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Adsorption equilibria and kinetics of CH₄ and N₂ on commercial zeolites and carbons

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Abstract

Adsorption equilibria and kinetics are two sets of properties crucial to the design and simulation of adsorption based gas separation processes. The adsorption equilibria and kinetics of N₂ and CH₄ on commercial activated carbon Norit RB3, zeolite 13X, zeolite 4A and molecular sieving carbon MSC-3K 172 were studied experimentally at temperatures of (273 and 303) K in the pressure range of (5 to 120) kPa. These measurements were in part motivated by the lack of consistent adsorption kinetic data available in the literature for these systems, which forces the use of empirical estimates with large uncertainties in process designs. The adsorption measurements were carried out on a commercial volumetric apparatus. To obtain reliable kinetic data, the apparatus was operated in its rate of adsorption mode with calibration experiments conducted using helium to correct for the impact of gas expansion on the observed uptake dynamics. Analysis of the corrected rate of adsorption data for N₂ and CH₄ using the non-isothermal Fickian diffusion (FD) model was also found to be essential; the FD model was able to describe the dynamic uptake observed to better than 1 % in all cases, while the more commonly applied isothermal Linear Driving Force model was found to have a relative root mean square deviation of around 10 %. The measured sorption kinetics had no dependence on gas pressure but their temperature dependence was consistent with an Arrhenius-type relation. The effective sorption rates extracted using the FD model were able to resolve inconsistencies in the literature for similar measurements.

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1. Introduction

Adsorption based processes are well-established technologies for the separation of gas mixtures in, for example, the air separation industry [1], the hydrogen production industry [2-4], and the capture of carbon dioxide from flue gases [5-9]. In the past several decades, adsorption based processes for separating nitrogen and methane have attracted significant attention in areas such as natural gas production [8, 10], landfill gas upgrading [11, 12], coalbed methane enrichment [13], and coal mine methane/ventilation air methane purification [14].

In the design of an adsorption process for nitrogen and methane separation, estimates of the lengths of the saturation and mass transfer zones are crucial to specifying the height of the adsorption bed. Equilibria data for nitrogen and methane mixtures, which are often available either from literature reports or from direct measurements, are the foremost information required for such estimates. Information about the effective sorption kinetics is also essential to properly estimate the length of the mass transfer zone in the bed because, for many adsorption based applications, the mass transfer from gas phase to solid phase is limited by sorption kinetics. This mass transfer limitation arises from the fact that the diffusion of gases into the porous interior of the adsorbent is restricted and that the intrinsic adsorption rate is usually much faster than the diffusion rate [15]. The kinetics are especially important when the adsorbents do not possess high equilibrium selectivity for the mixture components because for such scenarios the mass transfer fronts for different adsorbates could be very close to each other. Adsorption kinetics are even more vital to the design of pressure swing adsorption (PSA) separations for nitrogen and methane mixtures that exploit differences in their sorption rates, and are crucial parameters in the development of accurate and reliable simulations of industrial PSA processes intended to separate N_2 and CH_4 . However, kinetic parameters must often be estimated empirically for such applications since the relevant data in the literature are limited and inconsistent, even for commercial adsorbents. This is partly because of the difficulty associated with accurate measurements of adsorption kinetics [16].

In principle, adsorption kinetics can be measured experimentally using a variety of techniques, for example, by monitoring the time-dependence of volumetric or gravimetric sorption capacity [17, 18],

by the combined pressure-swing and volume-swing frequency response technique [19, 20], using a dynamic column breakthrough apparatus [21], and via zero length column (ZLC) experiments [22, 23]. However, the results of kinetic measurements made by different groups and/or with different techniques tend to have large deviations. A survey of literature (Figure 1) revealed that the reported effective sorption rates for N₂ and CH₄ on commercial adsorbents similar to those measured in this work have large variations, ranging in some cases over two orders of magnitude.

Figure 1 Variations in effective sorption rate (D/r^2) reported in the literature for N₂ and CH₄ on activated carbon (AC) [18, 21, 24, 25], zeolite 13X [26-28], carbon molecular sieve (CMS) [17, 20, 29] and zeolite 4A [30-32]

One possible reason for the large deviations present in the literature data is that kinetic measurements are often analysed under the assumption of a constant temperature throughout the adsorbent, usually on the basis that the sample mass is small (≤ 1 g). However, the adsorption rate observed in such measurements is generally non-isothermal because heat is evolved during the process and cannot be removed instantaneously due to heat transfer limitations. Temperature rises due to sorption can impact the apparent kinetics in different ways, such as increasing gas diffusivities while decreasing equilibrium capacities [33]. The non-isothermal effects associated with these adsorption kinetic measurements are often erroneously overlooked by extracting adsorption kinetics from the experimental data using the isothermal linear driving force model [21, 34, 35], which is widely implemented in simulations of adsorption processes. In particular, for volumetric sorption kinetics measurements the delay in signal

response caused by value effect or gas diffusion resistance were often ignored although several workers in the past have aimed to account for the dynamics of sorption uptake in volumetric experiments [36, 37].

In this work, the adsorption equilibria and kinetics of methane and nitrogen on four commercial adsorbents (Norit RB3, zeolite 13X, molecular sieve MSC-3K 172 and zeolite 4A) were measured to assess these adsorbents for potential applications in the separation of methane and nitrogen. The sample size (mass) of each adsorbent used was carefully chosen to give sufficient signal to noise ratio after it was confirmed that any heat and mass transfer limitations due to sample size were negligible. The kinetics were obtained from rate of adsorption measurements made using the volumetric method at two temperatures of 273 K and 303 K with gas pressures up to 120 kPa. Two important steps were applied to the analysis of the dynamic uptake data to extract reliable values of the effective sorption rate (D/r^2) for methane and nitrogen on each adsorbent: calibration of the effects at short time scales due to gas expansion using helium, and regression of a non-isothermal kinetic model to the measured data. The impact of adsorption heat on the apparent kinetics was evaluated by comparing the results of isothermal and non-isothermal kinetic models. The effect of temperature on the adsorption kinetics was also studied and compared to an Arrhenius-type correlation.

2. Experimental Section

2.1 Method and materials

The Norit RB3 extrude pellet used in this work is the same activated charcoal studied by Rufford et al. [21], supplied by IMCD Australia Ltd. Zeolite 13X APG extrude pellet was supplied by Shanghai MLC Molecular Sieve Co., Ltd. The Linde zeolite 4A extrude pellet was purchased from Sigma-Aldrich (Castle Hill, NSW, Australia). The granular molecular sieving carbon MSC-3K 172 was obtained from Japan EnviroChemicals, Ltd. (Osaka, Japan). The properties of these adsorbents relevant to the rate of adsorption measurements are summarised in Table 1; other properties for these materials can be found in elsewhere [21, 38, 39]. The sample mass to be used in these experiments was determined by first conducting ROA measurements for N₂ on zeolite 4A at 283 K. Two sample masses of 0.7704 g and 0.3694 g were tested for the measurements and the uptake data for these two masses are presented in

the supporting information (SI Figure 1). It is clear from the figure that the signal-to-noise for each of these two masses is much larger than for the other results presented in this work. One reason for these noisy data is the low overall N₂ adsorption that occurs for that amount of sample at 283 K, which is comparable to the measurement's uncertainty. Thus, for measurements at 303 K, one would expect the signals to be even noisier than those measured at 283 K if the same amount of adsorbent were used, since the adsorption capacity at 303 K is lower than that at 283 K. We then used 1 gram of zeolite 4A for the N₂ ROA measurement at 303 K and it was found this was an appropriate sample size for ROA measurements. Accordingly, we used about 1 gram of zeolite 4A for all our measurements and used a similar mass for all other adsorbents for the sake of comparison on an equivalent basis. All gases used for analysis were of high purity supplied by Coregas Australia, with the following specified molar purities: CH₄: 99.995 %; N₂: 99.999 % and He: 99.995%.

Table 1 Physical properties of the adsorbents

	Norit RB3	Zeolite 13X	Zeolite 4A	MSC-3K 172
Sample mass (g)	1.0077	0.8092	1.0328	1.0511
Particle Diameter* (mm)	3.2	1.4	2.0	1.0
Particle length* (mm)	4.0	4.0	3.6	2.0
Pore volume (cm ³ /g)	0.21	0.33	0.28	0.22
Pellet density* (g/cm ³)	0.85	1.12	1.09	0.90

