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Adsorption of Oxygen on Superactivated Carbon

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Twelve adsorption isotherms of oxygen on a high surface activated carbon have been collected with a volumetric apparatus for the range (118−313) K and (0−10) MPa. The isosteric enthalpy change of adsorption was evaluated on the basis of these isotherms. It shows a descending trend with the increased amount adsorbed. A model is presented for the experimental isotherms on the basis of the Gibbs definition and the determination of absolute adsorption. The model fits the isotherms well for the range of experiments. On the basis of the measurements, the enhancement effect of adsorption for the storage of oxygen was proven.

Introduction

Physical adsorption of supercritical gases on activated carbons has found many important applications, for example, in the pressure swing adsorption processes and the adsorptive storage of natural gas and hydrogen.[1−3] Because the adsorbate cannot be in the liquid state at above-critical temperatures, supercritical adsorption must assume a different mechanism than the adsorption at subcritical temperatures.[4] Different methods were applied to model the supercritical isotherms,[5−10] indicating the fact that the adsorption theory of supercritical gases has not been matured. Although molecular simulation of adsorption provides a tool to explore the nature of supercritical adsorption, experimental data are required to verify the simulation results. In addition, plenty of experimental data are usually the prerequisite condition for the development of a sophisticated theory. The experimental data of oxygen adsorption are available only for low pressures and isolated temperatures.[11] To complement the database of high pressure adsorption, the authors measured the adsorption of oxygen on an activated carbon with high surface area for a wide range of temperatures and pressures. Because oxygen is widely applied in practice for both industry and health care, this set of data provided the necessary information regarding the enhancement effect of adsorption for oxygen storage.

Experimental Section

The adsorption isotherms were collected with the same volumetric setup as was used previously for other measurements, and the details of the method were described elsewhere.[12−16] The activated carbon used was AX-21, although it is not commercially available presently. The specific surface area of the carbon is close to 3000 m^2/g. About 10 g of carbon sample was put in the adsorption cell, and the volume of the void space was determined at 25 °C with helium of 99.995% purity. The oxygen used in the experiments is of 99.95% purity. The carbon sample was dried to reach a constant weight in a vacuum drier at 120 °C before the adsorption measurements. Adsorption equilibrium was measured for a temperature range from 118.15 K to 313.15 K, covering the critical temperature of oxygen (154.58 K[17]). The temperature interval between isotherms was 15 K above 238.15 K and 20 K below this temperature. The adsorption pressure is from zero up to 10 MPa. The relative error of the measured amount adsorbed was analyzed on the basis of the calculation formula and the accuracy of instrumentation.[18] It was determined that the relative error in the adsorption measurement is 4% for the temperature below 158 K and 2.5% for higher temperatures.

Experimental Isotherms. The 12 isotherms obtained are shown in Figure 1, where dots are the experimental data and curves are the model predicted as described in the subsequent section. The values of the compressibility factor used for the calculation of the amounts adsorbed were derived with interpolation from the experimental data[19] for 118.15 K, 138.15 K, and 158.15 K, while those for the other temperatures were determined using the Lee−Kesler equation of state.[17] The two isotherms below the critical temperature show typical type-I features because AX-21 is a microporous activated carbon, for which the adsorption mechanism of volume filling functions.[20] All the isotherms above the critical temperature show typical features of supercritical adsorption. The amount adsorbed initially increases as the type-I isotherm behaves and then reaches a maximum, after which the amount adsorbed decreases with the increasing pressure. Noticeable is the isotherm for 158.15 K. The drastic descent of the isotherm indicates the transition of the adsorption mechanism from the volume filling to the monomolecular coverage in the vicinity of the critical temperature. [21]

Evaluation of the Adsorption Heat. The isosteric enthalpy change of adsorption, known also as the differential heat of adsorption, can be evaluated from these adsorption isotherms on the basis of the Clausius−Clapeyron equation:

$$q^{\mathrm{st}} = -\Delta H = -R\left[\frac{\mathrm{d}\ln f}{\mathrm{d}(1/T)}\right]_n \tag{1}$$

where T is the temperature, n is the amount adsorbed, and

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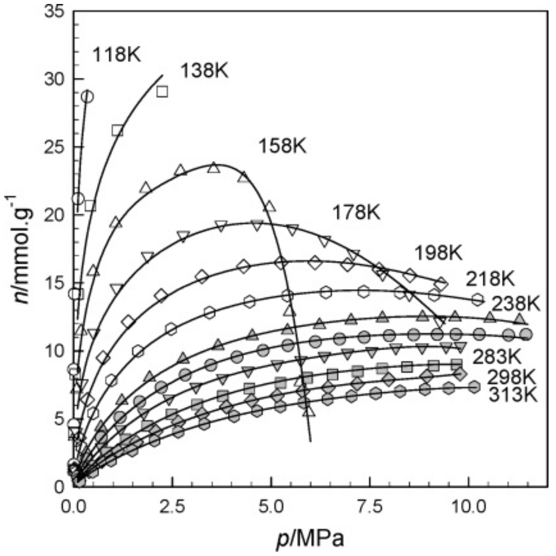

Figure 1. Adsorption isotherms of O_2 on activated carbon AX-21. Dots, experimental; curves, model predicted.

