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New experimental method for the determination of single-component isotherms: an application of the flow-rate retention time

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Abstract In this paper, we investigate adsorption of a single component (refrigerant) from the variation in the flow rate leaving the column. This requires evaluation of the flow-rate retention time—a measure of the net change in the amount adsorbed in the column, which can be positive or negative. The arrangement includes a system to deliver a fixed flow (30 mL/min) of helium through a column packed with 0.05 g of adsorbent. An experiment is initiated by adding a flow of refrigerant to the helium, and monitoring the outlet flow rate from the column. There are two main advantages of this approach: the experimental times are short (the order of 10 minutes) and the sensitivity is very high so that it can be used with very small as well as large amounts of adsorbent. Indeed, a sensitivity analysis suggests that the resolution is of the order of 10^{-5} g. The first results section considers the corrections required to the measured flow-rate retention time—these are small and determined by empty volume in the system. The second results section involves a determination of the adsorption isotherm of HFC-134A on an activated carbon at 35 °C up to a partial pressure of 0.25 bar.

Keywords Adsorption · Activated carbon · HFC-134A · Isotherm · Flow rate

1 Introduction

The importance of adsorption as a separation process is well established (Ruthven 1984). This has become more significant in recent years because of the synthesis of new adsorbents—as well as structure and chemical composition, the properties of an adsorbent can be changed by surface modification. Furthermore, another reason is the increasing applications for purification processes. A purification process is defined as the removal of a single component capable of adsorption from a non-adsorbed main flow: typically, this component is present at a composition of less than 5%. In order to select a suitable adsorbent and design a process, the adsorption isotherm for the particular adsorbent must be known. There are many traditional and established experimental methods in which the adsorption isotherm can be determined, and these are discussed and compared in a recent review by Sircar (2007). For the sake of this work, we are only concerned with pure-gas or single-component isotherms.

The experimental methods are conveniently divided into two categories: static (in which a fixed amount of gas is allowed to equilibrate with an adsorbent) and flow (in which a continuous stream of the gas flows across the adsorbent). The static category includes the gravimetric method: the weight of an adsorbent sample is measured before and after adsorption with a very sensitive balance. A recent application of the gravimetric method is the adsorption of methane on activated carbon fibres (Shao et al. 2007). Also classified under the static category is the volumetric method. From the initial and final gas pressures in the system and a suitable equation-of-state, a material balance enables the amount adsorbed to be determined. A recent application of the volumetric method is the adsorption of carbon-dioxide on various coals (Mazumder et al. 2006). The two main disadvan-

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tages with the static methods are that there is no control over the final equilibrium state and that the equilibration times can be significant. However, combination of the two methods to form a gravimetric–volumetric method could be classified as a gold standard of adsorption measurement since it involves both mass and molar measurements.

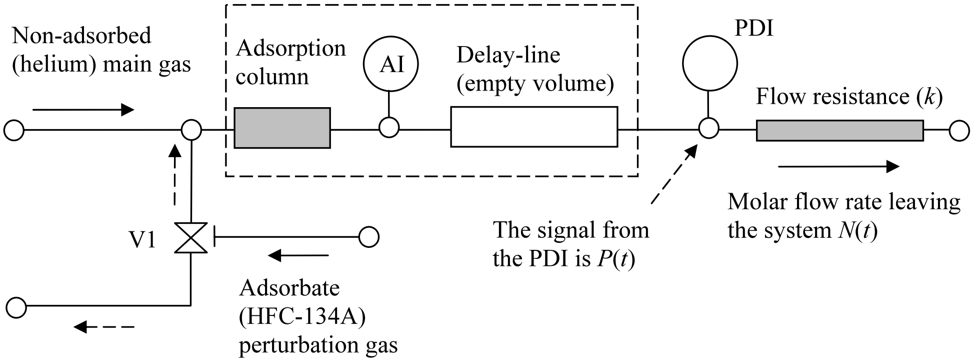
The advantage of the flow category is that the pressure and composition of the gas can be specified and maintained constant for the duration of the experiment. This tends to ensure that the experimental time is minimised, although the amount of gas required will be greater and this may have implications for situations where the feed is valuable. For the zero length column (ZLC) method, the flow to an adsorption column is a mixture consisting of a non-adsorbed gas (usually helium) and the component of interest (present at a low mole fraction, say 0.02). Then, at time zero, the flow to the column is switched to pure helium (at the same total flow rate). The concentration of the component in the outlet gas (c) is monitored until it reaches zero. If the flow rate is low enough, the Peclet number tends to infinity, and the variation of c with time depends *only* on the equilibrium isotherm and is *independent* of the kinetics. One advantage of this approach is that it allows determination of the complete isotherm at low concentration ranges from only one experiment. Brandani et al. (2003) have validated this method for the isotherms of carbon-dioxide on a range of zeolitic adsorbents. For the frequency response (FR) method (Sward and LeVan 2003), a single-component isotherm can be determined using only the component of interest (with no need for a non-adsorbed component). The molar flow rate into the column is maintained constant. Then, a sinusoidal variation is imposed on the column pressure and this leads to a similar variation in the outlet flow rate from the column. For *very low-frequency* variation, the outlet flow rate becomes independent of the kinetics and the variation in outlet flow rate can be used to determine the slope of the isotherm. The procedure is then repeated at a range of column pressures, and the corresponding slopes integrated to construct an isotherm.

The experimental approach of the group of Buffham and Mason at Loughborough has been to determine binary adsorption isotherms by monitoring the flow-rate changes as well as the composition changes that occur when a small perturbation flow is added to a main gas flowing through a column packed with an adsorbent (Mason and Buffham 1996a). This involves the definition of a *flow-rate retention time* (analogous to the standard chromatographic retention time) which can be positive or negative: the latter corresponds to a situation when the perturbation flow causes net desorption. Later papers followed showing how for a column with a reasonable pressure drop, it is necessary to take account of the pressure changes (Mason and Buffham 1996b) and the viscosity changes that occurs in the column (Mason et al. 1997). In order to determine *single-component* isotherms, it is simply necessary to ensure that one of the components is non-adsorbed (for example, helium).

The work presented in this paper is different from previous investigations in four ways.

