# Virial Modeling of Gas-Solid Joule-Thomson Effect for Argon-Carbon Aerosol

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From 1852 to 1862 James Prescott Joule and William Thomson (Lord Kelvin) carried out a series of experiments which demonstrated that a flowing gas (below its inversion temperature) undergoes cooling upon expansion from a higher to lower pressure. The theory and application of the Joule-Thomson effect has remained of interest to the present day. In addition to pure gas systems, a variety of theoretical and experimental studies on multicomponent gas systems have been made including work by Strakey et al. (1974), Ng and Mather (1976), Ahlert and Wenzel (1969), and Gustafsson (1970). More recently, it has been shown by Rybolt and Pierotti (1984) that an aerosol created by dispersing a fine powder in a gas can also display a Joule-Thomson effect.

Gas-solid aerosols have unique thermodynamic properties not found in pure or mixed gases. Of particular interest is the gas-solid Joule-Thomson cooling effect associated with a high surface area powder dispersed in a gas. The presence of such a powder can significantly enhance the Joule-Thomson cooling associated with a pressure drop in a flowing gas. Experimental measurements of aerosol cooling obtained by Rybolt and Pierotti (1984) were compared to a virial model utilizing chromatographic second gas-solid virial coefficients determined by Rybolt and Pierotti (1984). This model was based on the zero pressure limit in which it was necessary to consider terms only up to the second gas and gas-solid virial coefficients. The purpose of this study is to extend the application of this model to include the effects of higher order virial coefficients.

Pierotti and Rybolt (1984, 1989) showed that the Joule-Thomson effect associated with a gas-solid dispersion can be expressed in terms of gas and gas-solid virial coefficients, the heat capacity of the gas-solid mixture, and the concentration of the solid component. Microporous carbon adsorption data for argon, krypton, and xenon reported by Cole et al. (1974) are used in this study to obtain second and third gas-solid virial coefficients. Third gas virial coefficients are calculated using the method of De Santis and Grande (1979) and second gas virial coefficients are obtained from the data of Getzen (1956). These second and third gas and gas-solid virial coefficients and their temperature derivatives are used in conjunction with a statistical thermodynamic model to predict the magnitude of the aerosol cooling effect (gas-solid Joule-Thomson effect) as a function of temperature, pressure, and powder concentration.

## Theory and Analysis

Pierotti and Rybolt (1984) have previously derived an exact statistical thermodynamic equation for the gas-solid Joule-Thomson effect based on the following assumptions: the system is a two-component fluid phase consisting of a molecular gaseous component and a solid particulate component; the molecular component is an imperfect gas capable of interacting with the solid and itself through dispersion forces; and the solid particulate is dilute enough to exclude particle-particle interaction. This theoretical treatment is somewhat analogous to the two-component fluid treatment of Hill (1956). The starting gas and solid activities are replaced by gas and solid number densities and cluster integrals. The cluster integrals are in turn grouped together to give more familiar virial coefficients.

When the resultant virial equation of state for the gas-solid aerosol is substituted into the thermodynamic equation for the Joule-Thomson coefficient, expressed in terms of molar volume and the temperature derivative of the molar volume, then the gas-solid Joule-Thomson coefficient is expressed as

$$\mu_{gs}\bar{C}_{gs} = (TB'_{2g} - B_{2g}) + w(B_{2s} - TB'_{2s}) + (P/RT)(TB'_{3g} - 2TB_{2g}B'_{2g} - 2B_{3g} + 2B^2_{2g}) + w(P/RT)(2B_{3s} + 4B_{2g}B_{2s} - TB'_{3s} - 2TB_{2g}B'_{2s} - 2TB'_{2g}B_{2s}) + \cdots \quad (1)$$

where the low surface coverage heat capacity is given as

$$\bar{C}_{gs} = \bar{C}_g + wC'_s. \quad (2)$$

The zero pressure limit of the gas-solid Joule-Thomson coefficient is given as

$$\mu^\circ_{gs}\bar{C}^\circ_{gs} = (TB'_{2g} - B_{2g}) + w(B_{2s} - TB'_{2s}) \quad (3)$$

Note that if the powder concentration is zero, then Eqs. 1 and 2 are simplified to familiar virial expressions for the pure gas Joule-Thomson effect.