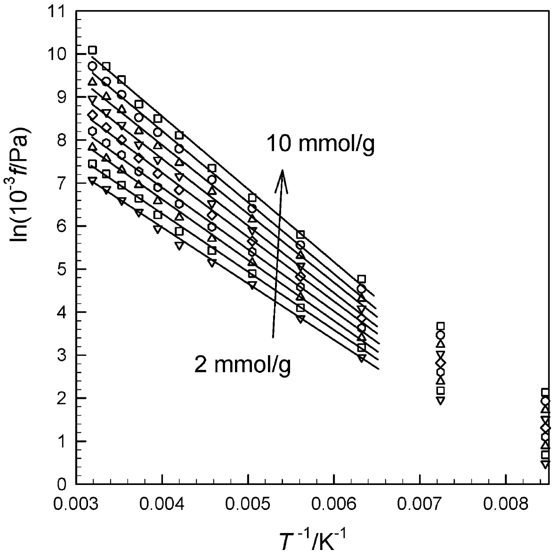

Figure 2. Isosteres of O_2 on activated carbon AX-21 for (118−313) K and (0−10) MPa.

f is the fugacity, which relates to the compressibility factor through the following equation:

$$\ln\left(\frac{f}{P}\right) = \int_0^P \frac{(Z-1)}{P}\,\mathrm{d}p \qquad (2)$$

Therefore, the value of fugacity was determined from the known values of the compressibility factor. The isosteric enthalpy change at different amounts adsorbed can be determined by the isosteres shown in Figure 2. The linear plots shown in the figure do not include the data for the 138.15 K and 118.15 K isotherms because the adsorption mechanism for the subcritical temperatures is different and, hence, yield a different magnitude of the enthalpy change of adsorption. The adsorbate molecules are preferably adsorbed on the sites with stronger potential, and the carbon surface is usually not energetically homogeneous; therefore, the isosteric enthalpy change decreases with the increasing amounts adsorbed, as shown in Figure 3.

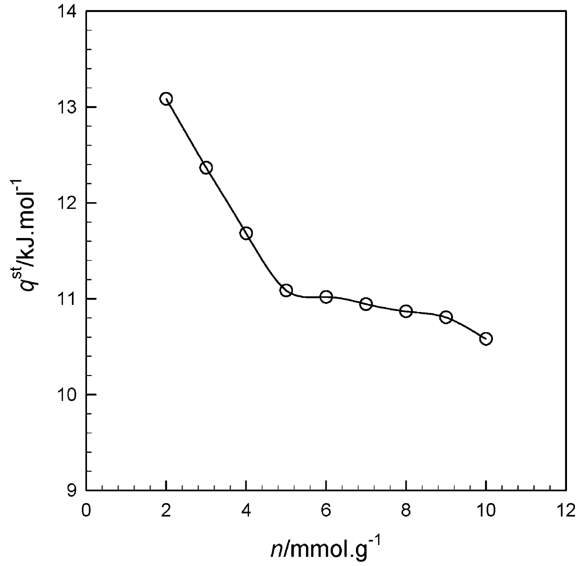

Figure 3. Variation of the isosteric enthalpy change of adsorption with the amount adsorbed.

Isotherm Modeling. To set up a model for the experimental isotherms, one has to understand the adsorption nature, and an appropriate model can usually provide valuable information of the adsorption system, as the Langmuir or BET models usually do. Different models have been presented for the supercritical isotherms that show a maximum and a descending section.[5−10] A different model was suggested on the basis of the classical adsorption theory.[14,22−24] The starting point of the model was the Gibbs definition of adsorption,[26] which applies for both above and below the critical temperature:

$$n = n^{\mathrm{s}} - \rho_{\mathrm{g}} V_{\mathrm{a}} = V_{\mathrm{a}}(\rho_{\mathrm{a}} - \rho_{\mathrm{g}}) \qquad (3)$$