*Assuming cylindrical, averaged over measurements of 20 particles

Equilibrium adsorption capacity in terms of pellet mass and adsorption rates of CH₄ and N₂ on four adsorbents were measured at two temperatures (273 and 303) K using a volumetric adsorption measurement system, the Micromeritics ASAP 2020, in Rate of Adsorption (ROA) mode. Prior to these measurements, each of the adsorbents was degassed under vacuum (1 Pa) in a sample tube for 12 hours at the recommended temperatures for the given adsorbents: 473 K for Norit RB3 and MSC-3K 172, 623 K for zeolite 13X and zeolite 4A [6, 21, 39, 40]. After degassing, the sample tube was backfilled with helium and transferred to the analysis port for measurement of the adsorption amount and rate of pure gases. The measurements were then carried out from low pressure (5 kPa) to high pressure (120 kPa) incrementally to ensure that upon a step pressure change the driving force of adsorption was sufficiently small to be considered linear as assumed by the Fickian diffusion model [37, 41]. In the ROA mode of the ASAP2020, the pressure in the sample tube was automatically monitored and recorded by the data

acquisition software on the instrument once a certain amount of gas was dosed. The pressure change in the sample tube was then converted to molar amount of gas adsorbed per unit mass of the adsorbent using the reference equation of state for the respective pure gases [42, 43]. In this work, the pressure change in the sample tube was recorded every 0.4 s immediately following the introduction of a gas dose (0.223 mmol gas per gram of adsorbent). The 0.4 s data acquisition period, which limits the fastest sorption rate that can be measured with the apparatus, is the smallest meaningful time interval that can be studied with the instrument even though the operating software allows a 0.1 s interval to be specified, because the data acquisition system on the ASAP 2020 executes a 400 ms averaging of the analogue pressure transducer signals. For all the rate of adsorption measurements, 1000 pressure data points (the maximum number allowable by the data acquisition software) were recorded following the introduction of the gas dose. Representative uptake curves of three consecutive equilibrium pressure points for “slow” and “fast” cases are shown in Figure 2. For systems with slow adsorption, the rate of adsorption over a pressure step was monitored for only the first 400 seconds ($0.4 \text{ s} \times 1000$) and then the uptake rate on the adsorbent was no longer recorded while the system was allowed to proceed towards equilibrium. Once the equilibrium criterion (a pressure change of less than 0.01 % in a time interval of 30 s) was satisfied, the measurement of the next pressure point was automatically initiated. For systems with faster adsorption where equilibrium could be obtained within 400 seconds, all of the uptake data of gas on the adsorbent were recorded.

Figure 2 Examples of rate of adsorption measurements for CH₄ on Norit RB3 (fast) and zeolite 4A (slow) for three consecutive pressure steps at 303 K. The solid curves correspond to ROA measurements, while the dashed curve indicates the pressure evolution that occurred prior to the attainment of equilibrium.

2.2 Calibration with helium

To properly analyse the data acquired during the rate of adsorption measurements, blank experiments with helium were carried out for each of the adsorbents with exactly the same run files as for CH₄ and N₂ at the same temperatures. This enabled measurement of the pressure in the sample tube following the opening of the dose valve due to the gas expansion and in the absence of any adsorption (assuming the adsorption of helium on the adsorbents was negligible [44]). The blank experiments were particularly important for two reasons: first, the very first pressure data point recorded for each rate of adsorption measurement by the ASAP 2020 data acquisition system actually corresponded to the pressure in the reference volume (solid red line in Figure 3) before Valve 12 (Figure 3) was opened to introduce gas into the sample tube and was not representative of the actual pressure in the sample tube. Second, for most measurements of gas adsorption kinetics based on the volumetric technique it is important to account for the time required for gas flow and expand into the sample tube. Determining the correct initial pressure in the sample tube is critical because it sensitively affects a key parameter (α^*) in the non-isothermal dynamic model to which the dynamic pressure data are regressed, as discussed further in Section 3.

Figure 3. Schematic of the volumetric adsorption system: red solid line represents the apparatus' reference volume, used to calculate the amount of gas dosed into the sample volume below V12. The four pressure transducers could also be isolated (valves not shown) from the manifold whenever the pressure exceeded their full scale.

3. Models for Adsorption Kinetics

The linear driving force (LDF) and Fickian diffusion (FD) equations are two kinetic models commonly used to extract adsorption kinetics information from experimentally measured rate of adsorption data [18, 26, 45, 46]. Commonly, the LDF model is used instead of the FD model to represent adsorption kinetics within adsorption process simulations even though LDF predictions often show larger deviations from experimentally measured kinetic data than those made with FD models. This results from the fact that in adsorption process simulations, the LDF model allows elimination of the integration step at the particle level which is required for the FD model and, thus, use of the LDF model significantly reduces computational time [45]. However, the widespread availability of high performance computers nowadays may enable the use of more accurate FD models to simulate cyclic adsorption processes even though they are more computationally intensive.

The linear driving force model was initially developed by Glueckauf and Coates [47] for interpreting the incomplete equilibrium of the front boundary in adsorption chromatography under isothermal conditions, and it has since been adopted for describing adsorption kinetics as summarised by Sircar [45]. The general form of the LDF model for a single adsorbate is given by:

$$\frac{dm_t}{dt} = k[m_\infty - m_t] \quad \text{Eqn. 1}$$

Here m_t is the molar adsorbed amount of adsorbate on the adsorbent particle at time t , and m_∞ is the equilibrium adsorbed amount of adsorbate at the gas phase pressure P and the adsorbent temperature T . The k is the effective LDF mass transfer coefficient for the equilibrium adsorbed amount of m_∞ . The analytical solution of the LDF model [45] is used for the regression of data obtained via constant volume-variable pressure experiments when the adsorption process can be assumed an isothermal process:

$$\frac{m_t - m_0}{m_\infty - m_0} = 1 - \exp[-(1 + \alpha^*)kt] \quad \text{Eqn. 2}$$

$$\frac{\alpha^*}{1 + \alpha^*} = \frac{P^{0+} - P^\infty}{P^{0+} - P^{0-}} \quad \text{Eqn. 3}$$

Here m_0 is the equilibrium adsorbed amount on the adsorbent at the start of a pressure step, α^* is dimensionless and related to the ratio of the amount gas adsorbed during the pressure step to the amount of gas introduced to the system at time zero of the pressure step as indicated in Eqn. 3, P^{0+} is the gas phase pressure immediately after opening the dosing valve, P^∞ is the final equilibrium pressure for a pressure step, P^{0-} is the gas phase pressure before opening the dosing valve. The mass transfer coefficient k can be correlated with the sorption rate D/r^2 using the commonly recommended relation $k = 15D/r^2$ for adsorption process design [48].

The Fickian diffusion (FD) model describes the mass transfer between the gas and adsorbed phases using Fick's law of diffusion in terms of the sorption rate (D/r^2) for a gas on given adsorbents. For a constant volume system, and under the assumptions (1) that the gas diffusivity is independent of the amount of adsorbed phase, and (2) the uptake is isothermal, the analytical solution to the dynamic mass balance equation is given as follows [37]:

$$\frac{m_t}{m_\infty} = 1 - \sum_{n=1}^{\infty} \frac{6(1+\alpha^*) \exp\left(-q_n^2 \frac{D}{r^2} t\right)}{9\alpha^*(1+\alpha^*) + q_n^2} \quad \text{Eqn. 4}$$

where

$$q_n = (1 + q_n^2/3\alpha^*)/\cot q_n \quad \text{Eqn. 5}$$

Here q_n is the root of transcendental equation (Eqn. 5). Eqn. 4 is strictly limited to the analysis of isothermal uptake data for cases where the heat resulting from the adsorption can be considered as being instantaneously dissipated to the environment. To account for situations where the heat released by adsorption cannot be dissipated fast enough to achieve an isothermal condition, the non-isothermal kinetic model developed by Kocirik et. al. [37] can be used. This model was obtained for non-isothermal, constant-volume but variable-pressure conditions, by deriving an analytical solution to the simultaneous mass and heat transport equations. The main assumptions for this model are that the adsorption rate was controlled by intracrystalline gas diffusion and heat (arising from heat of adsorption) transfer from the adsorbent surface to the surrounding environment. The analytical solution is as follows:

$$\frac{m_t}{m_\infty} = 1 - \sum_{n=1}^{\infty} \frac{9(1+\alpha^*) \left[\frac{Y_n}{-q_n^2} \right]^2 \exp(-q_n^2 \frac{D}{r^2} t)}{\frac{1}{\beta_n^*} + \frac{3}{2} \frac{\beta}{\beta_n^*} \left[q_n \cot q_n \left(\frac{Y_n}{q_n^2} \right) + 1 \right] + \frac{3\alpha^* B_n}{2q_n^4 \beta_n^*}} \quad \text{Eqn. 6}$$

Here q_n is given by the roots of the following equation:

$$(-q_n^2 + \alpha) + 3\beta Y_n - \frac{3\alpha^*}{q_n^2} (-q_n^2 + \alpha) Y_n = 0 \quad \text{Eqn. 7}$$

with:

$$Y_n = q_n \cot q_n - 1 \quad \text{Eqn. 8}$$

and with the additional parameters defined as follows:

$$\alpha = \frac{ha}{\rho_s c_s} / \frac{D}{r^2} \quad \text{Eqn. 9}$$

$$\beta = \frac{\Delta H}{c_s} \left(\frac{\partial q^*}{\partial T} \right)_{c_g(0), T_0} \quad \text{Eqn. 10}$$

$$\frac{1}{\beta_n^*} = \frac{1}{\beta} \left(1 - \frac{3\alpha^* Y_n}{q_n^2} \right) \quad \text{Eqn. 11}$$

$$B_n = Y_n [(q_n^2 - \alpha) q_n \cot q_n - 2\alpha] + q_n^2 (q_n^2 - \alpha) \quad \text{Eqn. 12}$$

Here h is the overall heat transfer coefficient between the external surface of the adsorbent and its surroundings, a is the external surface area per unit volume of the adsorbent, ρ_s is the adsorbent density, c_s is the heat capacity of the adsorbent at constant pressure, and ΔH is heat of adsorption.