As shown by Pierotti and Thomas (1971), the moles of gas adsorbed by a solid may be expressed as

$$n_{ad} = B_{2s}(P/RT) + (B_{3s} + B_{2s}B_{2g})(P/RT)^2 + \ldots. \quad (4)$$

where $B_{2s}$ is a measure of the interaction of isolated gas molecules with the surface, $B_{3s}$ is a measure of pairs of gas molecules interacting with the surface, etc. Thus the gas-solid virial coefficients treat gas-solid interactions in a manner analogous to the way gas virial coefficients treat gas-gas intermolecular interactions.

Previous virial modeling of the gas-solid Joule-Thomson effect was based on Eq. 3 and, higher-order effects were not considered. In this work, Eq. 1 is used to explore the effect of the linear term in pressure which includes the third gas and gas-solid virial coefficients. To utilize Eq. 1, it is first necessary to determine equations for $B_{2g}$, $B_{3g}$, $B_{2s}$, and $B_{3s}$ as a function of temperature.

Getzen (1956) reported the second, third, and fifth virial coefficients associated with argon compressibility data in the temperature range of 273 to 573 K up to a maximum pressure of 405 bar. After exploring various polynomial fitting schemes, a third-order expression was found to be most useful to fit Getzen's $B_{2g}$ data. For the purpose of this study, a third-order expression in temperature is used to fit the experimental $B_{2g}$ values from 273 to 450 K, giving

$$B_{2g} = -178.541 + 1.02239(T) - 0.00204853(T^2) + 1.50170 \times 10^{-6}(T^3) \quad (5)$$

The $B_{2g}$ values generated from Eq. 5 were compared to calculated values of $B_{2g}$ based on the Lennard-Jones (6, 12) potential as described by Hirschfelder et al. (1954) and found to agree within 0.05% over the temperature range of the fit.

Due to possible problems associated with series truncation in many experimental data sets, the $B_{3g}$ values for argon were obtained from the empirical equation of De Santis and Grande (1979) which is based on specific gas characteristics including: critical volume, critical temperature, dipole polarization, molecular volume, and an acentric factor.

Cole et al. (1971) reported adsorption isotherm data in the temperature range of 273 to 398 K for argon, krypton, and xenon with various carbons, in the form of

$$n_{ad} = K_1P + K_2P^2 + \ldots \quad (6)$$

One of the carbons reported is referred to as carbon C and it is a microporous carbon with a Brunaer-Emmett-Teller (BET) surface area of 1,279 $m^2/g$ formed from dehydrochlorination and activation of Saran 746 fiber. Comparing Eqs. 4 and 6, one can calculate $B_{2s}$ and $B_{3s}$ values as

$$B_{2s} = K_1RT \quad (7)$$

and

$$B_{3s} = K_2(RT)^2 - B_{2s}B_{2g} \quad (8)$$

The reported $K_1$ and $K_2$ values of Cole et al. were combined with $B_{2g}$ values obtained from Eq. 5 to generate $B_{2s}$ and $B_{3s}$ values for the Ar-carbon C system. The values of $B_{2s}$ were found to be best fit with the equation

$$B_{2s} = (0.052180) \exp(1691.49/T) \quad (9)$$

with $r = 0.999$. The values of $B_{3s}$ were fit with the equation

$$B_{3s} = (-1.0014) \exp(3306.33/T) \quad (10)$$

with $r = 0.993$. A variety of polynomial fits were examined but linear logarithmic fits for $B_{2s}$ and $B_{3s}$ were found to be much more effective.

To illustrate typical values, Table 1 gives values from 300 to 400 K for $B_{2g}$, $B_{3g}$, $B_{2s}$, and $B_{3s}$. Equations for temperature derivatives of the gas and gas-solid virial equations were obtained by taking the temperature derivative of Eq. 5 to find $B'_{2g}$, the DeSantis equation to find $B'_{3g}$, Eq. 9 to find $B'_{2s}$, and Eq. 10 to find $B'_{3s}$. Although not discussed in detail, specific virial equations for the Kr-carbon C and Xe-carbon C systems were developed by a method analogous to that discussed above for the argon system.

