The gas–solid Joule–Thomson Effect

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Abstract – The magnitude of interaction of a gas with a solid is expected to cause an aerosol created by dispersing a fine powder in a gas to have unique thermodynamic properties not found in pure or mixed gases. The virial equation of state associated with a gas-solid aerosol or dusty gas is obtained from statistical thermodynamic considerations. The theoretical model of the aerosol is that of a two component fluid made up of solid particles and gas molecules. The aerosol virial equation of state is used to derive an expression for the Joule-Thomson effect associated with a gas-solid dispersion. The magnitude of the gas-solid Joule-Thomson effect is expressed in terms of gas-gas and gas-solid virial coefficients. Previous adsorption data for an argon-porous carbon system is used to obtain gas-solid virial coefficients and to predict the magnitude of the gas-solid Joule-Thomson effect. A significant enhancement of the Joule-Thomson effect is predicted for gas-solid systems which display strong interactions. An apparatus was constructed to disperse a fine powder in a flowing gas and measure the thermal changes associated with a pressure drop across a glass orifice. The gas-solid Joule-Thomson effect was examined for 12 different gas-solid systems at a temperature of 302 K. Measurements for a series of aerosols composed of four different carbon adsorbents with argon, nitrogen and carbon dioxide confirm the effect and pose new questions.

INTRODUCTION

Over the years many theoretical and experimental studies of the Joule-Thomson effect have been carried out on a wide variety of pure and mixed gases. There has been no theoretical or experimental study of the Joule-Thomson effect associated with a gas-solid dispersion. In this paper a statistical thermodynamic theory of the Joule-Thomson effect for a two component fluid containing solid particles and gas molecules is presented. The Joule-Thomson coefficient associated with a gas-solid dispersion (aerosol) is expressed in terms of gas-gas and gas-solid virial coefficients, the heat capacity of the gas-solid mixture and the concentration of the solid component. A significant enhancement of the Joule-Thomson effect is predicted for those systems which display a favorable gas-solid interaction.

THEORY

General Conditions. In order to develop an expression for the Joule-Thomson coefficient of a gas-solid dispersion it is first useful to derive a virial equation of state for an aerosol (ref. 1). Statistical thermodynamic modeling of a gas-solid dispersion provides the best means of developing a proper virial equation of state. A correct statistical treatment will of necessity include the gas-gas interactions as manifest in deviations from gas ideality and the gas-solid interactions as manifest in physical adsorption.

Utilizing the ensemble method of Gibbs, a virial equation of state for a solid powder dispersed in a gas is derived. The treatment presented uses the grand partition function and is based on the following assumptions:

(a) The system of interest is a two component fluid phase composed of
     a molecular gaseous component and a particulate component. The
     solid particles are formally treated as giant molecules.
(b) The molecular component is an imperfect gas capable of inter-
     acting with the particulate component and itself through
     dispersion forces.
(c) The particulate component is dilute enough to exclude particle-
     particle interaction.

The grand partition function for a gas-solid mixture may be considered
analogous to the grand partition function of a two component imperfect gas
where the gaseous molecules of the second component are replaced by solid
particles. The appropriate grand partition function for the model above in
terms of canonical partition functions is given by (ref. 2)

$$\Xi\,(\lambda_g,\lambda_s,V,T)\;=\;\sum_{N_s>0}\;\;\sum_{N_g>0}\,Q_{N_g,N_{2s}}(V,T)\lambda_g^{N_g}\lambda_s^{N_s} \tag{1}$$

where λ_g is the absolute activity of the gas, λ_s is the absolute activity of
the particulate solid, N_g is the number of gas molecules, N_s is the number
of particles, and Q_{N_s,N_g} is the canonical partition N_s,N_g for N_s solid
particles and N_g gas molecules. As in the conventional statistical
treatment of fluids, it proves convenient to replace the canonical partition
functions with the appropriate configuration integrals. In addition, two
new activities, z_s activity of the particulate solid, and z_g activity of the
gas, are introduced. These activities become equivalent to their respective
number densities ρ_s number density of solid particles, and ρ_g number density
of gas molecules, in the limit as the densities go to zero.