Both the isothermal LDF model (Eqn. 2) and non-isothermal FD model (Eqn. 6) were regressed to the experimental uptake curves by adjusting the parameter D/r^2 in the LDF model and by adjusting the parameters α , β and D/r^2 in the non-isothermal FD to minimise the root mean squared deviation (RMSD) between the dynamic uptake data and the model according to Eqn.13.

$$RMSD = \sqrt{\frac{\sum_{i=1}^N [(1-m_t/m_\infty)_{exp} - (1-m_t/m_\infty)_{model}]^2}{N}} \quad \text{Eqn. 13}$$

where N is the number of experimental data points. Since $(1 - m_t/m_\infty)$ is normalised and dimensionless, the RMSD should have a value between 0 (indicating a perfect fit) and 1 (indicating a very bad fit).

4. Results and Discussion

4.1 Adsorption Equilibria

Figure 4 shows the measured pure component adsorption isotherms for CH₄ and N₂ on the four adsorbents, and Table 2 lists the data measured for these isotherms, together with their combined standard uncertainties which were calculated according to uncertainty propagation formula shown in Eqn. 14 [49]. Assuming that the input quantities are not correlated, the combined standard uncertainty in the adsorption capacity for the present measurements can be calculated as

$$u(Q_e) = \sqrt{\left[\left(\frac{\partial Q_e}{\partial m}\right)u(m)\right]^2 + \left[\left(\frac{\partial Q_e}{\partial P}\right)u(P)\right]^2 + \left[\left(\frac{\partial Q_e}{\partial T}\right)u(T)\right]^2 + \left[\left(\frac{\partial Q_e}{\partial V}\right)u(V)\right]^2} \quad \text{Eqn. 14}$$

where $u(x)$ denotes the standard uncertainty of a quantity x and V is sample tube volume. The uncertainty in the sample mass was estimated from the balance resolution, the uncertainty of the pressure was taken to be 0.15 % of the equilibrium reading, and the uncertainty of the temperature was set by the stability of the liquid bath. The uncertainty in the volume was estimated from the standard deviation in the free gas volume (≈ 20 mL) determined automatically by the apparatus corresponding to each equilibrium pressure measurement. Numerical values of these component uncertainties are listed in Table 2.

Figure 4 Measured adsorption capacity of pure methane (solid symbols) and pure nitrogen (hollow symbols) on four adsorbents at a) 303 K, and, b) 273 K for pressures up to 120 kPa

Table 2 Pure methane and nitrogen single component adsorption capacities, Q_e , along with their standard uncertainties, $u(Q_e)$, on the four adsorbents tested in this study. $u(Q_e)$ was calculated using Eqn. 14 with standard uncertainties for sample mass: 0.0001 g, pressure: 0.15 % of reading, temperature: 0.02 K, and volume: 0.074 mL

Temperature (K)	Pressure (kPa)	Q_e (mmol/g)	$u(Q_e)$ (mmol/g)	Temperature (K)	Pressure (kPa)	Q_e (mmol/g)	$u(Q_e)$ (mmol/g)
Zeolite 4A							
Methane				Nitrogen			
273.15	5.40	0.0735	0.0019	273.15	5.42	0.0418	0.0019
273.15	10.57	0.1393	0.0027	273.15	11.43	0.0830	0.0027
273.15	15.79	0.2037	0.0033	273.15	17.49	0.1230	0.0033
273.15	21.00	0.2679	0.0038	273.15	23.55	0.1615	0.0038
273.15	26.26	0.3299	0.0042	273.15	29.63	0.1985	0.0042
273.15	31.54	0.3911	0.0046	273.15	35.72	0.2346	0.0046
273.15	36.88	0.4506	0.0050	273.15	41.82	0.2694	0.0050
273.15	42.35	0.5106	0.0053	273.15	48.10	0.3038	0.0053
273.15	47.91	0.5680	0.0056	273.15	54.41	0.3371	0.0056
273.15	53.52	0.6231	0.0059	273.15	60.71	0.3690	0.0059
273.15	59.15	0.6774	0.0062	273.15	67.05	0.4000	0.0062
273.15	64.73	0.7307	0.0065	273.15	73.41	0.4296	0.0065
273.15	70.48	0.7817	0.0068	273.15	79.82	0.4588	0.0068
273.15	76.33	0.8314	0.0070	273.15	86.20	0.4861	0.0070
273.15	82.13	0.8802	0.0073	273.15	92.61	0.5124	0.0073
273.15	87.98	0.9246	0.0075	273.15	99.03	0.5375	0.0075
273.15	93.95	0.9680	0.0078	273.15	105.49	0.5619	0.0078
273.15	99.87	1.0131	0.0080	273.15	111.96	0.5853	0.0080
273.15	105.88	1.0547	0.0082				
273.15	111.97	1.0940	0.0084				
303.15	5.54	0.0362	0.0016	303.15	5.16	0.0186	0.0016
303.15	11.82	0.0737	0.0022	303.15	12.05	0.0394	0.0022
303.15	18.13	0.1108	0.0027	303.15	18.92	0.0593	0.0027
303.15	24.52	0.1475	0.0031	303.15	25.77	0.0783	0.0031
303.15	30.85	0.1837	0.0035	303.15	32.61	0.0966	0.0035
303.15	37.28	0.2195	0.0038	303.15	39.45	0.1142	0.0038
303.15	43.68	0.2546	0.0042	303.15	46.31	0.1306	0.0042
303.15	50.19	0.2895	0.0044	303.15	53.28	0.1466	0.0044
303.15	56.73	0.3238	0.0047	303.15	60.28	0.1620	0.0047
303.15	63.30	0.3572	0.0050	303.15	67.31	0.1764	0.0050
303.15	69.82	0.3902	0.0052	303.15	74.26	0.1899	0.0052
303.15	76.33	0.4223	0.0054	303.15	81.27	0.2026	0.0054
303.15	82.93	0.4543	0.0057	303.15	88.29	0.2147	0.0057
303.15	89.54	0.4856	0.0059	303.15	95.36	0.2259	0.0059
303.15	96.12	0.5158	0.0061	303.15	102.37	0.2363	0.0061
303.15	102.72	0.5455	0.0063	303.15	109.39	0.2458	0.0063
303.15	109.36	0.5750	0.0065				
Zeolite 13X APG							
Methane				Nitrogen			
273.15	5.38	0.0684	0.0016	273.15	4.76	0.0393	0.0016
273.15	9.85	0.1206	0.0022	273.15	9.67	0.0747	0.0022
273.15	14.34	0.1717	0.0027	273.15	14.60	0.1090	0.0027

1	273.15	18.90	0.2227	0.0031	273.15	19.54	0.1421	0.0031
2	273.15	23.39	0.2723	0.0035	273.15	24.50	0.1740	0.0035
3	273.15	27.95	0.3217	0.0038	273.15	29.46	0.2052	0.0038
4	273.15	32.53	0.3707	0.0041	273.15	34.43	0.2351	0.0041
5	273.15	37.12	0.4186	0.0044	273.15	39.43	0.2646	0.0044
6	273.15	41.70	0.4656	0.0047	273.15	44.53	0.2932	0.0047
7	273.15	46.39	0.5124	0.0049	273.15	49.64	0.3210	0.0049
8	273.15	51.07	0.5592	0.0052	273.15	54.75	0.3481	0.0052
9	273.15	55.81	0.6047	0.0054	273.15	59.89	0.3742	0.0054
10	273.15	60.55	0.6501	0.0056	273.15	65.05	0.3994	0.0056
11	273.15	65.28	0.6946	0.0058	273.15	70.21	0.4239	0.0058
12	273.15	70.06	0.7383	0.0060	273.15	75.39	0.4475	0.0060
13	273.15	74.85	0.7816	0.0062	273.15	80.55	0.4703	0.0062
14	273.15	79.64	0.8241	0.0064	273.15	85.75	0.4925	0.0064
15	273.15	84.47	0.8657	0.0066	273.15	90.98	0.5137	0.0066
16	273.15	89.28	0.9061	0.0068	273.15	96.21	0.5344	0.0068
17	273.15	94.11	0.9466	0.0070	273.15	101.42	0.5546	0.0070
18	273.15	98.97	0.9864	0.0071	273.15	106.67	0.5738	0.0071
19	273.15	103.84	1.0255	0.0073	273.15	111.93	0.5922	0.0073
20	273.15	108.68	1.0636	0.0075				
21	273.15	113.57	1.1010	0.0076				
22	303.15	4.93	0.0317	0.0019	303.15	5.24	0.0200	0.0019
23	303.15	10.14	0.0611	0.0027	303.15	10.77	0.0378	0.0027
24	303.15	15.35	0.0899	0.0033	303.15	16.29	0.0549	0.0033
25	303.15	20.57	0.1187	0.0038	303.15	21.82	0.0715	0.0038
26	303.15	25.76	0.1468	0.0043	303.15	27.33	0.0873	0.0043
27	303.15	30.98	0.1746	0.0047	303.15	32.93	0.1025	0.0047
28	303.15	36.35	0.2029	0.0051	303.15	38.48	0.1171	0.0051
29	303.15	41.70	0.2308	0.0054	303.15	44.00	0.1310	0.0054
30	303.15	47.06	0.2584	0.0058	303.15	49.62	0.1444	0.0058
31	303.15	52.39	0.2857	0.0061	303.15	55.22	0.1572	0.0061
32	303.15	57.78	0.3127	0.0064	303.15	60.85	0.1695	0.0064
33	303.15	63.18	0.3395	0.0066	303.15	66.46	0.1811	0.0066
34	303.15	68.58	0.3660	0.0069	303.15	72.08	0.1920	0.0069
35	303.15	73.90	0.3921	0.0072	303.15	77.73	0.2022	0.0072
36	303.15	79.17	0.4175	0.0074	303.15	83.37	0.2121	0.0074
37	303.15	84.55	0.4429	0.0077	303.15	89.03	0.2211	0.0077
38	303.15	89.96	0.4683	0.0079	303.15	94.69	0.2296	0.0079
39	303.15	95.33	0.4933	0.0081	303.15	100.33	0.2373	0.0081
40	303.15	100.72	0.5179	0.0084	303.15	106.00	0.2447	0.0084
41	303.15	106.02	0.5419	0.0086	303.15	111.66	0.2514	0.0086
42	303.15	111.42	0.5661	0.0088				
43	MSC-3K 172							
44	Methane				Nitrogen			
45	273.15	4.86	0.0820	0.0018	273.15	5.87	0.0544	0.0018
46	273.15	9.03	0.1823	0.0026	273.15	11.87	0.1019	0.0026
47	273.15	13.69	0.2665	0.0032	273.15	17.99	0.1458	0.0032