The $\bar{C}_{gs}$ value can be determined from $\bar{C}_g$, $C'_s$, and $w$. Based on the data of Whalley (1955), $\bar{C}_g$ for argon is essentially constant at 20.8 J/mol · K over the pressure range (0 to 2 bar) and temperature range (300 to 400 K) considered. The maximum

**Table 1. Virial Parameters**

| $T$<br>K | $B_{2g}$<br>cm³/mol | $B_{3g}$<br>cm⁶/mol² | $B_{2s}$<br>cm³/g | $B_{3s}$<br>cm⁶/g · ol |
|---|---|---|---|---|
| 300 | −15.65 | 1,109 | 14.66 | −61,237 |
| 310 | −13.73 | 1,077 | 12.22 | −42,915 |
| 320 | −11.94 | 1,047 | 10.31 | −30,751 |
| 330 | −10.27 | 1,020 | 8.78 | −22,484 |
| 340 | −8.72 | 996 | 7.55 | −16,746 |
| 350 | −7.26 | 974 | 6.55 | −12,683 |
| 360 | −5.91 | 954 | 5.73 | −9,756 |
| 370 | −4.64 | 937 | 5.05 | −7,612 |
| 380 | −3.44 | 922 | 4.47 | −6,017 |
| 390 | −2.31 | 908 | 3.99 | −4,813 |
| 400 | −1.24 | 895 | 3.58 | −3,894 |

increase in the constant pressure heat capacity of argon on going from 0 to 2 bar is approximately 0.5% at 273 K and about 0.2% at 400 K. Rather than explicitly representing the $P$ and $T$ dependence of $\bar{C}_g$, it was taken as a constant. Over the narrow pressure range considered for Kr and Xe (from 0 to less than 1 bar), their $\bar{C}_g$ values are within 1% of the value for argon. Based on differential scanning calorimeter measurements of Rybolt and Pierotti (1984) for several different microporous carbons, the value of $C_s'$ was found to be 0.9 J $\cdot$ $g^{-1}$ $\cdot$ $K^{-1}$. Using the previously indicated values of $\bar{C}_g$ and $C_s'$, $\bar{C}_{gs}$ can be calculated from Eq. 2 for any value of $w$.

## Results and Discussion

Using equations developed for $B_{2g}$, $B_{3g}$, $B_{2s}$, $B_{3s}$, $B'_{2g}$, $B'_{3g}$, $B'_{2s}$, $B'_{3s}$, and the Ar-carbon C values for $\bar{C}_g$ and $C_s'$ indicated previously, it is possible to use Eq. 1 to calculate $\mu_{gs}$ as a function of $T$, $P$, and $w$. For the Ar-carbon C aerosol system, $\mu_{gs}$ was calculated over the range of $T$ from 300 to 400 K, $P$ from 0 to 2 bar, and $w$ from 0 to 20 g/mol. The key results of this analysis for the Ar-carbon C system are shown in Figures 1 and 2.

Figure 1 shows the value of $\mu_{gs}$ at $P = 101$ kPa as a function of $T$ for $w = 0$, 5, 10, and 20 g/mol. As the temperature is decreased, the value $\mu_{gs}$ increases and the effect is enhanced as the powder concentration is increased. According to Michels (1951), the value of $\mu_g$ is 0.44 K/bar at $T = 273$ K, 0.38 K/bar at $T = 298$ K, and 0.24 K/bar at 373 K. These values are in agreement with the predicted $\mu_g$ values shown in Figure 1. Note that the pure gas-solid Joule-Thomson effect is significantly enhanced by the addition of a high surface area carbon powder. At 300 K and $w = 20$ g/mol, the cooling effect is increased by about a factor of eight relative to the pure gas.

The $\bar{C}_{gs}$ value increases with $w$ and tends to attenuate the cooling effect. For a high surface area powder the other virial factors in Eq. 1 are sufficient to more than offset this gas-solid heat capacity effect. For low surface area powders with small gas-solid virial coefficients, however, the heat capacity effect can be sufficiently large to actually cause $\mu_{gs}$ to be smaller than $\mu_g$. This is predicted from Eqs. 1 and 3 and has been observed experimentally by Rybolt and Pierotti (1984).