The statistical thermodynamic treatment developed is applicable to any two
component fluids. This generalization is lost by assuming the particulate
component is very dilute. If the particulate component is dilute enough to
exclude particle-particle interaction then any system within the grand
ensemble contains either no particle or one particle. Thus, i is allowed
only values of zero or one. As in the treatment of an imperfect gas, there
is no restriction on the number of gas molecules within any system of the
ensemble. Following established procedures and utilizing the characteristic
function for the grand ensemble, $PV/RT = \ln \Xi$ and replacing Ξ, one may
expand the logarithm, divide by V, and group like powers of the z activities
and obtain

$$P/kT\;=\;z_s\;+\;\sum_{j>1}\;(b_{1j}z_s\,+\,b_{0j})z_s^{\,j} \tag{2}$$

where b_{ij} is a cluster integral, i is the number of solid particles, and j
is the number of gas molecules. The cluster integrals are related to the
configuration integrals for mixtures in the usual manner (ref 2).

Virial Equation for an Aerosol. To obtain a useful equation of state it is
necessary to express the preceding equation as a power series in the number
density of the gas, ρ_g and the number density of solid particles, ρ_s and
eliminate the use of the z activities. The number densities and activities
are related by

$$\rho_i\;=\;z_i[\partial(P/kT)/\partial z_i]_{\{z\},V,T} \tag{3}$$

Utilizing equations (2) and (3) yields after mathematical manipulation

$$P/kT\;=\;\rho_s\;+\;\sum_{j>1}\;C_j(T)\rho_g^{\,j} \tag{4}$$

where the C_j's are collections of cluster integrals (ref. 1).

To develop a statistical theory of the gas-solid Joule-Thomson effect it is
necessary to consider the influence of both gas-gas and gas-solid

interactions. Gas-solid interactions due to van der Waals forces give rise to physical adsorption. In physical adsorption the number of molecules adsorbed is defined as the excess number of molecules in a volume due to the interaction of gas molecules with the adsorbent (ref. 3). In the virial coefficient treatment of physical adsorption, the number of moles adsorbed per gram of adsorbent, n_a is given by

$$n_a = \sum_{i \geq 2} B_{is}(f/RT)^{i-1} \tag{5}$$

where f is the fugacity, R is the gas constant and B_{is} is the (i)th gas-solid virial coefficient (ref. 4). The interaction of a single gas molecule with a solid adsorbent is reflected in B_{2s}, the second gas-solid virial coefficient, while B_{3s}, the third gas-solid virial coefficient involves a pair of molecules interacting with the solid, B_{4s} involves a triplet of gas molecules, etc. It should be noted that the gas-solid virial coefficients are usually expressed in terms of per gram of solid.

Combining equations (6) and (7) and rearranging yields

$$PV/RT = 1 + \{(B_{2g} - wB_{2s})(P/RT)\} + O\{P^2\} \tag{6}$$

where $O\{P^2\}$ are terms of order of P^2 or greater and w is the mass of solid per mole of gas. Equation (8) is the virial equation of state for the gas-solid dispersion (aerosol) (ref. 1).

Gas-Solid Joule-Thomson Coefficient. The virial equation of state for an aerosol can be used to obtain the gas-solid Joule-Thomson coefficient since

$$\mu_{gs}C_P = T(\partial V/\partial T)_p - V \tag{7}$$

where C_P is the constant pressure molar heat capacity and µJT is the Joule-Thomson coefficient. Solving (8) for V and substituting the result into (9) gives

$$\mu_{gs}C_{gs} = \{(TB_{2g}' - B_{2g}) + w(B_{2s} - TB_{2s}')\} + O\{P\} \tag{8}$$

where C_{gs} is the constant pressure heat capacity for a gas-solid dispersion consisting of w grams of particulate solid in one mole of gas and where B_{2s}' is the temperature derivative of B_{2s} (ref. 1). The first term in brackets represents the limiting value of the gas-solid Joule-Thomson coefficient at zero pressure.