273.15	18.70	0.3407	0.0036	273.15	24.21	0.1866	0.0036
273.15	23.55	0.4197	0.0041	273.15	30.51	0.2250	0.0041
273.15	29.78	0.4583	0.0045	273.15	36.87	0.2609	0.0045
273.15	34.18	0.5552	0.0048	273.15	43.35	0.2948	0.0048
273.15	40.21	0.6030	0.0052	273.15	49.84	0.3271	0.0052
273.15	45.80	0.6645	0.0055	273.15	56.45	0.3571	0.0055
273.15	51.67	0.7174	0.0058	273.15	63.02	0.3857	0.0058
273.15	57.54	0.7699	0.0060	273.15	69.60	0.4115	0.0060
273.15	63.82	0.8085	0.0063	273.15	76.26	0.4363	0.0063
273.15	69.82	0.8554	0.0066	273.15	82.94	0.4602	0.0066
273.15	76.36	0.8863	0.0068	273.15	89.66	0.4833	0.0068
273.15	82.52	0.9304	0.0071	273.15	96.39	0.5046	0.0071
273.15	88.99	0.9640	0.0073	273.15	103.16	0.5247	0.0073
273.15	95.42	0.9997	0.0075	273.15	109.94	0.5432	0.0075
273.15	102.20	1.0252	0.0077				
273.15	108.76	1.0576	0.0079				
273.15	115.39	1.0875	0.0081				
303.15	5.15	0.0782	0.0016	303.15	6.90	0.0276	0.0016
303.15	10.33	0.1530	0.0023	303.15	13.79	0.0527	0.0023
303.15	15.73	0.2204	0.0028	303.15	20.71	0.0762	0.0028
303.15	21.26	0.2836	0.0033	303.15	27.65	0.0985	0.0033
303.15	27.00	0.3402	0.0037	303.15	34.61	0.1193	0.0037
303.15	32.96	0.3966	0.0040	303.15	41.57	0.1391	0.0040
303.15	39.06	0.4472	0.0043	303.15	48.66	0.1575	0.0043
303.15	45.26	0.4943	0.0046	303.15	55.76	0.1750	0.0046
303.15	51.40	0.5398	0.0049	303.15	62.89	0.1911	0.0049
303.15	57.83	0.5807	0.0052	303.15	70.10	0.2066	0.0052
303.15	64.34	0.6208	0.0054	303.15	77.25	0.2203	0.0054
303.15	70.89	0.6587	0.0057	303.15	84.43	0.2332	0.0057
303.15	77.41	0.6942	0.0059	303.15	91.63	0.2449	0.0059
303.15	83.99	0.7306	0.0061	303.15	98.85	0.2558	0.0061
303.15	90.73	0.7620	0.0064	303.15	106.05	0.2655	0.0064
303.15	97.52	0.7928	0.0066	303.15	113.29	0.2744	0.0066
303.15	104.31	0.8237	0.0068				
303.15	111.16	0.8522	0.0070				
Norit RB3							
Methane				Nitrogen			
273.15	3.69	0.1129	0.0017	273.15	6.16	0.0368	0.0017
273.15	7.82	0.2106	0.0024	273.15	12.37	0.0697	0.0024
273.15	12.18	0.3000	0.0029	273.15	18.58	0.1009	0.0029
273.15	16.72	0.3836	0.0034	273.15	24.81	0.1306	0.0034
273.15	21.41	0.4615	0.0038	273.15	31.08	0.1590	0.0038
273.15	26.23	0.5353	0.0041	273.15	37.37	0.1860	0.0041
273.15	31.18	0.6053	0.0045	273.15	43.78	0.2125	0.0045
273.15	36.32	0.6734	0.0048	273.15	50.25	0.2379	0.0048
273.15	41.57	0.7391	0.0051	273.15	56.69	0.2623	0.0051

273.15	46.87	0.8018	0.0053	273.15	63.17	0.2856	0.0053
273.15	52.26	0.8615	0.0056	273.15	69.66	0.3079	0.0056
273.15	57.69	0.9198	0.0058	273.15	76.11	0.3292	0.0058
273.15	63.22	0.9762	0.0061	273.15	82.66	0.3500	0.0061
273.15	68.85	1.0310	0.0063	273.15	89.19	0.3699	0.0063
273.15	74.43	1.0833	0.0065	273.15	95.74	0.3888	0.0065
273.15	80.08	1.1343	0.0067	273.15	102.32	0.4070	0.0067
273.15	85.77	1.1844	0.0069	273.15	108.90	0.4241	0.0069
273.15	91.51	1.2328	0.0071	273.15	115.50	0.4409	0.0071
273.15	97.21	1.2795	0.0073				
273.15	103.02	1.3255	0.0075				
273.15	108.87	1.3705	0.0077				
273.15	114.76	1.4146	0.0079				
303.15	5.28	0.0689	0.0016	303.15	6.89	0.0212	0.0016
303.15	10.73	0.1294	0.0022	303.15	13.74	0.0398	0.0022
303.15	16.37	0.1867	0.0027	303.15	20.62	0.0572	0.0027
303.15	22.10	0.2410	0.0032	303.15	27.47	0.0737	0.0032
303.15	27.89	0.2920	0.0035	303.15	34.32	0.0894	0.0035
303.15	33.72	0.3408	0.0039	303.15	41.18	0.1043	0.0039
303.15	39.71	0.3882	0.0042	303.15	48.24	0.1186	0.0042
303.15	45.74	0.4338	0.0045	303.15	55.11	0.1319	0.0045
303.15	51.83	0.4777	0.0048	303.15	62.13	0.1446	0.0048
303.15	57.98	0.5202	0.0050	303.15	69.05	0.1564	0.0050
303.15	64.18	0.5615	0.0053	303.15	76.06	0.1674	0.0053
303.15	70.31	0.6008	0.0055	303.15	83.07	0.1778	0.0055
303.15	76.56	0.6396	0.0057	303.15	90.07	0.1870	0.0057
303.15	82.87	0.6774	0.0059	303.15	97.06	0.1956	0.0059
303.15	89.17	0.7142	0.0061	303.15	104.11	0.2036	0.0061
303.15	95.49	0.7497	0.0063	303.15	111.14	0.2108	0.0063
303.15	101.86	0.7846	0.0065				
303.15	108.23	0.8185	0.0067				
303.15	114.64	0.8517	0.0069				

Figure 4 clearly shows that all of these adsorbents have higher CH₄ capacities than N₂ capacities at the same temperature and pressure. At 303 K, MSC-3K 172 and Norit RB3 exhibited a similar adsorption capacity for methane, which is about 40% higher than the corresponding methane capacities observed for zeolite 4A and zeolite 13X at around 100 kPa. The nitrogen adsorption capacity for MSC-3K 172, Norit RB3, zeolite 4A and zeolite 13X were essentially identical at 303 K. At 273 K, both MSC-3K 172 and Norit RB3 displayed slightly higher (~20%) capacities for methane than those for the other adsorbents at pressures up to 40 kPa. The nitrogen adsorption capacity for MSC-3K 172, zeolite 4A and zeolite 13X were essentially identical at 273 K, and about 30% higher than that for Norit RB3.