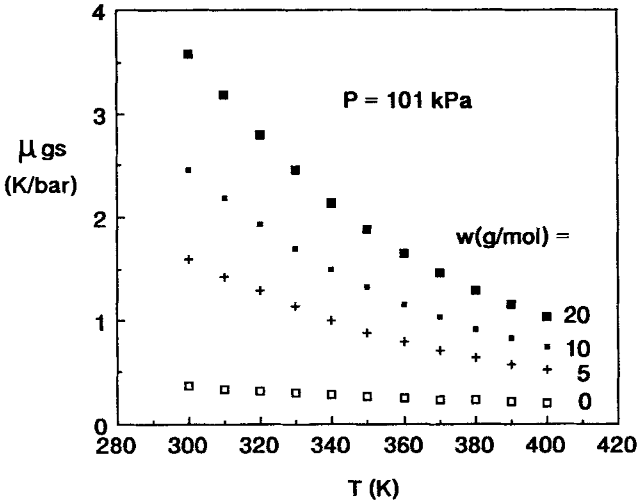

Figure 1. Argon-carbon C gas-solid Joule-Thomson effect as powder concentration varied (Eq. 1).

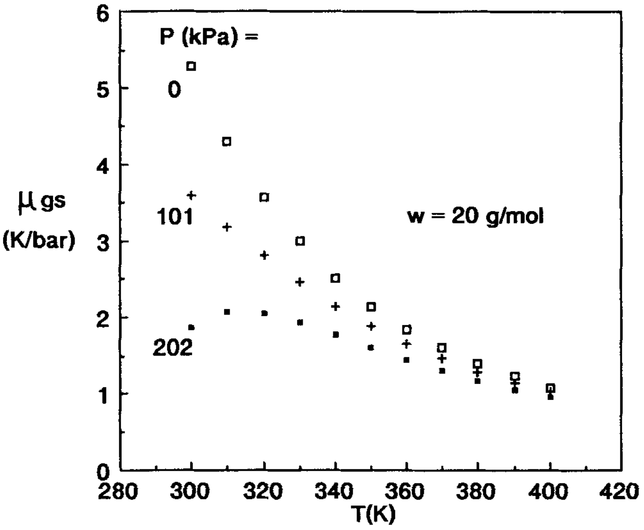

Figure 2. Argon-carbon C gas-solid Joule-Thomson effect as pressure varied (Eq. 1).

Figure 2 shows the effect of holding $w$ constant at 20 g/mol and varying $T$ at $P = 0$, 101, and 202 kPa. Note that the zero pressure limit of the effect is significantly raised at $w = 20$ g/mol from the pure gas effect. As the pressure is increased to 101 and 202 kPa, there is a significant attenuation of the effect. Therefore, it is clear that the higher order linear term in $P$ found in Eq. 1 makes a net negative contribution to $\mu_{gs}$ to reduce this value. As $P$ is increased, $\mu_{gs}$ decreases over the temperature range examined.

Figure 3 shows the argon-carbon C adsorption isotherms calculated from Eq. 4 and the appropriate virial coefficients, $B_{2s}$, $B_{3s}$, and $B_{2g}$. Note that over the pressure range, 0 to 2 bar, and temperature range, 300 to 400 K, the Ar-carbon C system is in the Henry's law region and first deviation from Henry's law so that higher virial coefficients are not needed.

An analogous treatment to the one outlined previously for Ar-carbon C was used to model similar Kr-carbon C and Xe-carbon C data. Virial coefficient equations were determined and $\mu_{gs}$ values found, over a range of temperature, pressure, and powder concentration. The basic trends are the same as noted previously

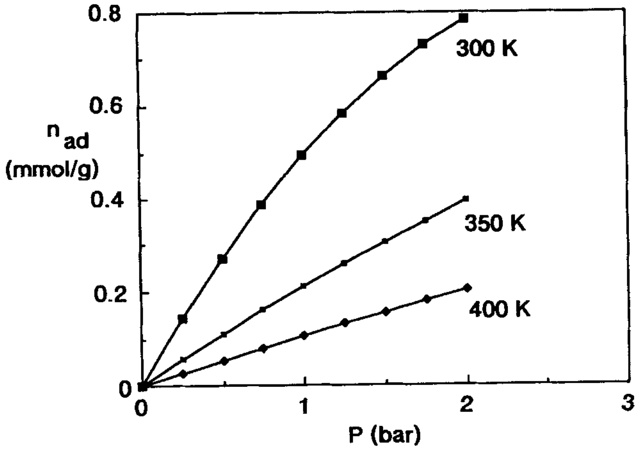

Figure 3. Calculated adsorption isotherms for argon-carbon C (Eq. 4).