1. For the method of Sward and LeVan (2003), the input to the column is a constant flow of the *adsorbate only* at a particular pressure. An experiment is carried out by imposing a very low-frequency sinusoidal variation on the column pressure (with an amplitude of about 1%), which causes a sinusoidal variation in the outlet flow rate. The *isotherm slope* is then determined from analysis of this flow rate variation. For this paper, however, the initial feed to the adsorption column is the non-adsorbed component (helium). An experiment is carried out by adding a particular perturbation flow of the adsorbate, and the column material balance gives the *isotherm chord*. Sward and LeVan (2003) investigated the adsorption of carbon-dioxide on BPL activated carbon, with an adsorbent mass of about 5 g and a cycle time of the order of a few hours. In this work, we have used an adsorbent mass of 0.05 g and experimental times of the order of a few minutes.
2. In order to obtain a critical assessment of the method presented in this paper, it is necessary to carry out a *detailed* investigation of the flow-rate retention time. The results would suggest that the presence of volume in the system gives a contribution to the measured flow-rate retention time. This will be achieved by repeating the experiment in two modified arrangements: firstly without the adsorption column and then without the delay-lines.
3. The second point is significant, because the intention is for the new theory to determine the isotherm from measurements in flow rate only—with the intention of avoiding use of a composition detector. The key question is whether we are able to determine a single-component isotherm by flow rate measurements alone and without the use of a device to measure composition such as a thermal conductivity detector (TCD).
4. The work presented in this paper is distinctive from the traditional approach at Loughborough, which has been to use *small* perturbation flows and *vary* the composition of the main flow. The experimental method in this work involves adding large perturbation flows to a non-adsorbed carrier gas, rather than adding 1% perturbation flows to a carrier gas of varying compositions. This concept was first considered by Brandini (2005), who measured the concentration of the adsorbed component in the outlet flow and used this to estimate the variation in the outlet flow rate. The work presented here is also distinctive from the approach at Loughborough in that it considers the effect of a non-ideal gas phase: the compressibility (Z) will not be exactly equal to unity, but will vary with the composition of the binary mixture.

Fig. 1 Schematic of experimental arrangement used for adsorption experiments



2 Theory

2.1 Determination of molar flow rate from pressure measurement

In the next section we will describe the determination of the molar flow rate of a gas mixture leaving an adsorption column. Here we show how this can be obtained simply from a pressure measurement. Consider the schematic experimental arrangement shown in Fig. 1. At this stage, we are only concerned with the molar flow rate *leaving* the system through the flow resistance: this has the symbol $N(t)$. Assuming that the flow regime is *laminar*, the pressure drop across the resistance is given by the Hagen-Poiseuille equation:

$$P^2(t) - P_{\mathrm{atm}}^2 = k\mu NRT, \tag{1}$$

where k is a tubing constant, related to the length and internal diameter, and μ is the viscosity. In general, k is large for a long pipe of small bore. Indeed, the value of k is very sensitive to the bore of the tube. We note that in general the viscosity *cannot* be considered constant since viscosity for a binary system is a function of composition.

If we assume that the atmospheric pressure (P_{atm}) and viscosity remain *constant*, we can differentiate (1) to obtain

$$\frac{\mathrm{d}P}{\mathrm{d}N} = \frac{k\mu RT}{(P_{\mathrm{atm}}^2 + k\mu NRT)^{0.5}}. \tag{2}$$

Obviously, the value of P will increase with flow rate (N). However, we require that the gradient in (2) should be constant over a large range in N. It can be shown that for a flow-resistance with a small pressure drop (low value of k), the second term in the denominator becomes insignificant compared to the first term: this should ensure that the gradient can be taken as a constant. For example, for a flow resistance with a pressure drop of 0.01 bar—which is a typical value for our experimental arrangements—the value of the derivative in (2) changes by 0.1% if the value of N changes by 10%. Obviously, the arrangement can be made more sensitive to changes in flow rate by increasing the value of k, although at the expense of detector linearity. This means that we can state confidently that

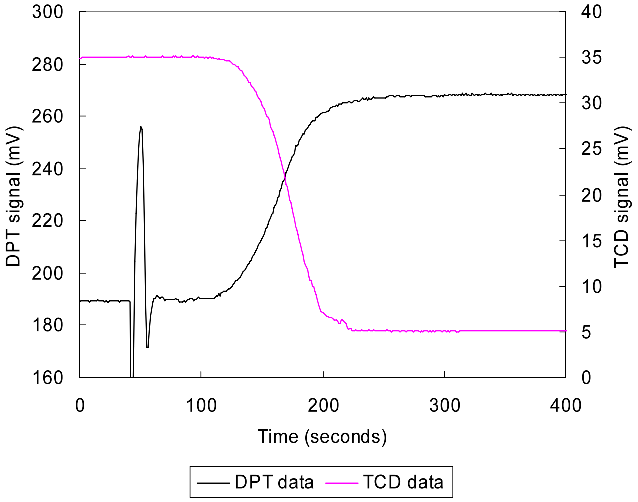


Fig. 2 Record for Experiment 1. This involved adding an HFC-134A flow rate of 0.74 mL/min to a helium carrier flow of 30 mL/min with an adsorbent mass of 0.05 g

$$P(t) \propto N(t). \tag{3}$$

As we shall see later, the calibration constant in (3) is not required for the determination of the adsorption isotherms. We are reminded that the above sequence ending with (3) involved a requirement that the viscosity of gas in the *flow resistance* (for measurement of P) should remain *constant* during the experiment. This is achieved in practical terms by placing a long length of tubing (termed a delay line) between the adsorption column and the flow resistance. In effect, for the whole duration of the experiment (consider, for example, the records in Fig. 2), the gas in the flow resistance is helium only.

2.2 Material balance on column and determination of isotherm

We now consider Fig. 1 in more detail. It is schematic because the actual experimental arrangement is twin-sided, similar to a gas chromatograph, with matched delay-lines and measurement resistances, and a differential pressure transducer (DPT) with differential inputs. The theory is based on a material balance over the system:

input = output + accumulation.

Note that the system is the experimental arrangement surrounded by the dashed line and necessarily includes the delay lines.