Calculations of the Joule-Thomson Effect. At this point, one may anticipate the possibility of greatly enhancing the Joule-Thomson effect of a gas by dispersing a fine powder into it. This effect is to be expected since the gas-solid interaction is typically much stronger than the gas-gas interaction. To explore this possibility specific numerical examples based on available data for an argon-powder systems are considered.

Cole and Everett (ref. 5) have reported experimental adsorption data for nitrogen and inert gases interacting with activated porous carbons. This data is in the temperature range of 275 to 400 K and pressure range up to 1 atm. Their reported Henry law constants as a function of temperature for the adsorption of argon by carbon C (a Saran carbon with a BET area of 1280 m^2/g) were used to obtain the values of B_{2s} which were found to be described by the following equation

$$B_{2s} = 0.0521 \exp(-1692/T) \tag{9}$$

Calculated values of B_{2s} based on (9) agreed with the experimental values within 0.1 to 0.5%. This equation was used to calculate B_{2s}'. The values of μ_{JT} calculated using equation (8) are shown in Fig. 1.

Data for adsorption of argon on a 5A-zeolite were determined by Yang and Pierotti (ref. 6) over a wide temperature range and the procedure used in treating the Cole and Everett data were followed. Adsorption data for argon

on P33 graphitic carbon determined by Sams, Constabaris and Halsey were used to include a low surface area powder (ref. 7). Values of μ_{JT} for these systems are shown in Fig. 1.

There are several comments worth making concerning Fig. 1. All calculations are based upon w equal to one gram of solid per liter of gas. The curve labelled Ar-Ar represents the Joule-Thomson coefficient for pure gaseous argon. The curve labelled Ar-P33 is the Joule-Thomson coefficient for argon interacting with a non-porous low surface area graphitic carbon and is based upon the data of Sams, Constabaris and Halsey. The curve labelled Ar-Porous C is based on the Cole and Everett data while the curve labelled Ar-5A is based upon the zeolite data of Yang and Pierotti. Clearly, the calculated effect indicates a major enhancement over the pure gas for the high surface area solids. The insert in Fig. 1 shows that for the non-porous graphite there is an attenuation in the Joule-Thomson effect at temperature above about 150 K. The attenuation is primarily a heat capacity effect. The substantial effect indicated that it would be worthwhile directly measuring gas-solid Joule-Thomson coefficients and accordingly an apparatus was designed and constructed to do this (ref. 8).
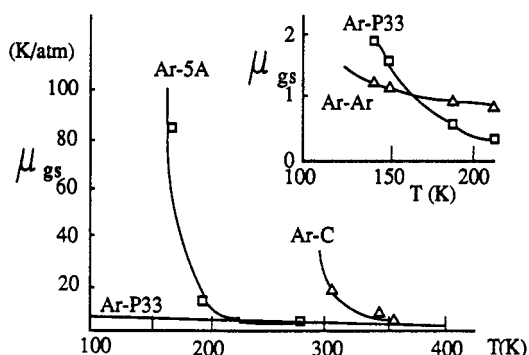

Fig. 1. Gas-solid Joule-Thomson Coefficients calculated for Argon interacting with charcoal (C), zeolite (5A) and graphite (P33).
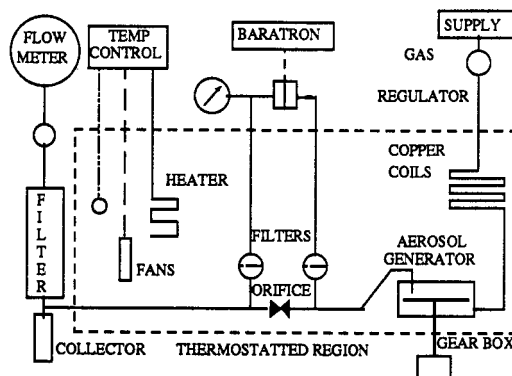

Fig. 2. Schematic diagram of apparatus for the measurement of gas-solid Joule-Thomson coefficients.

