experimental results for B vs T , ϕ^0 vs T , and the calorimetric data very well; whereas (b) our best fit, Eq. (11), based on the ϕ^0 -vs- T data only, although leading to reasonable values for σ and R and an excellent fit of the ϕ^0 -vs- T data, did rather poorly at reproducing the experimental B -vs- T results.

In order to elucidate this discrepancy we looked for a second "best fit" to Eq. (10) (again using only the ϕ^0 -vs- T data) in the region of FMW's values for R , σ , and ϵ . This led to the results listed in column 4 of Table II.

It is not the point of this note to explore this problem, but the benzene example does illustrate, albeit fortuitously, some of the difficulties associated with such calculations. An unambiguous computation of the potential parameters for a particular function requires a large amount of highly accurate experimental data, preferably from different complementary measurements. It would also seem that a search for multiple "best fits" is called for. Furthermore, it is well known that the second virial and Joule-Thomson coefficients are rather insensitive to the exact shape of the potential function. Indeed, as Klein and Hanley⁷ have shown, the second virial coefficient and to a lesser extent the zero-pressure Joule-Thomson coefficient are incapable of even differentiating between potential functions within certain temperature ranges. This is unfortunate since both μ^0 and B provide a direct connection between experiment and $U(r)$ which does not involve a concomitant test of a theoretical expression of unknown validity.

¹ H. N. Davis, *Phys. Rev.* **5**, 359 (1915).

² E. A. Guggenheim, *Thermodynamics* (North-Holland, Amsterdam, 1967), pp. 92-101.

³ The coefficients C and D are not, strictly speaking "virial coefficients" since generally the virial coefficients are defined by expressing PV as a power series in $1/V$. The second virial coefficient B , however, has the same form in either case (see Ref. 4, p. 131).

⁴ J. O. Hirschfelder, C. F. Curtiss, and R. B. Boyd, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954), p. 160.

In any case, we see that experimental Joule-Thomson data can provide a probe for obtaining information about molecular interactions, although the analysis is far from straightforward.

Readers interested in the general topic of intermolecular forces and potential functions are referred to Refs. 7-10. For a detailed discussion of the Joule-Thomson coefficient with other potential functions as well as the application to mixtures, Ref. 4 should be consulted. Reference 11 contains an excellent discussion of the thermodynamics of the Joule-Thomson expansion.

SUMMARY

We have seen that the Joule-Thomson coefficient is amenable to a simple theoretical description from which one can rationalize, at the molecular level, the details of the throttling process. In particular, the occurrence of heating and cooling on expansion depends on the sensitive balance between the forces of attraction and repulsion between molecules. Furthermore, it is interesting to note that even for as simple a potential function as a square well, the agreement between experiment and theory was satisfactory.

Finally, it was shown how one can use the experimental Joule-Thomson coefficient to obtain information about interactions in the gas phase.

ACKNOWLEDGMENTS

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⁵ J. Kestin, *A Course in Thermodynamics* (Blaisdell, Waltham, Mass., 1968), Vol. II, pp. 245-249.

⁶ P. G. Francis, M. L. McGlashan, and C. J. Wormald, *J. Chem. Thermodynamics* **1**, 441 (1969).

⁷ M. Klein and H. J. M. Hanley, *Trans. Faraday Soc.* **64**, 2927 (1968).

⁸ *Advanced Chem. Phys.* **12**, 1 (1967).

⁹ *Discussions Faraday Soc.* **40**, 1 (1965).

¹⁰ D. D. Fitts, *Ann. Rev. Phys. Chem.* **17**, 59 (1966).

¹¹ M. W. Zermansky, *Heat and Thermodynamics* (McGraw-Hill, New York, 1968), pp. 335-346.