4.2 Kinetic Measurement Calibration

To accurately measure sorption kinetics using a volumetric system, the time delay in recorded data caused by the effects of the valve and the sensors' response needs to be accounted for when processing the uptake data. In the work of Hu et al. [36], for example, the initial 5 seconds of pressure data were discarded by the authors presumably because, as we found, the dynamics of the early transient is not captured correctly by existing models. The objective of this work is to explicitly account for those very early dynamics through the use of a helium blank run at the corresponding pressures where measurements with CH₄ and N₂ (which both adsorb but also experience similar transient dynamics) were acquired. Helium was used to calibrate the effects of gas expansion upon dosing for all the kinetic measurements conducted in this work to enable correction of the initial condition (time origin and pressure) for the subsequent analysis of the dynamic uptake. Figure 5 shows an example of why the helium calibration was necessary to obtain accurate sorption kinetics from the raw pressure readings acquired with the apparatus, through the comparison of ROA data obtained for helium and methane on Norit RB3 at 80 kPa and 273 K. At 273 K, the methane pressure dropped quickly from 86.74 kPa at $t = 0$ to 80.63 kPa at $t = 0.8$ s, with the final equilibrium pressure being 80.08 kPa. These raw pressure data superficially indicate that 92 % of the sorption capacity at 273 K was reached within 0.8 seconds of gas dosage, which could be interpreted erroneously as extremely fast sorption kinetics if these raw data were used. However, comparison of these raw pressure data for methane with those obtained during the corresponding helium calibration experiment shows that those initial rapid pressure changes were more likely caused by gas expansion rather than adsorption given that the experiment with helium also exhibited a similar rapid pressure drop within the first 0.8 seconds, with a negligible pressure decrease thereafter. Clearly then, the pressure drop occurring in the first 0.8 seconds is dominated by gas expansion, and the condition from which the initial time and pressure datum should be taken for the analysis of sorption kinetics is $t = 0.8$ s and $p \approx 80.63$ kPa. To capture a more precise estimate of the initial pressure, which accounts for any possible methane adsorption that did occur during the first 0.8 s, the pressure ratio obtained for helium between $t = 0.8$ s and $t = 0$ s can be applied to the methane pressure recorded at $t = 0$ s. Across all the experiments conducted, the time scale of the gas expansion effect as

measured with helium ranged from 0.8 to 5.6 s, and it was found to be important to perform helium calibration runs for each adsorbent.

Figure 5 Pressure readings in methane rate of adsorption measurements on Norit RB3 at around 80 kPa at 273 K together with corresponding helium calibration pressure readings.

4.3 Sorption Rate Determination from Dynamic Uptake with Kinetic Models

The objective of this paper is to demonstrate a new robust method of extracting effective reliable sorption kinetic data for materials that may be used in industrial adsorption process design. Accordingly, we do not discuss extensively the mechanisms governing the observed uptake rates, in part because it is well known that the controlling mechanism for nitrogen and methane diffusion in Norit RB3 and zeolite 13X is macropore diffusion [21, 26, 36] and that for zeolite 4A and molecular sieve carbon is micropore diffusion [17, 30].

Figure 6 shows pairs of representative CH₄ and N₂ uptake data obtained at 273 K and about 100 kPa for Norit RB3, zeolite 13X, MSC 3K-172 and zeolite 4A. For both gases, the non-isothermal Fickian diffusion models resulting from the regression to the CH₄ and N₂ uptake data are presented along with the experimental data. Additionally, the results of the isothermal LDF model regression to the CH₄ data are shown.

The LDF model is the most widely-used correlation for representing gas adsorption kinetics in adsorption process simulations. Therefore, fits of this model to the gas uptake data were tested for each

of the adsorbents. However, the LDF fit had particularly large deviations from the experimental data for Norit RB3 (RMSD = 12.26 %) and zeolite 13X (RMSD = 7.44 %) measured in this study. The LDF model tends to predict an overall faster approach to equilibrium for these large pore sized adsorbents but a slower adsorption rate at the initial stage of the adsorption. The deviations of the LDF model from the experimental data can be explained by the fact that in the experiments, the approach to adsorption equilibrium was initially accelerated by faster gas diffusion due to the temperature rise associated with heat-transfer limitations, before the reduction in the adsorbent's equilibrium capacity adversely affected the sorption driving force [41]. The isothermal LDF model cannot capture such heat related effects, and instead assumes that the rate of adsorption depends solely on the initial driving force for adsorption. The deviations of the LDF model from the experimental data for MSC-3K 172 (RMSD = 1.27 %) and zeolite 4A (RMSD = 2.6 %) are smaller compared to those for the other two adsorbents, which can be attributed to the small micropores within MSC-3K 172 and zeolite 4A, which slow gas diffusion therein. This enables the heat of adsorption to be dissipated to the environment relatively rapidly in comparison with the time scale for sorption, thereby maintaining the system at near constant temperature.

Figure 6 Experimental and theoretical (black solid lines representing FD model for both CH₄ and N₂, and blue dash line representing LDF model for CH₄) uptake curves of CH₄ and N₂ on a) Norit RB3, b) Zeolite 13X, c) carbon molecular sieve MSC-3K 172, and d) zeolite 4A pellet at 273 K with pressure around 100 kPa

When the non-isothermal FD model was used to regress the experimental uptake data, the respective RMSDs were much smaller than that for LDF model: 0.91 % for Norit RB3, 0.82 % for zeolite 13X, 0.95 % for MSC-3K 172 and 0.96 % for zeolite 4A. The effective sorption rates obtained with the LDF model were 10 to 20 times smaller than those obtained with the FD model for Norit RB3 and zeolite 13X, and differed by about a factor of two for MSC-3K 172 and zeolite 4A. Clearly, the non-isothermal FD model provided a much better description of the experimental uptake curves on all four adsorbents than the LDF model and for this reason we exclusively used the FD model in all subsequent analysis.

4.4 Kinetic Adsorption Results

Figure 7 shows the effective sorption rate of CH₄ and N₂ on Norit RB3, zeolite 13X, zeolite 4A and MSC-3K 172 as a function of pressure at 303 K and 273 K. The effective sorption rates for CH₄ are of the same order of magnitude for adsorbents Norit RB3 and zeolite 13X, which are approximately 10³ times faster than that of CH₄ in zeolite 4A and 10⁴ times faster than that of CH₄ in MSC-3K 172. The effective sorption rates for N₂ are also of the same order of magnitude for adsorbents Norit RB3 and zeolite 13X, which are approximately 10² times faster than that of N₂ in zeolite 4A and 10³ times faster than that of N₂ in MSC-3K 172. The effective sorption rate showed only a weak dependence on pressure, which is consistent with the assumption of the FD model that the sorption rates are independent of loading of adsorbed phase on the adsorbents [37] in the range of pressures studied in this work.

Figure 7 Effective diffusion time constant for CH₄ and N₂ on Norit RB3, zeolite 13X, zeolite 4A and carbon molecular sieve MSC-3K 172 obtained by non-isothermal Fickian diffusion model at 303 K

(solid) and 273 K (hollow) at various pressures: a) effective sorption rate constant for CH₄, b) effective sorption rate constant for N₂

Values of the effective sorption rate for Norit RB3 are listed in Table 3, ranging from (0.13 to 0.15) s⁻¹ for CH₄ and being no smaller than 0.16 s⁻¹ for N₂ at 273 K. At 303 K they ranged from (0.31 to 0.35) s⁻¹ for CH₄ but the rate of N₂ adsorption was too fast (more than 90 % of adsorption capacity over the pressure step was achieved within 1 second) to obtain meaningful values given the limited temporal resolution of the apparatus. To the best of our knowledge, there has been only one work reporting the kinetics of CH₄ and N₂ on activated carbon Norit RB3 by Rufford et al. [21]. They used an isothermal linear driving force model to extract mass transfer coefficients for CH₄ and N₂ from breakthrough experiments conducted in a fixed bed column. However, even the largest effective sorption rate derived from their reported mass transfer coefficients are about 100 times smaller than our results. We suspect that the apparent sorption rates extracted from the measurements of Rufford et al. [21] were significantly afflicted by heat transfer limitations in the fixed bed, and we have since updated our approach to such DCB sorption rate measurements [50, 51]. Meanwhile, our results are similar to that of a work by Malek and Farooq [25] for CH₄ on an activated carbon. Their measurements were performed at temperatures from (299 to 338) K and pressures in the range of (199 to 651) kPa with dynamic breakthrough experiments using dilute CH₄ mixtures. The effective sorption rate reported by them for these conditions ranged from (0.41 to 0.66) s⁻¹. In addition, our measurements are consistent with effective sorption rates obtained from N₂+CH₄ breakthrough experiments conducted on a Maxsorb activated carbon at 300 K and 1 atm by Sheikh et. al. [24] (0.197 s⁻¹ for CH₄ and 0.55 s⁻¹ for N₂). More recently, Ju et al. [18] reported the kinetics of pure CH₄ and N₂ on cylindrical activated carbon granules with effective sorption rate of (0.06 to 0.08) s⁻¹ for CH₄ in the pressure range of (25 to 78) kPa and (0.06 to 0.08) s⁻¹ for N₂ in the pressure range of (20 to 90) kPa at 308 K. These values for methane are about 30 to 50 times smaller than our results at 303 K. However, we note that the dynamic uptake data shown graphically in reference [18] for CH₄ on activated carbon are reasonably consistent with our dynamic uptake data. Figure 3 of reference [18] suggests that 90 % of the uptake occurred in about 20 seconds, which is even faster than our observations of 80 % uptake within 20 seconds for CH₄ on activated carbon. As indicated above,

systematically low estimates of the effective sorption rate can occur if the LDF model is used to analyse data with appreciable heating effects. However, Ju et al. [18] stated they used the non-isothermal FD model to regress their data. Bulow [52] has suggested alternative reasons for the apparently low sorption rates reported by Ju et al. [18], such as neglecting to deduct the overall response time of the apparatus or the delay caused by forcing the gas to pass through a 0.5 micron ceramic frit on top of the adsorbent.

Table 3. Effective sorption rate and associated parameters for the non-isothermal FD model in eqs (6)-(12) for CH₄ and N₂ on activated carbon Norit RB3. Values are not reported for conditions where 90% of the uptake occurred within 1 s.