EXPERIMENTAL

Apparatus. A schema of the gas-solid Joule-Thomson apparatus is shown in Fig. 2. With this apparatus it is possible to disperse a fine powder into a gas stream, flow the resultant mixture through an orifice, measure the absolute pressure and temperature of the flowing aerosol, measure the pressure drop and temperature change across the orifice, filter out the solid powder, and determine the flow rate of the gas. The portion of the apparatus which required temperature control was placed inside a thermostated box. The aerosol generator consisted of a metal chamber containing a rotating powder container, retaining partition, and pickup valve. Powder was entrained and deagglomerated by gas passing upward through the multiple small diameter passages in the pickup valve.

The flow system was designed for the gas-solid mixture to flow through a glass constriction. A filter collected the particulate solid, and a wet test meter measured the flow rate of the gas. The gas passed through an inlet valve and was thermally equilibrated prior to entering the aerosol generator. The gas-solid mixture passed through a glass constriction tube (6 mm I.D. and 9.4 mm O.D. with a 1 mm I.D. orifice). Branches off the central tube were 10 cm before and after the constriction. Powder filters using medium porosity fritted glass disks were placed at each of these side tubes. The solid was separated from the gas by means of a filter and was weighed while the gas volume was measured with the wet test meter.

An MKS Baratron capacitance manometer was used to measure the pressure difference across the glass orifice. The high pressure and low pressure sides of the capacitance head were connected to the upstream and downstream filters, respectively. A Bourdon Gauge was used to measure the pressure downstream of the orifice relative to atmospheric pressure. Atmospheric pressure was determined with a mercury barometer.

Twelve copper-constantan thermocouples were used in these measurements. The main thermocouples of interest were placed in the middle of the glass flow tube 6.3 cm upstream and downstream of the orifice, respectively. Other thermocouples were placed throughout the apparatus to make sure that the interior of the thermostated box had reached thermal equilibrium.

Procedure. The gas and gas-solid Joule-Thomson data were taken in a temperature range of 298-303 K. The initial procedure which was used for a solid aerosol was the same as for a pure gas. After the gas flowed for about 15 minutes and the data were obtained for the pure gas, the aerosol generator was started. While a gas-powder mixture was flowing the measurements of ΔT, ΔP, T, and P were made. In addition, the average concentration of the aerosol was calculated from the mass of powder transported to the collector and moles of gas flowed through the flowmeter during the time interval the aerosol generator was operating.

Results. Experimental Joule-Thomson data were obtained for 12 gas-solid systems (ref. 9). The gaseous component was either argon, nitrogen, or carbon dioxide. The particulate component was either Mexican Graphite (MG), Nuchar S-C (SC), Nuchar S-A (SA), or Super Sorb (SS). Two sets of data were taken for each gas-solid system including values of ΔT, ΔP, P, and T. One set of data was obtained from measurements made when the aerosol generator was not operating and thus represents pure gas flow. The powders were selected to span a range of surface area and porosity. The nitrogen BET surface areas were 26, 903, 1661, and 3169 m^2/g for Mexican Graphite (MG), Nuchar S-C (SC), Nuchar S-A (SA), and Super Sorb (SS), respectively. Pore size distributions were determined. The pore volumes for pores in the 2 to 60 nm range were 0.118, 0.572, 0.925, and 0.797 cm^3/g for MG, SC, SA, and SS, respectively. The results of the measurements are given in Table I which includes values for μ_{JT} determined at 302 K and a loading (w) of 10 grams of solid per mole of gas. Gas-solid chromatography was used to determine values of B_{2s} between 265 and 325 K for each of these systems.

From gas-solid chromatography measurements (ref. 10) the temperature dependences of the second gas-solid virial coefficients were determined. As expected, it was found that ln B_{2s} versus 1/T was linear.