Initially (at time t less than zero), the system is at steady-state with the non-adsorbed component (helium) throughout. The steady-state is confirmed by the two detector signals being constant. The molar flow rate *entering* the system ($M(0)$) is equal to that *leaving* the system ($N(0)$). Then at time zero, some change is made to the system such that the hold-up (H) is changed. Eventually, the system reaches a new steady-state, and the change in hold-up (ΔH) is represented by:

$$\Delta H = \int_0^\infty (M(t) - N(t))\mathrm{d}t. \tag{4}$$

The use of the limit infinity should not be taken literally: it simply means the time taken to reach the new steady-state, and is typically the order of minutes.

For this investigation, the state of the system is changed by adding a small and *constant* molar flow ($m = n(\infty)$) of the *adsorbed component* at time zero. It is found convenient to represent the variation in molar flow rate leaving the system by the perturbation variable $n(t)$, and the material balance can be re-written as

$$\Delta H = \int_0^\infty [(M(0) + n(\infty)) - (N(0) + n(t))]\mathrm{d}t. \tag{5}$$

Initially, since the system is at steady-state, the values of $M(0)$ and $N(0)$ are equal and so:

$$\Delta H = \int_0^\infty (n(\infty) - n(t))\mathrm{d}t. \tag{6}$$

Note here that the change in hold-up for the experiment includes the adsorbed phase, the space within the column, and all the other empty space between the position at which the perturbation is added and the position at which the flow rate is measured. If we consider that the addition of the perturbation changes the *total* gas concentration in the column by Δc_{T} and the adsorbed-phase concentration by Δq_{T} we can state that

$$\Delta H = (V_{\mathrm{delay}} + V_{\mathrm{void}})\Delta c_{\mathrm{T}} + W\Delta q_{\mathrm{T}}, \tag{7}$$

where V_{delay} is the volume of the delay-lines, V_{void} is the voidage in the column and W is the mass of the adsorbent. At first impression, it might appear that the Δc_{T} term should be zero since we are only adding a small flow to a larger flow at supposedly constant pressure. However, as we shall see, this term will turn out to have a finite value.

We remember that the experiment consists of adding a small flow of the adsorbed component to a large flow of the non-adsorbed component. For convenience we assign component A as the adsorbed component. We are interested in developing an expression for the change in gas-phase concentration of component A since we will then divide this into (7) to obtain a point on the isotherm. The gas-phase concentration of component A is written as

$$c_{\mathrm{A}} = c_{\mathrm{T}} y_{\mathrm{A}} \tag{8}$$

from which we can write the change in concentration (Δc_{A}) for a *finite* change to the system

$$\Delta c_{\mathrm{A}} = c_{\mathrm{T}}\Delta y_{\mathrm{A}} + y_{\mathrm{A}}\Delta c_{\mathrm{T}} + \Delta y_{\mathrm{A}}\Delta c_{\mathrm{T}}. \tag{9}$$

In our case, we start with a non-adsorbed main flow so that y_{A} is equal to zero. From a simple material balance at the point of mixing, the change in mole fraction (Δy_{A}) can be written as

$$\begin{aligned} &(m \times 1) + (M \times 0) = (M + m)\Delta y_{\mathrm{A}} \\ &\quad \to \Delta y_{\mathrm{A}} = \frac{m}{M + m}. \end{aligned} \tag{10}$$

Equations (7), (9) and (10) are then combined to give:

$$\begin{aligned} &\left[(V_{\mathrm{delay}} + V_{\mathrm{void}})\frac{\Delta c_{\mathrm{T}}}{\Delta c_{\mathrm{A}}}\right] + W\frac{\Delta q_{\mathrm{A}}}{\Delta c_{\mathrm{A}}} \\ &\quad = \frac{M + m}{c_{\mathrm{T}} + \Delta c_{\mathrm{T}}}\int_0^\infty \frac{n(\infty) - n(t)}{n(\infty) - n(0)}\mathrm{d}t. \end{aligned} \tag{11}$$

The integral is termed the *flow-rate retention time*, and the formal definition is

$$t_n = \int_0^\infty \frac{n(\infty) - n(t)}{n(\infty) - n(0)}\mathrm{d}t \tag{12}$$

From the findings of (3), the pressure (P) is proportional to the molar flow rate passing through the resistance. This gives an alternative (and useful) definition for t_n:

$$t_n = \int_0^\infty \frac{p(\infty) - p(t)}{p(\infty) - p(0)}\mathrm{d}t \to p(t) = P(t) - P(0), \tag{13}$$

where p is the deviation from the initial value, analogous to n.

This is important, because the value of the flow-rate retention time can be obtained from measuring an area in the flow rate record and dividing by the offset.

We now return to the subject of the gas-phase concentration. The multiplier for t_n is the molar flow rate of the mixture divided by the gas-phase concentration in the column. This is simply the volumetric flow rate through the column *after the perturbation flow has been added*, which gives:

$$\left[(V_{\text{delay}}+V_{\text{void}})\frac{\Delta c_{\text{T}}}{\Delta c_{\text{A}}}\right]+W\frac{\Delta q_{\text{A}}}{\Delta c_{\text{A}}}=Q_{\text{sys}}t_n. \tag{14}$$

The term in square brackets is the correction term that needs to be evaluated. Obviously, the value of this term will be minimised if the volume is reduced and the change in gas concentration (Δc_{T}) is as small as possible. For practical reasons, the value of this term should not be excessive: the longer the delay line, the longer the experimental time. Importantly, (14) is valid for both small and large perturbation flows. Note that the use of "Δ" rather than "d" is to represent the *chord* of the isotherm rather than the gradient. Note also that any heat of adsorption effects will not affect the solution of the integral to determine t_n; the inference is that the column temperature is able to return to the starting value of 35 °C *before* the integration is complete. This is one of the reasons for the delay line. Note finally that assuming the new steady-state is achieved after adding the perturbation flow—that is, the plateau at $n(\infty)$ is *properly attained*—then the integral to determine t_n should be independent of the mass transfer effects.

