

Application of the New equation of state to the Joule-Thomson effect

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In a recent paper¹⁾ I proposed an equation of state which equally satisfies the three criteria for state equations: $RT_c/p_c V_c$, T_R/T_c and $T_c/p_c \cdot (dp/dT)_c$. One more criterion with technical importance is the Joule-Thomson effect which is formulated thermodynamically

1) This *Bulletin*, **23**, 78 (1953).

by the aid of van der Waals' equation of state, but results in a qualitative formula:

$$\mu = \frac{2a_{corr}/RT - b_{corr}}{C_p}, \quad a_{corr} = \frac{27R^2T_c^2}{64p_c},$$

$$b_{corr} = \frac{RT_c}{8p_c} \quad \dots(1)$$

where μ is the Joule-Thomson coefficient, C_p the molecular heat, R the gas constant, and T the temperature, these together with a_{corr} and b_{corr} being expressed in liters, atmospheres, moles, deg. absolute.

I will communicate in this letter the applicability of my equation of state to this problem.

Taking my equation, $p + a/V^2 = RT/(V - b)$, in the deduction of the above formula, it readily follows that

$$\mu = \frac{2aV^{\epsilon'}/RT - b}{C_p}, \quad a = 3p_cV_c^2,$$

$$b = V_c/3, \quad \dots(2)$$

here a , b &c. are expressed in the same units as above.

It is noticed here that ϵ in the preceding paper where V is expressed in cc./mole, and ϵ' denoted here where V is expressed in liter/mole are related by $\epsilon = \epsilon' \times \log V/(\log V + 3)$.

From International Critical Tables III, V, and Henning's "Warmetechnische Richtwerte", five available data of H_2 , CO_2 , N_2 , O_2 and air can be taken, among which, however, only air may serve as a test case for pressure effect.

To compare with (2- ϵ) directly from the equation of state, the test for its validity being the present purpose, estimate ϵ' from formula (2) and transform it into ϵ , from which (2- ϵ) from formula (2) is obtained.

| | | | | |
|---|------------------|-------|-------------------|-------|
| | Hydrogen | | | |
| | 0°C | | 100°C | |
| (2— ϵ) from formula (2) | 1.979 | | 2.005 | |
| (2— ϵ) from equation of state | 2.000 | | 2.009 | |
| | (p=50 atm.) | | (p=50 atm.) | |
| Divergence in % | 1.1 | | 0.2 | |
| | Carbon dioxide | | | |
| | 0°C | | 100°C | |
| (2— ϵ) from formula (2) | 1.890 | | 1.910 | |
| (2— ϵ) from equation of state | 1.900 | | 1.930 | |
| | (extrapolated) | | (p=50—1000 atm.) | |
| Divergence in % | 0.5 | | 1.0 | |
| | Nitrogen | | | |
| | 0°C | | 100°C | |
| (2— ϵ) from formula (2) | 1.944 | | 1.965 | |
| (2— ϵ) from equation of state | 2.007 | | 2.039 | |
| | (p=50—1000 atm.) | | (p=50—1000 atm.) | |
| Divergence in % | 3.1 | | 3.6 | |
| | Oxygen | | | |
| | 0°C | | 100°C | |
| (2— ϵ) from formula (2) | 1.941 | | 1.959 | |
| (2— ϵ) from equation of state | 1.967 | | 2.026 | |
| | (p=36—62 atm.) | | (p=100—1000 atm.) | |
| Divergence in % | 1.3 | | 3.3 | |
| | Air at 0°C | | | |
| | | | p (atm.) | |
| | 1 | 20 | 60 | 100 |
| (2— ϵ) from formula (2) | 1.977 | 1.969 | 1.973 | 1.987 |
| (2— ϵ) from equation of state | 1.987 | 1.997 | 2.000 | 2.002 |
| Divergence in % | 0.5 | 1.4 | 1.4 | 0.8 |
| | Air at 100°C | | | |
| | | | p (atm.) | |
| | 1 | 20 | 60 | 100 |
| (2— ϵ) from formula (2) | 1.995 | 1.995 | 2.005 | 2.019 |
| (2— ϵ) from equation of state | 1.986 | 2.019 | 2.025 | 2.029 |
| Divergence in % | 0.4 | 1.2 | 1.0 | 0.5 |

The agreements between these two are fairly good as seen from the above tables, and even the greatest divergence arising in the cases of N_2 and O_2 is less than 4%, where the mean values of $(2-\epsilon)$ from the equation of state at 50 or 100—1000 atms. are presumably the same as those at 1 atm. These results lead to the conclusion that the Joule-Thomson effect is formulated with accuracy by making use of my equation of state.

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