DISCUSSION

The effectiveness of the powders in producing a gas-solid Joule-Thomson cooling effect are in the order SS > SA >SC > MG. The effectiveness of the gases in producing a gas-solid Joule-Thomson cooling effect was in the order CO_2 > N_2 > Ar. Basically, these results correlate with the surface area of the powders and the expected strength of the gas-solid interaction. A direct comparison of the theoretical predictions and the experimental results found for the gas-solid Joule-Thomson effect requires an independent measurement of the second gas-solid virial coefficient and its temperature dependence for each of the twelve gas-solid systems which had been studied. Using the results from the gas-solid chromatography values were predicted and are included in Table I. A comparison of the values obtained from the gas-solid Joule-Thomson experiments (meas) and the values obtained from the gas-solid chromatography (pred) experiments reveals that the former values are always less than the latter values.

The apparent discrepancies between these two methods may be reconciled by considering the influence of the gas-solid interaction energy on the kinetics of desorption. The Joule-Thomson coefficient, as defined, is an equilibrium thermodynamic *property*. *In a Joule-Thomson experiment for a pure gas*, the flowing gas reaches equilibrium just beyond the orifice. Because the molecules are weakly interacting through the van der Waals forces, there is no significant barrier to prevent the rapid attainment of equilibrium. However, the gas-solid interaction energies are 10 to 20 times as strong as the pure gas interaction energies. For the gas-powder systems, especially the porous powders, there is an energetic barrier to the desorption process. Thus as the gas-solid aerosol flows past the downstream thermocouple, the equilibrium distribution of adsorbed and desorbed gas molecules may not have been attained. Therefore, the observed deltaT is smaller than the expected value based on equilibrium measurements such as those made with gas-solid chromatography.

Based on an Arrhenius type relation, the rate of desorption should be dependent on the exponential of the energy of activation of desorption. If the attenuation of the expected (GSC) Joule-Thomson coefficient is due to the time required for desorption in the actual gas-solid Joule-Thomson experiment, then the ratio of μ_{gs}(meas)/μ_{gs}(pred) should be related to the rate of desorption. The energy of activation for desorption can be approximated by the isosteric heat since the gas-solid systems are in the region of low coverage. Therefore, it is expected that the logarithms of μ_{gs}(meas)/μ_{gs} (pred) will be linearly proportional to the isosteric heats of gas-porous carbon systems. Figure 3 shows the suggested linear relation. An additional consideration is that higher order virial coefficients may be required to correctly predict values of μ_{gs}'s even at these temperatures and coverages.
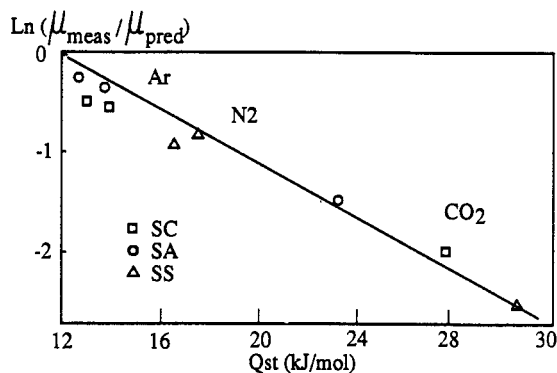

Fig. 3. Ratio of measured to predicted gas-solid Joule-Thomson coefficients as related to the isosteric heat of adsorption.

Table I. Joule-Thomson Coefficients at 302 K and 10 grams of solid per mole of gas. (units are deg/atm)

Gas-Solid	Measured	Predicted
Ar-MG	-0.05	0.28
-SA	0.88	1.01
-SS	1.15	1.65
N2-MG	0.03	0.18
-SA	0.64	0.81
-SS	0.93	1.42
CO2-MG	0.84	0.96
-SA	3.27	18.8
-SS	5.14	19.8

CONCLUSION

It is clear from the preliminary theoretical and experimental results presented that the gas-solid Joule-Thomson effect is one worthy of further exploration. The effect appears to be sufficiently large that measurements of gas-solid Joule-Thomson coefficients could provide information about the nature of the interaction potential between gases and solids in addition to possibly having a practical value in thermodynamic cycles for heat engines and other thermodynamic devices (ref. 11). There can be no doubt that gas-solid aerosols can be viewed as fluids having very interesting and unique thermal properties. The discrepancies between the predicted and measured values and the clear trend associated with those discrepancies are areas for further study and investigation.

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