2.3 Correction due to empty volume in system

We now consider evaluation of the correction term in more detail. This involves the possibility of non-ideality in the gas phase, and is best achieved using the compressibility (Z). The equation-of-state for a real gas is

$$P_{\text{sys}}=c_{\text{T}}RTZ. \tag{15}$$

The value of c_{T} can be changed in two ways. The more recognisable way is by increasing the system pressure. We note that the pressure downstream of the flow resistance is fixed, and so the increase in total flow rate caused by adding the perturbation flow will necessarily increase the system pressure. The other way is by changing the compressibility of the mixture. The change in the total gas concentration is then given by

$$\Delta c_{\text{T}}=\frac{\Delta n}{V}=\frac{1}{RTZ}\left[\Delta P_{\text{sys}}-P_{\text{sys}}\frac{\Delta Z}{Z}\right] \tag{16}$$

For pure helium, the value of Z can be taken to be exactly 1. The value of Z for HFC-134A at ambient pressure and temperature is 0.985. There are two approaches to working out the value of Z for a mixture. The "worst case" (likely to give the larger value of ΔZ) scenario is Amagats law in which there is no volume of mixing. In this case, the value of Z for the mixture is determined from a weighted function of the pure-component values according to the mole fractions. The other case (Daltons law) requires that Z values are used at the *partial-pressures* of the mixture, for which the value of Z for HFC-134A would be much closer to unity. Information on helium–HFC-134A mixtures is not available in the literature and so will form part of the error analysis.

For the correction term, we also require the value of c_{A}. This is given in (9) and is shown here in a more convenient form

$$\Delta c_{\text{A}}=\frac{m}{M+m}(c_{\text{T}}+\Delta c_{\text{T}}). \tag{17}$$

Equations (16) and (17) can be substituted into the correction term shown in square brackets in (14). The form of (14) would suggest that the correction term can also be written as the product of Q_{sys} multiplied by a correction to the retention time (t_{corr}).

$$t_{\text{corr}}=\left[\frac{V_{\text{delay}}+V_{\text{void}}}{Q_{\text{sys}}}\right]\left[\frac{\Delta P_{\text{sys}}}{P_{\text{sys}}}-\frac{\Delta Z}{Z}\right]\frac{M+m}{m}. \tag{18}$$

We now make the approximation that the molar flow rate is proportional to the pressure drop across the resistance:

$$M\propto(P_{\text{sys}}-P_{\text{at}}),\qquad m\propto\Delta P_{\text{sys}}.$$

These give a working form which will allow the two parts to the correction to be evaluated.

$$t_{\text{corr}}=\left[\frac{V_{\text{delay}}+V_{\text{void}}}{Q_{\text{sys}}}\right]\left[\frac{P_{\text{sys}}-P_{\text{at}}}{P_{\text{sys}}}-\frac{\Delta Z}{Z}\frac{M+m}{m}\right]. \tag{19}$$

At its simplest—when dealing with ideal systems—the value of ΔZ is zero, and the value of t_{corr} is simply determined from the tubing volume, system pressure and pressure drop across the flow resistance (typically of the order of millibar). For the case when ΔZ is finite (as it will be in this investigation), the value of ΔZ might be expected to increase with the perturbation flow (value of m). This will be covered in point 2 of the Discussion.

3 Experimental arrangement and procedure

We now refer to the experimental arrangement shown in Fig. 1. The helium carrier flow is set by a fixed pressure drop across a fixed resistance. The pressure drop is set using two Porter back-pressure regulators (BPR: type 9000). The helium flow into the apparatus is set using a Porter pressure regulator (PR: type 8286) and a Porter mass-flow controller (MFC: type VCD-1000), and any excess gas vented through the upstream BPR. The actual system was arranged in a twin-sided mode, but for convenience it is shown as single-sided in Fig. 1. The controls were adjusted to give a flow through each side of the system of 30 mL/min measured at the ambient conditions for the day (20 °C and 765 mbar). The adsorbent is 607C activated carbon supplied by Sutcliffe Speakman. This was supplied as granules and ground down to a size fraction of 250 to 500 µm. Approximately 0.05 g was placed into a short length of ¼-inch stainless-steel tubing to act as a column. The outlet flow from the adsorption column then passes through a Shimadzu GC-8A oven with a thermal conductivity detector (TCD): this is shown as a composition indicator (AI) in Fig. 1. The flow leaving the TCD then passes through a 15-m length of nylon tubing with an outside diameter of ¼-inch and an internal diameter of 4 mm giving a volume of about 189 mL. Finally, the flow leaving the delay line passes through the flow resistance: this is actually a Nupro ½-micron filter which gives a pressure drop of about 5 mbar.

A Porter MFC is used to deliver a range of flow rates of adsorbate (refrigerant HFC-134A) from 0.3 mL/min up to around 10 mL/min. The essential requirement is that the perturbation flow should remain *constant* for the duration of the experiment. The perturbation flow is added to the main flow using a Whitey 3-port valve. The experimental data is measured using a differential pressure transducer (DPT: type FCO332) supplied by Furness Controls with a pressure range of ±100 Pa corresponding to ±1000 mV: this is shown as a pressure indicator (PDI). The experimental data is recorded using a Pico ADC-16 (16 bit) data acquisition system. The choice of experimental temperature deserves special mention. We were not able to use the heating facility in the oven, and so we had to rely on the heat generated by the high-speed oven fan (which could not be switched off). This gave a steady-state temperature of 35 °C.

The experimental results are conveniently divided into two sections. The first section is an investigation of the correction factor to the measured flow rate retention time. This was achieved by carrying out *three* experiments, for each of which the perturbation flow was fixed. In the first, a perturbation flow of 0.6 mL/min was used with the actual experimental arrangement shown in Fig. 1. After completion, the adsorption column was removed from the system and replaced with connecting tubing, and the second experiment was initiated by adding the same perturbation flow. Finally, the delay line was removed (removing most of the empty volume in the system) and replaced with connecting tubing, and the third experiment involved the same perturbation flow. The second section is a determination of the isotherm for HFC-134A on 607C activated carbon at 35 °C. This involved a number of experiments. The main flow was helium, and each experiment involved progressively larger perturbation flows (ranging from 0.3% to 30%).