Norit RB3									
Methane					Nitrogen				
273.15 K					273.15 K				
P (kPa)	$ha/\rho_s c_s$ (s ⁻¹)	β	D/r ² (s ⁻¹)	u(D/r ²) (s ⁻¹)	P (kPa)	$ha/\rho_s c_s$ (s ⁻¹)	β	D/r ² (s ⁻¹)	u(D/r ²) (s ⁻¹)
21.41	0.033	0.249	0.14	0.02	24.81	—	—	—	—
41.57	0.033	0.345	0.15	0.02	43.78	—	—	—	—
63.22	0.032	0.541	0.14	0.01	63.178	—	—	—	—
80.08	0.033	0.653	0.14	0.01	82.66	0.034	0.257	0.16	0.04
103.02	0.034	0.736	0.13	0.01	102.32	0.034	0.253	0.16	0.03
303.15 K					303.15 K				
22.10	0.032	0.155	0.34	0.04	20.62	—	—	—	—
39.71	0.034	0.203	0.34	0.04	41.18	—	—	—	—
64.18	0.034	0.334	0.32	0.05	62.13	—	—	—	—
82.87	0.035	0.384	0.32	0.05	83.07	—	—	—	—
101.86	0.032	0.358	0.31	0.05	104.11	—	—	—	—

The effective sorption rates measured for CH₄ and N₂ on zeolite 13X are listed in Table 4, and range from (0.11 to 0.29) s⁻¹ and (0.13 to 0.43) s⁻¹, respectively. These are broadly consistent with kinetic results reported in the literature. Delgado et al. used pulse experiments to measure the effective sorption rate for CH₄ at 289 K and 324 K on a zeolite 13X with results ranging from (0.18 and 0.33) s⁻¹ [28]. Dantas et al. [27] obtained N₂ mass transfer coefficients on a zeolite 13X using binary gas breakthrough experiments at 1 bar of pressure at various temperatures, and at about 303K, the effective sorption rate reported for N₂ was 0.18 s⁻¹. However, Park et al. [26] recently reported the kinetics of pure CH₄ and N₂ on spherical pelletised UOP zeolite 13X with effective time of 0.05-0.07 s⁻¹ for CH₄ and 0.01-0.08 s⁻¹ for N₂ in the pressure range of 10-80 kPa and temperature range of (293 to 323) K. These values are about 3~20 times smaller than our results, which might be explained by the fact that Park et al. [26] used the same apparatus and method as Ju et al. [18].

Table 4 Effective sorption rate of CH₄ and N₂ on zeolite 13X obtained from the non-isothermal FD model
Values are not reported for conditions where 90% of the uptake occurred within 1 s.

Zeolite 13X									
Methane					Nitrogen				
273.15 K					273.15 K				
P (kPa)	$ha/\rho_s c_s$ (s ⁻¹)	β	D/r ² (s ⁻¹)	u(D/r ²) (s ⁻¹)	P (kPa)	$ha/\rho_s c_s$ (s ⁻¹)	β	D/r ² (s ⁻¹)	u(D/r ²) (s ⁻¹)
18.9	0.027	0.258	0.11	0.03	19.5	—	—	—	—
42.1	0.029	0.404	0.14	0.02	39.4	0.029	0.271	0.19	0.05
60.6	0.027	0.484	0.12	0.02	59.9	0.028	0.334	0.16	0.03
79.6	0.026	0.468	0.11	0.01	80.6	0.027	0.380	0.16	0.03
103.2	0.029	0.583	0.11	0.01	101.7	0.028	0.338	0.13	0.02
303.15 K					303.15 K				
20.6	—	—	—	—	21.8	—	—	—	—
41.7	—	—	—	—	38.5	—	—	—	—
63.2	0.026	0.169	0.29	0.09	60.9	0.030	0.178	0.43	0.08
79.2	0.025	0.167	0.27	0.07	83.4	0.029	0.149	0.40	0.07
100.7	0.027	0.217	0.23	0.05	100.3	0.028	0.138	0.34	0.05

The values of effective sorption rate for MSC-3K 172 are listed in Table 5, and at pressures from (20 to 120) kPa range from $(0.95 \text{ to } 27.8) \times 10^{-5} \text{ s}^{-1}$ for CH₄ and $(3.61 \text{ to } 5.57) \times 10^{-4} \text{ s}^{-1}$ for N₂ at 273 K, and from $(1.72 \text{ to } 2.95) \times 10^{-5} \text{ s}^{-1}$ for CH₄ and $(0.88 \text{ to } 1.35) \times 10^{-3} \text{ s}^{-1}$ for N₂ at 303 K. Our results are consistent with the data of Bae and Lee [29] for CH₄ and N₂ on a CMS-T3A carbon molecular sieve. Their measurements were performed at 303 K with pressures in the range of 0-1500 kPa with a volumetric-type apparatus. The effective sorption rate reported by them for these conditions ranged from $(0.05 \text{ to } 8) \times 10^{-5} \text{ s}^{-1}$ for CH₄ and $(2 \text{ to } 30) \times 10^{-4} \text{ s}^{-1}$ for N₂. More recently, Yang et. al. [17] reported the kinetics of pure CH₄ and N₂ on carbon molecular sieve CMS-131510 with pellet diameters of (0.11 to 0.13) cm using a magnetic suspension microbalance. The effective time constants reported were $(4.25 \text{ to } 6.71) \times 10^{-6} \text{ s}^{-1}$ for CH₄ at 343 K and $(1.44 \text{ to } 2.56) \times 10^{-4} \text{ s}^{-1}$ for N₂ at 303 K in the pressure range of (0 to 100) kPa. In addition, Hossain [20] measured the effective sorption rate for N₂ using volume swing frequency response method at temperatures between (293 and 332) K on MSC-3K 172 with values ranging from $(4.9 \text{ to } 13.0) \times 10^{-4} \text{ s}^{-1}$, which fall in the range of our results for N₂.

Table 5 Effective sorption rate of CH₄ and N₂ on carbon molecular sieve MSC-3K 172 obtained from the non-isothermal FD model

MSC-3K 172									
Methane					Nitrogen				
273.15 K					273.15 K				
P (kPa)	$ha/\rho_s c_s$ (s ⁻¹)	β	D/r ² ×10 ⁵ (s ⁻¹)	u(D/r ²) ×10 ⁵ (s ⁻¹)	P (kPa)	$ha/\rho_s c_s$ (s ⁻¹)	β	D/r ² ×10 ⁴ (s ⁻¹)	u(D/r ²) ×10 ⁴ (s ⁻¹)
23.55	0.010	79.915	0.95	0.36	24.21	0.012	0.672	3.61	0.01
40.21	0.014	69.746	1.94	0.38	43.35	0.011	0.881	4.25	0.02
63.82	0.012	32.067	2.49	0.39	63.02	0.010	0.664	4.85	0.02
82.52	0.012	39.470	2.76	0.75	82.94	0.010	0.540	5.41	0.02
102.20	0.012	12.481	2.78	0.39	101.7	0.012	0.213	5.57	0.02
303.15 K					303.15 K				
21.26	0.011	40.567	1.72	0.32	20.71	0.102	0.025	8.81	0.08
39.06	0.013	39.197	2.04	0.54	41.57	0.011	0.038	10.30	0.09
64.34	0.013	24.557	2.95	0.42	62.89	0.010	0.033	11.89	0.37
83.99	0.010	10.558	3.28	0.32	84.43	0.011	0.020	12.69	0.34
104.31	0.011	12.781	4.24	0.72	106.05	0.012	0.003	13.51	0.73

The effective sorption rates measured for CH₄ and N₂ on zeolite 4A are listed in Table 6, and at pressures from (20 to 120) kPa range from $(1.30 \text{ to } 1.48) \times 10^{-4} \text{ s}^{-1}$ for CH₄ and $(1.11 \text{ to } 1.15) \times 10^{-3} \text{ s}^{-1}$ for N₂ at 273 K, and from $(2.68 \text{ to } 3.12) \times 10^{-4} \text{ s}^{-1}$ for CH₄ and $(2.96 \text{ to } 3.16) \times 10^{-3} \text{ s}^{-1}$ for N₂ at 303 K. The values obtained in this work are similar to kinetic results reported for zeolite 4A in the work by Haq and Ruthven [32]. They used the chromatographic method to study the diffusion of N₂ and CH₄ on zeolite 4A at various temperatures and obtained sorption rates of $(2.95 \text{ to } 11.5) \times 10^{-3} \text{ s}^{-1}$ for N₂ at temperatures from (298 to 363) K and $(6.06 \text{ to } 59.2) \times 10^{-4} \text{ s}^{-1}$ for CH₄ at temperatures from (323 to 473) K. Mohr et al. [31] measured pure and binary gas adsorption kinetics of CH₄ and N₂ on zeolite 4A by the isotope exchange technique, and stated that the experiments were carried out isothermally. They used the isothermal Fickian diffusion model to extract the “self-diffusivities” of CH₄ and N₂ which are effectively the sorption kinetics as we used in this work. They measured the diffusion of pure N₂ and pure CH₄ at three temperatures and obtained sorption rates of $3.0 \times 10^{-3} \text{ s}^{-1}$ for N₂ and $2.5 \times 10^{-4} \text{ s}^{-1}$ for CH₄ at 273 K. They also measured binary N₂/CH₄ diffusion at the same temperature and obtained values of $(2.34 \text{ to } 2.61) \times 10^{-4} \text{ s}^{-1}$ for CH₄ and $(2.86 \text{ to } 3.52) \times 10^{-3} \text{ s}^{-1}$ for N₂. These measured sorption rates are reasonably consistent with our results considering the adsorbents were from different manufacturers.