for the argon. The pressure range for Kr was limited to 0.5 bar and for Xe was limited to 0.2 bar because, for these larger adatoms, the van der Waals attraction is greater and deviations from Henry's law become significant at lower pressures.

One must be cautious not to try to extend Eq. 1 to higher pressure regions than there are virial coefficients available to fit the adsorption behavior. It is necessary to be certain that the adsorption isotherm can be fit with the available virial coefficients over the pressure range of interest. To extend Eq. 1 to higher pressure $\mu_{gs}$ values, one must have available higher virial coefficients for higher pressure terms. Since this becomes more complicated at higher pressure, there are rather restrictive limits on how high a pressure can be modeled exactly.

From Eq. 3 for the pure gases, the values of $\mu_g$ (K/bar) at $T = 400$ K and $P = 0$ bar are $\mu_g(\mathrm{Ar}) = 0.21$, $\mu_g(\mathrm{Kr}) = 0.49$, and $\mu_g(\mathrm{Xe}) = 1.10$. As an example of the values obtained for these monatomic gas-carbon C systems, one may compare the following $\mu_{gs}$(K/bar) values at $T = 400$ K and $w = 10$ g/mol: for $P = 0$ bar, $\mu_{gs}(\mathrm{Ar}) = 0.77$, $\mu_{gs}(\mathrm{Kr}) = 3.55$, and $\mu_{gs}(\mathrm{Xe}) = 28.0$; for $P = 2$ bar, $\mu_{gs}(\mathrm{Ar}) = 0.69$; for $P = 0.5$ bar, $\mu_{gs}(\mathrm{Kr}) = 2.88$; and for $P = 0.2$ bar, $\mu_{gs}(\mathrm{Xe}) = 11.6$. In the zero pressure limit there is a significant predicted enhancement of the effect as one goes from Ar to Kr to Xe. However, the linear term in pressure causes an attenuation of the cooling effect in all cases and this attenuation occurs more rapidly as the gas-solid interaction energy is increased in going from Ar to Kr to Xe.

The results of this work make it clear that the extrapolation of the effect from the zero pressure limit to higher pressures is clearly not simply additive. As the pressure is increased, there is an attenuation of the cooling effect. Even with this attenuation, however, it appears that the addition of a high surface area powder can significantly enhance the Joule-Thomson cooling effect. To determine the application of this effect either in practical refrigeration devices as suggested by Pierotti and Rybolt (1982), or as a novel method to examine gas-solid interactions, will require the determination of extensive experimental values of the gas-solid Joule-Thomson effect for a variety of gas-solid aerosol systems.

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## Notation

$B_{2g}$ = second gas virial coefficient
$B_{2s}$ = second gas-solid virial coefficient
$B_{3g}$ = third gas virial coefficient
$B_{3s}$ = third gas-solid virial coefficient
$C_g$ = constant pressure heat capacity of 1 mol gas
$C_s$ = constant pressure heat capacity of 1 g solid
$C_{gs}$ = constant pressure gas-solid aerosol heat capacity for $w$ g solid dispersed in 1 mol gas
$K_1$ = Henry's constant in pressure series adsorption isotherm
$K_2$ = second constant in pressure series adsorption isotherm
$n_{ad}$ = mol gas adsorbed/g adsorbent
$P$ = pressure of adsorbate
$R$ = universal gas constant
$r$ = correlation coefficient
$T$ = absolute temperature
$w$ = powder concentration, g powder/mol gas

### *Greek letters*

$\mu_g$ = gas Joule-Thomson coefficient
$\mu_{gs}$ = gas-solid Joule-Thomson coefficient

### *Superscripts*

$^\circ$ = zero pressure-limiting value
$'$ = first derivative of temperature

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