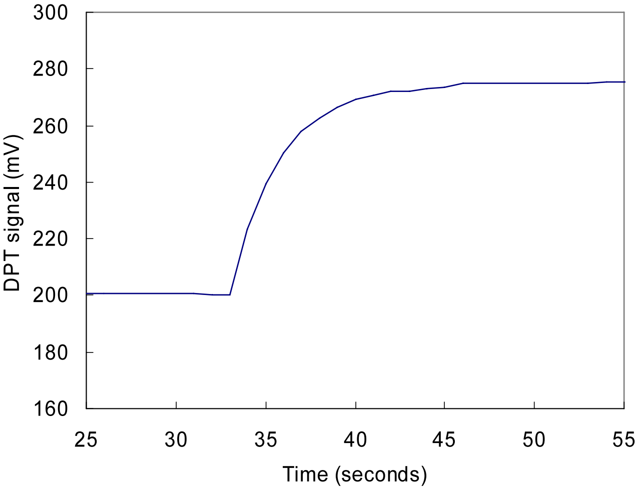


Fig. 3 Record for Experiment 2. This involved adding an HFC-134A flow rate of 0.74 mL/min to a helium carrier flow of 30 mL/min *without* the adsorbent

4 Results

4.1 Effect of empty volume in system and correction to retention time

Figure 2 shows the recorded data obtained for the first experiment. It can be seen that there are two traces. The conventional one (represented by the secondary-axis) is that obtained from the composition (TCD) detector. The TCD information was not processed in this work, but is included as an indication of how the flow rate and composition changes are related. The initial TCD baseline is around 35 mV, and the composition change caused the baseline to move to around 5 mV. The DPT signal tells us that the HFC-134A perturbation flow was added at a time of around 42 seconds. The initial downward spike was caused by the experimental arrangement, for which switching the valve causes a temporary interruption in the carrier flow and adds a small pulse of gas as well. It can be seen that the final baseline is achieved well within 400 seconds. The flow-rate retention time (t_n) was calculated according to the integral in (13) by determining the area between the $p(\infty)$ level and the signal starting at 42 seconds and running to 400 seconds. From Fig. 2, the $n(0)$ level is at 189.4 mV and the $n(\infty)$ level is at 267.9 mV. The integration is carried out using the trapezoidal rule and gives an area of 9510 mVs. The change in baseline is 79.2 mV, and these values are used in (13) to obtain a flow-rate retention time (t_n) of 120.1 s.

Figure 3 shows the experimental data for the second experiment, obtained without the adsorption column. As can be seen, the perturbation flow was added at a time of 33 seconds, and the new steady-state achieved by a time of 50 seconds. This is certainly a faster response without the adsorption column, but the response is far from instantaneous—it is

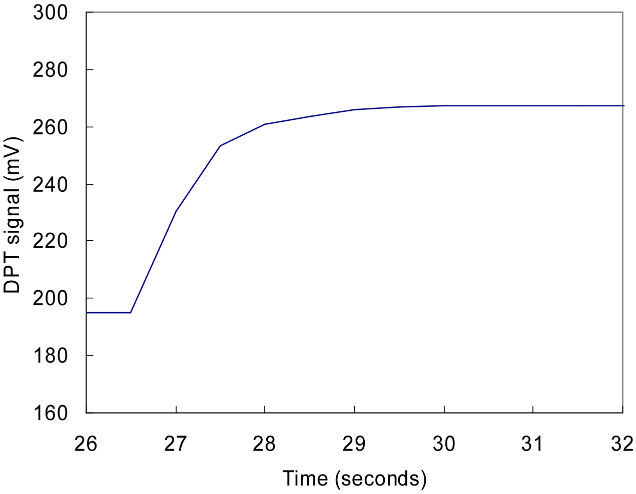


Fig. 4 Record for Experiment 3. This involved adding an HFC-134A flow rate of 0.74 mL/min to a helium carrier flow of 30 mL/min *without* the adsorbent and *without* the delay-line

certainly not a vertical step. The initial baseline is 200.0 mV and the final baseline is 275.1 mV, which means that the perturbation flow rate is slightly lower than for the first experiment. The area according to the integral in (13) is 265 mVs and the baseline shift is 75.1 mV so that the value of t_n is 3.5 seconds. The flow record appears slightly jagged because of the sampling rate. In any case, the important finding from this graph is that there is still a finite area, despite the absence of the adsorption column.

Figure 4 shows the experimental data obtained without either the adsorption column or the long nylon delay line. This time it can be seen that the response is even faster: the valve is switched at a time of 26.5 seconds and the new steady-state is achieved by 33 seconds. The initial baseline is around 195.0 mV and the final baseline is 267.2 mV meaning that the perturbation flow rate is slightly lower than for Fig. 3. This is because over a long time spell it is difficult to maintain a constant perturbation flow rate. The area in the DPT record is estimated to be 67.0 mVs, and this gives a t_n value of 0.9 seconds.

It is appropriate now to check the derivation for the correction to the measured retention time, shown as (19). We consider the difference in measured t_n values between Experiment 2 (Fig. 3) and Experiment 3 (Fig. 4). The delay-line volume is 189 mL, assuming an internal diameter of 4 mm. We note also that the carrier flow rate is 30 mL/min measured at ambient conditions, whereas Q_{sys} in the volumetric flow rate measured at column conditions (where the temperature and pressure are 35 °C and 1050 mbar). Finally, the pressure in the column was measured to be 1.05 bar (using a barometer and pressure gauge). The two volumetric flow rates are related by

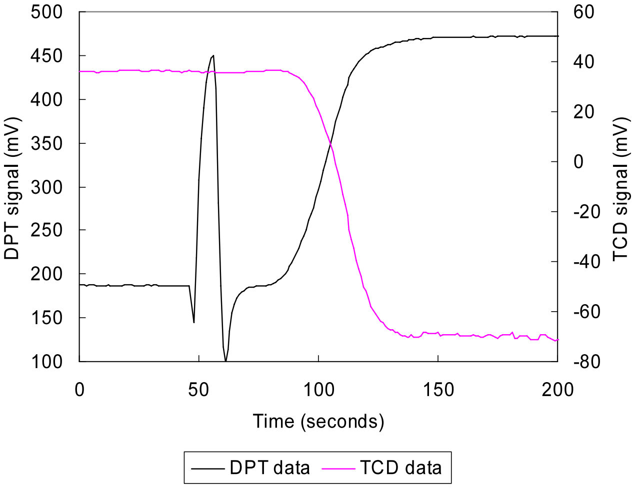


Fig. 5 Record for Experiment 8. This involved adding an HFC-134A flow rate of 2.69 mL/min to a helium carrier flow of 30 mL/min with an adsorbent mass of 0.05 g