No obvious pressure dependence in the effective sorption rate was observed by Mohr et al. [31] for either CH₄ or N₂.

Table 6 Effective sorption rate of CH₄ and N₂ on Zeolite 4A obtained from the non-isothermal FD model

Zeolite 4A									
Methane					Nitrogen				
273.15 K					273.15 K				
P (kPa)	$ha/\rho_s c_s$ (s ⁻¹)	β	$D/r^2 \times 10^4$ (s ⁻¹)	$u(D/r^2) \times 10^4$ (s ⁻¹)	P (kPa)	$ha/\rho_s c_s$ (s ⁻¹)	β	$D/r^2 \times 10^3$ (s ⁻¹)	$u(D/r^2) \times 10^3$ (s ⁻¹)
21.00	0.027	27.779	1.30	0.03	17.49	0.024	0.769	1.15	0.08
42.35	0.024	19.365	1.34	0.01	41.82	0.023	0.604	1.15	0.06
59.15	0.028	19.398	1.48	0.01	60.71	0.025	0.567	1.12	0.05
82.13	0.027	16.149	1.46	0.01	79.82	0.024	0.951	1.14	0.04
99.87	0.028	11.070	1.37	0.01	99.03	0.028	0.456	1.11	0.04
303.15 K					303.15 K				
18.13	0.024	5.692	2.68	0.02	18.92	0.025	0.233	3.16	0.38
43.68	0.024	5.009	3.29	0.02	39.45	0.024	0.298	3.14	0.50
63.30	0.029	5.520	3.01	0.02	60.28	0.026	0.304	3.12	0.47
82.93	0.029	5.221	3.11	0.02	81.27	0.026	0.338	2.98	0.45
102.72	0.028	4.244	3.12	0.03	102.37	0.028	0.385	2.96	0.50

The temperature dependence of the effective sorption rate for the four adsorbents is shown in Figure 8 with higher sorption rates observed at higher temperatures. The sorption rate of CH₄ for all the adsorbents showed a strong temperature dependence, as did the sorption rate of N₂ for the three adsorbents measured at both temperatures (zeolite 13X, zeolite 4A and MSC-3K 172). The activation energies of CH₄ and N₂ diffusion were estimated using an Arrhenius type equation [30], and were found to be (10 – 20) kJ·mol⁻¹, which is comparable with the enthalpy of adsorption for these systems.

Figure 8 Temperature dependence of effective sorption rate

5. Conclusions

Equilibrium capacities and sorption kinetics for pure CH₄ and N₂ were measured for several widely-available adsorbents using a commercial volumetric system at pressures from (5 to 100) kPa and temperatures of (273 and 303) K. Literature values for the effective sorption rate, D/r^2 of both gases on these adsorbents varied in all cases by nearly an order of magnitude or more. Accurate measurements of the sorption rate in this work were found to require two key elements in the method and analysis of the dynamic uptake data. First, correction of the dynamic uptake data for the effects of gas expansion by calibrating the system response with helium was important to the accurate determination of the initial condition. Second, use of the non-isothermal Fickian diffusion model was found to be essential for reliable analysis of the ROA data, even for the small sample masses studied here. For adsorbents with small heat-to-mass transfer ratios (i.e. small values of α as defined in Eq (9)), such as activated carbon Norit RB3 and zeolite 13X, use of the isothermal linear driving force model results in apparent sorption rate values at least an order of magnitude too small. A small pressure dependence was observed only for the adsorbents MSC-3K 172 and zeolite 4A, with an increased (but still small) effective sorption rate observed at higher pressures. The sorption rates of both CH₄ and N₂ for all four adsorbents showed a clear temperature dependence with Arrhenius-type activation energies around (10 - 20) kJ·mol⁻¹.

For the adsorbents studied here, Norit RB3 and zeolite 13X have such fast and similar kinetics that any separation of N₂ and CH₄ would rely on their equilibrium selectivity for CH₄ over N₂. However, while zeolite 4A and MSC-3K 172 are also methane selective at equilibrium, their uptake of N₂ is sufficiently faster than that of CH₄ that they are kinetically selective for N₂ over CH₄. In both cases the kinetic selectivity $\left(\beta_{N_2/CH_4} = \frac{1}{\alpha_{CH_4/N_2}} \sqrt{\frac{D_{N_2}}{D_{CH_4}}}\right)$ [53] is modest (1.4 to 2.2) at the conditions studied in this work, in comparison for example with those reported for Sr-UPRM-5 [54] (β_{N_2/CH_4} =25.42) and Sr-ETS-4 [55] (β_{N_2/CH_4} =21.62). However, both zeolite 4A and MSC-3K 172 are more readily available and lower in price than these specialised adsorbents, and might be engineered for N₂ removal from CH₄ rich gas streams using novel cycle designs such as dual reflux pressure swing adsorption [10].

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References:

- [1] S. Sircar, Air fractionation by adsorption, *Separation Science and Technology* 23 (1988) 2379-2396.
- [2] D.-K. Moon, Y.-H. Kim, H. Ahn, C.-H. Lee, Pressure swing adsorption process for recovering H₂ from the effluent gas of a melting incinerator, *Industrial & Engineering Chemistry Research* 53 (2014) 15447-15455.
- [3] K.B. Lee, M.G. Beaver, H.S. Caram, S. Sircar, Novel thermal-swing sorption-enhanced reaction process concept for hydrogen production by low-temperature steam methane reforming, *Industrial & Engineering Chemistry Research* 46 (2007) 5003-5014.
- [4] J. Yang, C.-H. Lee, J.-W. Chang, Separation of hydrogen mixtures by a two-bed pressure swing adsorption process using zeolite 5A, *Industrial & Engineering Chemistry Research* 36 (1997) 2789-2798.
- [5] G. Xiao, R. Singh, A. Chaffee, P. Webley, Advanced adsorbents based on MgO and K₂CO₃ for capture of CO₂ at elevated temperatures, *International Journal of Greenhouse Gas Control* 5 (2011) 634-639.
- [6] G. Xiao, P. Xiao, S. Lee, P.A. Webley, CO₂ capture at elevated temperatures by cyclic adsorption processes, *RSC Advances* 2 (2012) 5291-5297.
- [7] N. Hedin, L. Andersson, L. Bergström, J. Yan, Adsorbents for the post-combustion capture of CO₂ using rapid temperature swing or vacuum swing adsorption, *Applied Energy* 104 (2013) 418-433.
- [8] T.E. Rufford, S. Smart, G.C.Y. Watson, B.F. Graham, J. Boxall, J.C. Diniz da Costa, E.F. May, The removal of CO₂ and N₂ from natural gas: A review of conventional and emerging process technologies, *Journal of Petroleum Science and Engineering* 94-95 (2012) 123-154.
- [9] A. Samanta, A. Zhao, G.K.H. Shimizu, P. Sarkar, R. Gupta, Post-combustion CO₂ capture using solid sorbents: A review, *Industrial & Engineering Chemistry Research* 51 (2011) 1438-1463.
- [10] T.L. Saleman, G. Li, T.E. Rufford, P.L. Stanwix, K.I. Chan, S.H. Huang, E.F. May, Capture of low grade methane from nitrogen gas using dual-reflux pressure swing adsorption, *Chemical Engineering Journal* 281 (2015) 739-748.
- [11] V.P. Mulgundmath, F.H. Tezel, F. Hou, T.C. Golden, Binary adsorption behaviour of methane and nitrogen gases, *J Porous Mater* 19 (2012) 455-464.
- [12] G. Spoorthi, R.S. Thakur, N. Kaistha, D.P. Rao, Process intensification in PSA processes for upgrading synthetic landfill and lean natural gases, *Adsorption* 17 (2011) 121-133.
- [13] A. Olajossy, Effective recovery of methane from coal mine methane gas by vacuum pressure swing adsorption: a pilot scale case study, *Chemical Engineering and Science* 1 (2013) 46-54.
- [14] J.-S. Bae, S. Su, X.X. Yu, Enrichment of ventilation air methane (VAM) with carbon fiber composites, *Environmental Science & Technology* 48 (2014) 6043-6049.
- [15] D. Do, Analysis of adsorption kinetics in a single homogeneous particle, *Adsorption Analysis: Equilibria and Kinetics*, Imperial College Press, 2011, pp. 519-602.
- [16] R.M. Rynders, M.B. Rao, S. Sircar, Isotope exchange technique for measurement of gas adsorption equilibria and kinetics, *AIChE Journal* 43 (1997) 2456-2470.
- [17] Y. Yang, A.M. Ribeiro, P. Li, J.-G. Yu, A.E. Rodrigues, Adsorption equilibrium and kinetics of methane and nitrogen on carbon molecular sieve, *Industrial & Engineering Chemistry Research* 53 (2014) 16840-16850.
- [18] Y. Ju, Y. Park, D. Park, J.-J. Kim, C.-H. Lee, Adsorption kinetics of CO₂, CO, N₂ and CH₄ on zeolite LiX pellet and activated carbon granule, *Adsorption* 21 (2015) 419-432.
- [19] T.J. Giesy, Y. Wang, M.D. LeVan, Measurement of mass transfer rates in adsorbents: new combined-technique frequency response apparatus and application to CO₂ in 13X zeolite, *Industrial & Engineering Chemistry Research* 51 (2012) 11509-11517.