$$Q_{\mathrm{sys}} = Q_{\mathrm{amb}} \frac{P_{\mathrm{atm}}}{P_{\mathrm{sys}}} \frac{T_{\mathrm{sys}}}{T_{\mathrm{atm}}}$$

$$\rightarrow Q_{\mathrm{sys}} = Q_{\mathrm{amb}} \times \frac{1000}{1050} \times \frac{308}{293} \rightarrow Q_{\mathrm{sys}} = 1.001 \times Q_{\mathrm{amb}}$$

which means the two values are virtually the same. The correction is then approximated as

$$t_{\mathrm{corr}} \approx \left[\frac{V_{\mathrm{delay}} + V_{\mathrm{void}}}{Q_{\mathrm{sys}}}\right] \frac{P_{\mathrm{sys}} - P_{\mathrm{atm}}}{P_{sys}}$$

$$\rightarrow t_{\mathrm{corr}} \approx \left[\frac{189}{30}\right] \times \frac{5}{1050} \times 60 = 1.8(\mathrm{s}),$$

where the factor of 60 is the conversion factor from minutes to seconds.

This compares well with the actual value of $3.5 - 0.9 = 2.6$ s, considering that this is only an approximation. At this stage, we have not considered the contribution of the ΔZ term, and this will be revisited in the Discussion.

4.2 Determination of HFC-134A isotherm using varying perturbation flows

The points on the isotherm were determined from eight experiments. The recorded experimental data for three of the eight experiments are shown in Figs. 2, 5 and 6. These correspond to increasing perturbation flows. For the first seven experiments, the helium carrier flow rate was maintained constant at 30 mL/min, and for the last case it was reduced in order to give a larger value of adsorbate partial pressures. Comparing Figs. 5 and 6 with Fig. 1, it can be seen that as the perturbation flow is *increased*, the experimental time

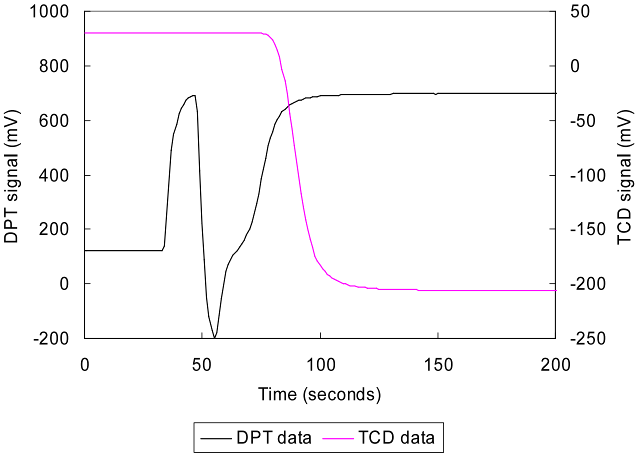


Fig. 6 Record for Experiment 10. This involved adding an HFC-134A flow rate of 5.4 mL/min to a helium carrier flow of 15 mL/min with an adsorbent mass of 0.05 g

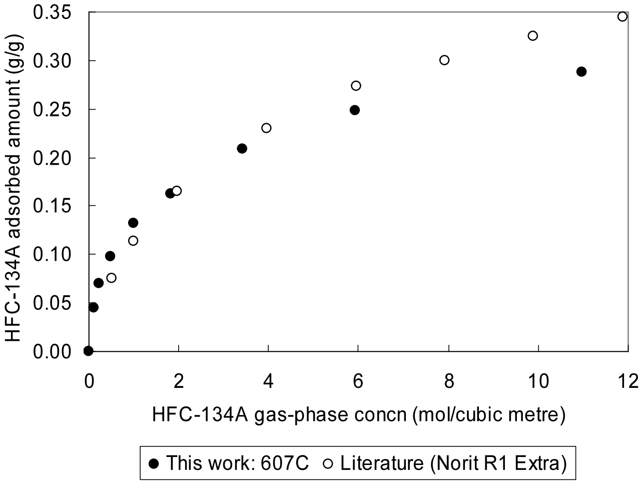


Fig. 7 Pure-component isotherm for HFC-134A on Sutcliffe-Speakman 607C activated carbon at 35 °C plotted with a literature investigation for a different carbon at 30 °C

is *reduced*. Note that we have only used the dark-coloured DPT experimental data; the light-coloured TCD data has not been used for the isotherm determination, but will be covered in the Discussion.

The calculations used to determine the isotherm points are summarised in Table 1. We can also measure the volumetric flow rate of the perturbation—also at ambient conditions—which will vary from about 0.1 mL/min to about 10 mL/min. It is important to know these values accurately in order to determine the mole fraction of the mixture (and the value of Δy_A). This is best achieved by measuring the *largest* perturbation volumetric flow rate, and then using the step-change in the flow-rate record—the difference between $n(0)$ and $n(\infty)$—to calculate the volumetric flow rate of the perturbation for the other experiments. This is more accurate than using a bubble-flow meter to measure trickle flows. The asterisk in two columns of Table 1 refers to volumetric flow rates measured at *ambient* conditions.

The reason for the strange numbering of experiments in Table 1 is that Experiments 2 and 3 correspond to the first section of results. The adsorption column and delay-line were then replaced before starting on Experiment 4 (with the lowest perturbation flow) and progressing to Experiment 9 (with the largest perturbation flow). The amounts adsorbed are calculated in the final column, and these results are shown graphically as Fig. 7.

5 Discussion

For convenience, this section is divided into six parts. The first part is a comparison with data from the literature, albeit on different activated carbon adsorbents. The second part is a consideration of the correction to the retention time (t_{corr}) in more detail. The third part is a sensitivity analysis, to determine what is the smallest change in adsorbed amount the apparatus is capable of detecting. The fourth part is an error analysis, which also goes on to consider how the experimental arrangement might be improved for further investigations. The fifth part considers how the experimental procedure might be adapted to deal with a higher range of adsorbate partial pressures. The final part is a consideration of the composition record of the flow leaving the adsorption column, and how this might compare with the flow rate record.

1. The calculated isotherm is shown in Fig. 7 along with an isotherm for HFC-134A on a different activated carbon at a slightly higher temperature (Heggs et al. 1995). The literature investigation was carried out using a gravimetric method. The isotherms are comparable, but there are notable differences. For the 607C activated carbon, the gradient in the Henry's law region is steeper, but the Norit carbon has a higher capacity. A similar investigation was carried out by Akkimaradi et al. (2001) but using a volumetric apparatus and three different activated charcoals (Fluka, Chemviron and Maxsorb). Comparisons are more difficult, because this work involved a much higher range of partial pressure (up to about 6 bar). For experiments comparable with our largest partial-pressure of HFC-134A, the following adsorbed amounts are reported at 40 °C: Chemviron [0.239 g/g at 53 mbar], Fluka [0.225 g/g at 52 mbar] and Maxsorb [0.627 g/g at 39 mbar]. Lin and Lin (1999) also determined the pure-component isotherms for HFC-134A on various activated carbon adsorbents, but at a much lower partial-pressure range (6 to 25 mbar).

2. The measured retention time (t_n) includes a contribution from the empty volume in the system. The approximate value of the correction to the measured retention time (t_{corr})

Table 1 Summary of calculations to determine isotherm

Expt	Q^*_{He}	m(mV)	Q^*_{Pert}	Q_{sys}	Δy_{A}	Δc_{A}(mol/m^3)	t_n(s)	t_{corr}(s)	Δq_{A}(g/g)
4	30	8.3	0.08	30.1	0.003	0.12	381	1.8	0.046
5	30	17.0	0.16	30.1	0.006	0.24	(275)	1.8	0.070
6	30	38.7	0.36	30.4	0.012	0.49	181	1.8	0.097
1	**30**	**79.2**	**0.74**	**30.8**	**0.024**	**0.98**	**120.1**	**1.8**	**0.132**
7	30	145.5	1.37	31.4	0.044	1.81	80.8	1.7	0.163
8	30	286.0	2.69	32.7	0.083	3.41	53.3	1.7	0.209
9	30	532.0	5.00	35.0	0.144	5.92	34.7	1.6	0.249
10	15	578.0	5.40	20.4	0.268	10.43	36.5	1.6	0.287

was calculated to be 1.8 s (compared to a measured value of 2.6 s). We now consider the contribution of the ΔZ term. The compressibility of a mixture (Z_{mix}) is determined from the Z values of the pure components and the respective mole fractions. Note that component A is the adsorbate (HFC-134A) and component B is the non-adsorbed gas (helium).

$$Z_{\mathrm{mix}} = Z_{\mathrm{A}} y_{\mathrm{A}} + Z_{\mathrm{B}}(1 - y_{\mathrm{A}}) \rightarrow \Delta Z = Z_{\mathrm{mix}} - Z_{\mathrm{B}}. \qquad (20)$$

The difference (ΔZ) is relative to Z_{B} since initially the system contains the non-adsorbed gas only.

It is convenient to make (19) more accessible. Combining (10), (19) and (20) we have:

$$t_{\mathrm{corr}} = \left[\frac{V_{\mathrm{delay}} + V_{\mathrm{void}}}{Q_{\mathrm{sys}}}\right]\left[\frac{P_{\mathrm{sys}} - P_{\mathrm{at}}}{P_{\mathrm{sys}}} - \frac{Z_{\mathrm{A}} - Z_{\mathrm{B}}}{Z_{\mathrm{B}}}\right]. \qquad (21)$$

There are two approaches to calculate the pure-component values of Z_{A} and Z_{B}: either at the partial pressures (Dalton's law of partial pressures) or at the total (system) pressure (Amagat's law of additive volumes). For each case, since helium can be considered a perfect gas, we can take the value of Z_{B} equal to 1. However, the value of Z_{A}(HFC-134A) is of particular interest. At ambient conditions, the value of Z_{A} is equal to 0.985. Substituting this value into (21) will give a time correction (t_{corr}) of about 8 seconds. If we consider the Dalton's law case, we require the value of Z_{A} at the *partial pressure* of the adsorbate (which will give a value much closer to 1) and which will vary with perturbation flow rate. For a 1% perturbation flow ($y_{\mathrm{A}} = 0.01$), the value of Z_{A} is estimated to be 0.999. Substituting this value into (21) will give a time correction (t_{corr}) of about 2.2 seconds—much closer to the experimental value. Furthermore, the thermodynamic literature would tend to suggest that the Dalton's law model should be used at system pressures below 50 bar—and this confirms the findings in the first section of the results.

3. We now consider the resolution of the experimental arrangement: that is, what is the smallest change in amount adsorbed that might be detected. Consider Experiment 1 in which the actual change in amount adsorbed is 5×10^{-5} mol and 5×10^{-3} g. This amount adsorbed corresponds to a DPT area in Fig. 2 of about 9000 mVs. The area in Fig. 2 can be measured to 0.1% and the change in baseline signal to 0.5%, in which case we should be able to detect a change in the amount adsorbed of 5×10^{-7} mol and 5×10^{-5} g. This DPT area is based on downstream resistances with a pressure drop of 5 mbar. Increasing this resistance by a factor of two will increase both the area in the DPT record and the change in baseline signal, and the implication is that this approach might allow the resolution to be improved to the order of 10^{-6} g. Interestingly, the resolution of this arrangement can be *increased* by *increasing* the amount of adsorbent. This is in stark contrast to conventional gravimetric arrangements where the resolution tends to decrease with a larger mass of adsorbent.

4. In order to carry out an error analysis, it is convenient to rearrange (14) so that we obtain Δq_{A} explicitly and arrange the other relevant equations on the same line:

$$\Delta q_{\mathrm{A}} = \Delta c_{\mathrm{A}} \frac{Q_{\mathrm{sys}}(t_n - t_{\mathrm{corr}})}{W}$$

$$\rightarrow \Delta c_{\mathrm{A}} = \Delta y_{\mathrm{A}}(c_{\mathrm{T}} + \Delta c_{\mathrm{T}})$$

$$\rightarrow t_{\mathrm{corr}} = \frac{V}{Q_{\mathrm{sys}}}\left[\frac{P_{\mathrm{sys}} - P_{\mathrm{atm}}}{P_{sys}} - \frac{Z_{\mathrm{A}} - Z_{\mathrm{B}}}{Z_{\mathrm{B}}}\right].$$

In order to determine overall confidence limits, it is a case of determining the confidence limits in each of three terms, and using the appropriate error combination rules.