- [20] M.I. Hossain, Volumetric swing frequency response method for determining mass transfer mechanisms in microporous adsorbents (Doctoral dissertation) College of Engineering and Computing, University of South Carolina, 2014.
- [21] T.E. Rufford, G.C.Y. Watson, T.L. Saleman, P.S. Hofman, N.K. Jensen, E.F. May, Adsorption equilibria and kinetics of methane + nitrogen mixtures on the activated carbon Norit RB3, *Industrial & Engineering Chemistry Research* 52 (2013) 14270-14281.
- [22] J.A.C. Silva, K. Schumann, A.E. Rodrigues, Sorption and kinetics of CO₂ and CH₄ in binderless beads of 13X zeolite, *Microporous and Mesoporous Materials* 158 (2012) 219-228.
- [23] D. Friedrich, E. Mangano, S. Brandani, Automatic estimation of kinetic and isotherm parameters from ZLC experiments, *Chemical Engineering Science* 126 (2015) 616-624.
- [24] M.A. Sheikh, M.M. Hassan, K.F. Loughlin, Adsorption equilibria and rate parameters for nitrogen and methane on Maxsorb activated carbon, *Gas Separation & Purification* 10 (1996) 161-168.
- [25] A. Malek, S. Farooq, Kinetics of hydrocarbon adsorption on activated carbon and silica gel, *AIChE Journal* 43 (1997) 761-776.
- [26] Y. Park, Y. Ju, D. Park, C.-H. Lee, Adsorption equilibria and kinetics of six pure gases on pelletized zeolite 13X up to 1.0 MPa: CO₂, CO, N₂, CH₄, Ar and H₂, *Chemical Engineering Journal* 292 (2016) 348-365.
- [27] T.L.P. Dantas, F.M.T. Luna, I.J. Silva Jr, A.E.B. Torres, D.C.S. De Azevedo, A.A. Rodrigues, R.F.P.M. Moreira, Modelling of the fixed-bed adsorption of carbon dioxide and a carbon dioxide-nitrogen mixture on zeolite 13X, *Brazilian Journal of Chemical Engineering* 28 (2011) 533-544.
- [28] J.A. Delgado, V.I. Águeda, M.A. Uguina, J.L. Sotelo, P. Brea, C.A. Grande, Adsorption and diffusion of H₂, CO, CH₄, and CO₂ in BPL activated carbon and 13X zeolite: Evaluation of performance in pressure swing adsorption hydrogen purification by simulation, *Industrial & Engineering Chemistry Research* 53 (2014) 15414-15426.
- [29] Y.S. Bae, C.H. Lee, Sorption kinetics of eight gases on a carbon molecular sieve at elevated pressure, *Carbon* 43 (2005) 95-107.
- [30] H. Ahn, H.-K. Yoo, Y. Shul, S. Hyun, C.-H. Lee, Diffusion mechanism of N₂ and CH₄ in pelletized zeolite 4A, 5A and CaX, *Journal of Chemical Engineering of Japan* 35 (2002) 334-345.
- [31] R.J. Mohr, D. Vorkapic, M.B. Rao, S. Sircar, Pure and binary gas adsorption equilibria and kinetics of methane and nitrogen on 4A zeolite by isotope exchange technique, *Adsorption* 5 (1999) 145-158.
- [32] N. Haq, D.M. Ruthven, Chromatographic study of sorption and diffusion in 4A zeolite, *Journal of Colloid and Interface Science* 112 (1986) 154-163.
- [33] D.M. Ruthven, L.-K. Lee, H. Yucel, Kinetics of non-isothermal sorption in molecular sieve crystals, *AIChE Journal* 26 (1980) 16-23.
- [34] C. Guan, C. Yang, K. Wang, Adsorption kinetics of methane on a template-synthesized carbon powder and its pellet, *Asia-Pacific Journal of Chemical Engineering* 6 (2011) 294-300.
- [35] Z. Zhang, W. Zhang, X. Chen, Q. Xia, Z. Li, Adsorption of CO₂ on zeolite 13X and activated carbon with higher surface area, *Separation Science and Technology* 45 (2010) 710-719.
- [36] X. Hu, E. Mangano, D. Friedrich, H. Ahn, S. Brandani, Diffusion mechanism of CO₂ in 13X zeolite beads, *Adsorption* 20 (2014) 121-135.
- [37] M. Kocirik, P. Struve, M. Bulow, Analytical solution of simultaneous mass and heat transfer in zeolite crystals under constant-volume/variable-pressure conditions, *Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases* 80 (1984) 2167-2174.
- [38] M.I. Hossain, Volume swing frequency response method for determining mass transfer mechanisms in microporous adsorbents (Doctoral dissertation). Retrieved from <http://scholarcommons.sc.edu/etd/2585>, 2014.
- [39] N.K. Jensen, T.E. Rufford, G. Watson, D.K. Zhang, K.I. Chan, E.F. May, Screening zeolites for gas separation applications involving methane, nitrogen, and carbon dioxide, *Journal of Chemical & Engineering Data* 57 (2011) 106-113.
- [40] J.-G. Jee, M.-B. Kim, C.-H. Lee, Pressure swing adsorption processes to purify oxygen using a carbon molecular sieve, *Chemical Engineering Science* 60 (2005) 869-882.
- [41] L.-K. Lee, D.M. Ruthven, Analysis of thermal effects in adsorption rate measurements, *Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases* 75 (1979) 2406-2422.

- [42] R. Span, E.W. Lemmon, R.T. Jacobsen, W. Wagner, A reference quality equation of state for Nitrogen, *International Journal of Thermophysics* 19 (1998) 1121-1132.
- [43] U. Setzmann, W. Wagner, A new equation of state and tables of thermodynamic properties for methane covering the range from the melting line to 625 K at pressures up to 100 MPa, *Journal of Physical and Chemical Reference Data* 20 (1991) 1061-1155.
- [44] T.H. Saleman, G.Y. Watson, T. Rufford, P. Hofman, K.I. Chan, E. May, Capacity and kinetic measurements of methane and nitrogen adsorption on H⁺-mordenite at 243–303 K and pressures to 900 kPa using a dynamic column breakthrough apparatus, *Adsorption* 19 (2013) 1165-1180.
- [45] S. Sircar, J.R. Hufton, Why does the linear driving force model for adsorption kinetics work?, *Adsorption* 6 (2000) 137-147.
- [46] M.S. Shafeeyan, W.M.A. Wan Daud, A. Shamiri, A review of mathematical modeling of fixed-bed columns for carbon dioxide adsorption, *Chemical Engineering Research and Design* 92 (2014) 961-988.
- [47] E. Glueckauf, J.I. Coates, 241. Theory of chromatography. Part IV. The influence of incomplete equilibrium on the front boundary of chromatograms and on the effectiveness of separation, *Journal of the Chemical Society (Resumed)* (1947) 1315-1321.
- [48] D.M. Ruthven, *Principles of adsorption and adsorption processes*, Wiley 1984.
- [49] B.N. Taylor, C.E. Kuyatt, Guidelines for evaluating and expressing the uncertainty of NIST measurement results, *National Institute of Standards and Technology*, 1994.
- [50] T.L. Saleman, G. Xiao, E.F. May, Key adsorbent properties for N₂/CH₄ separations measured with a specialised breakthrough column apparatus, to be submitted to *Adsorption*, (2016).
- [51] T.L. Saleman, *Adsorption-based separations of gaseous nitrogen and methane mixtures*, School of mechanical and chemical engineering, The University of Western Australia, Perth, Western Australia, 2016.
- [52] M. Bulow, Comments on the publication " Adsorption kinetics of CO₂ , CO, N₂ and CH₄ on zeolite LiX pellet and activated carbon granule " by Youngsan Ju, Yongha Park, Dooyoung Park, Jae-Jeon Kim and Chang-Ha Lee, *Adsorption*, 21, 419-432 (2015), https://www.researchgate.net/publication/293333947_Comments_on_the_publication_Adsorption_kinetics_of_CO2_CO_N2_and_CH4_on_zeolite_LiX_pellet_and_activated_carbon_granule_by_Youngsan_Ju_Yongha_Park_Dooyoung_Park_Jae-Jeon_Kim_and_Chang-Ha_Lee_Adsorption, 2016.
- [53] D.M. Ruthven, S. Farooq, K.S. Knaebel, *Pressure swing adsorption*, VCH Publishers, Inc., New York, 1994.
- [54] M. Yu, J.N. Primera-Pedrozo, M.E. Marcano-González, A.J. Hernández-Maldonado, Selective adsorption of N₂ over CH₄ in flexible Sr²⁺- and Ba²⁺-UPRM-5 (TEA) titanium silicates: Effect of activation temperature, *Chemical Engineering Journal* 252 (2014) 311-319.
- [55] A. Jayaraman, A.J. Hernandez-Maldonado, R.T. Yang, D. Chinn, C.L. Munson, D.H. Mohr, Clinoptilolites for nitrogen/methane separation, *Chemical Engineering Science* 59 (2004) 2407-2417.

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