The value of c_{T} is known very accurately from the absolute pressure and absolute temperature in the system. The value of Δc_{T} is very small compared with c_{T}. The change in mole fraction (Δy_{A}) requires the ratio of the helium to HFC-134A volumetric flow rates. This ratio is determined from measurements with a bubble flow meter, and by using the baseline change in the DPT record (since this is proportional to the perturbation flow rate): our confidence limits in the value of Δc_{A} are estimated to be ±0.5%. Likewise, the value of Q_{sys}—which is the total volumetric flow rate measured at ambient conditions—is measured with a bubble flow meter. A typical flow rate of 30 mL/min would take 50 seconds to pass through a volume of 25 mL, and would be known to ±0.5%. Finally, we consider the value of $(t_n - t_{\mathrm{corr}})$. The value of t_n is determined from an area and a change in baseline, and for our series of experiments this quantity varies from 40 up to 400 seconds. Any error in the value of t_n will be caused by baseline drift during the experiment and so will depend on the length of the experiment: a value of ± 0.1 mV is more than reasonable. The value of t_{corr} is typically 2 seconds. However, because of the doubt about which definition of Z_{A} to use, the value of t_{corr} is probably known to $\pm 10\%$ (that is ± 0.2 s). This implies that the error in the value of $(t_n - t_{\mathrm{corr}})$ varies from about $\pm 0.5\%$ for the low perturbation flows to $\pm 1\%$ for the larger perturbation flows. From the rules of error combination, the confidence limits in the values of Δq_{A} vary from $\pm 1\%$ to $\pm 1.5\%$.

5. For this work, in order to obtain the highest value of gas-phase concentration (Δc_{A}), the helium flow was reduced from 30 to 15 mL/min and the perturbation flow rate was increased to the maximum value of 5.4 mL/min. We now consider how the procedure might be adapted to give even higher values of Δc_{A}. It is first helpful to state (9) in a different form:

$$\Delta c_{\mathrm{A}} = \Delta y_{\mathrm{A}}(c_{\mathrm{T}} + \Delta c_{\mathrm{T}}).$$

For example, an increased perturbation flow of 15 mL/min would give a mole fraction of approximately 0.5 and an increased value of Δc_{A}. However, this increased value of Δc_{A} would also be obtained by adding 10 to 10 mL/min, or even 5 to 5 mL/min. Furthermore, an alternative approach to obtain this increased value of Δc_{A} would be to use a *lower* perturbation flow (reduced value of Δy_{A}) but at a *higher* value of system pressure (higher value of Δc_{T}). This apparent "dilemma" highlights the advantage of the perturbation approach to the determination of adsorption isotherms, where the *same* change in gas-phase concentration (Δc_{A}) can be obtained in a different number of ways. For a particular value of flow-measuring resistance (k), the change in DPT baseline for adding 10 to 10 mL/min would be greater than for adding 5 to 5 mL/min, and the experimental time would be greater for the second case. However, if the change in baseline is too great, then this will compromise the linearity of the detector given in (2), although this can be remedied by reducing the value of k; that is, by using a lower value of resistance. One advantage of the reduced experimental time is that there is less potential for drifting in the baseline.

6. In this work, there is little mention of the composition detector, although the TCD data is shown in Figs. 2, 5 and 6. According to the material balance, the amount adsorbed can *either* be obtained by monitoring the variation in flow rate from the column (as we have done in this work using the flow-rate retention time) or the standard composition detector (using the composition retention time). In fact, these retention times are similar for the smaller perturbation flows, although there are systematic (but not large) differences for the larger perturbation flows. This is likely to be because the composition detector signal will not vary linearly with composition over large step changes: there are very few binary systems for which the thermal conductivity varies linearly with composition.

6 Conclusions

We have shown that the adsorption of a single component (HFC-134A on an activated carbon) can be determined from the flow-rate changes that occur in the outlet of an adsorption column, avoiding the need for a composition detector. An experiment is carried out by adding a perturbation flow of adsorbate to a non-adsorbed (helium) carrier gas. Successive experiments involve increasing perturbation flow rates: these vary from 0.3% to 30% of the helium flow rate. The material balance is conveniently rearranged to define a flow-rate retention time (t_n). It is necessary to make a small correction (t_{corr}) to the measured retention time due to the change in hold-up in the system volume (189 mL): this is mainly due to the increase in system pressure. The validity of this time correction has been confirmed in three ways: an equation derived from first principles, a series of experiments and accepted properties of gas mixtures. The constructed isotherm compares well to isotherms presented in the literature for other activated carbons. One advantage of the flow-rate approach is the sensitivity of the equipment: the mass of adsorbent was only 0.05 g and we estimate the resolution to be of the order of 10^{-5} g. A particular advantage is that the resolution can be increased by increasing the amount of adsorbent: using the order of 0.5 g should enable the resolution to be improved to the order of 10^{-6} g. Other advantages are that an experiment can be completed relatively quickly, typically the order of 10 minutes.

Nomenclature

c_{T}	Total gas concentration in system (mol/m^3)
c_{A}	Gas concentration of component A in system (mol/m^3)
H	Total hold-up in system (mol)
k	Resistance of flow-measuring capillary
m	Molar flow rate of perturbation (refrigerant) (mol/s)
M	Molar flow rate of carrier gas (helium) (mol/s)
$M(t)$	Total molar flow rate entering system (mol/s)
$N(t)$	Total molar flow rate leaving system (mol/s)
$n(t)$	Change in molar flow rate from initial baseline value (mol/s)
$P(t)$	Pressure signal at DPT (mV)
$p(t)$	Change in pressure signal from baseline value (mV)
P_{sys}	Absolute pressure in system (mbar)

P_{amb}	Atmospheric pressure (mbar)
q_{A}	Adsorbed concentration in column of component A at steady-state (mol/g)
Q_{atm}	Volumetric flow rate measured at ambient conditions (mL/s)
Q_{sys}	Volumetric flow rate at system conditions (slightly elevated pressure) (mL/s)
t_{corr}	Correction to measured retention time due to empty volume (s)
t_n	Flow-rate retention time caused by adding perturbation flow (s)
V_{delay}	Volume of delay lines (mL)
V_{column}	Empty voidage in the column (mL)
W	Mass of adsorbent (g)
y_{A}	Mole fraction of component A in system
Z	Compressibility of gas in system

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