where n^{s} is the total of adsorptive molecules included in the adsorption space (or adsorbed phase), which is equal to the product of the volume and the density of the space, $V_{\mathrm{a}}\rho_{\mathrm{a}}$, or the sum of the excess adsorption measured experimentally, n, and the product of the adsorbed phase volume and the gas phase density, ρ_{g}. However, neither V_{a} nor ρ_{a} can be experimentally measured; therefore, the quantity of the absolute adsorption, n^{s}, is difficult to determine. On the other hand, should the quantity of absolute adsorption be determined on the basis of the experimental data, the Gibbs definition would be a good starting point to model the supercritical isotherm, and the classical adsorption theory would have thus been extended to the above-critical temperatures. The principle of our method relies on the fact that both the excess and the absolute quantity of adsorption are equal provided the adsorbate concentration on the sorbent surface is dilute. Therefore, the experimental data of the excess adsorption corresponding to the condition of dilute surface concentration were used to formulate the absolute adsorption quantity. The formulation established in this way applies certainly for all ranges of the adsorption phenomenon where eq 3 applies. The modeling procedure is basically a two-step data screening. First, a general isotherm was constructed for different temperatures as the one shown in Figure 4 for the present set of data. The Henry law constant, K, used in the construction of the general isotherm was determined on the basis of the virial equation of isotherms:

$$\frac{aP}{n} = \exp\left(2c_1 n + \frac{3}{2}c_2 n^2 + \ldots\right) \qquad (4)$$

The plot of $\ln(p/n)$ versus n will be linear as n approaches

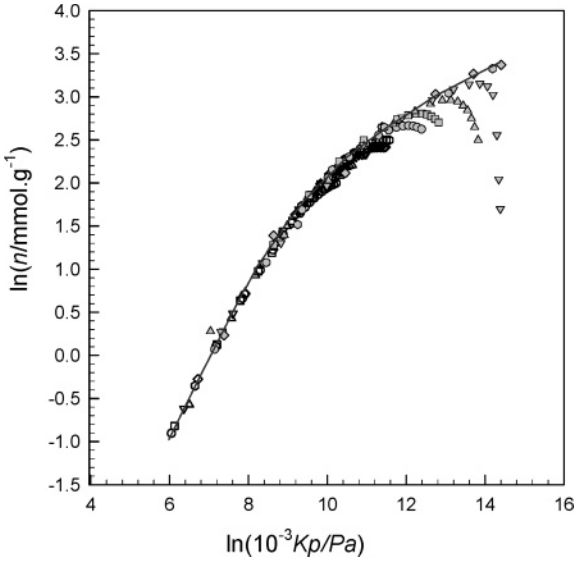

Figure 4. General isotherm of the oxygen adsorption data for (118−313) K.

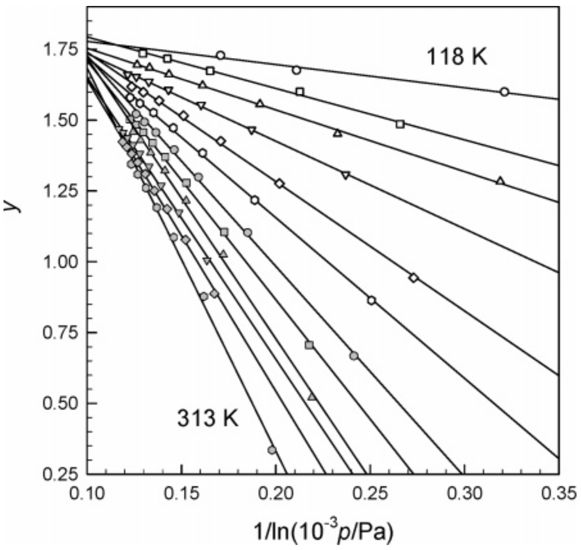

Figure 5. Plots for the formulation of absolute adsorption.

Table 1. Model Parameter Values

T/K	n_0^{s}/mmol·g^{-1}	b	q
118.15	47.6336	1.4935	0.4319
138.15	42.6913	0.8827	0.4134
158.15	36.1	0.7319	0.4456
178.15	36.1	0.5037	0.4599
198.15	36.1	0.3501	0.5315
218.15	36.1	0.2496	0.6125
238.15	36.1	0.1760	0.7043
253.15	36.1	0.1385	0.7565
268.15	36.1	0.1106	0.7893
283.15	36.1	0.0888	0.8114
298.15	36.1	0.0725	0.8115
313.15	36.1	0.0598	0.7942

zero, and the value of K can be determined from the intercept of the plot.[27] Some data in Figure 4 are not on the smooth curve. However, they correspond to a higher surface concentration of adsorbate[28] and were discarded in the next step of data screening. Next, the model equation of the general isotherm was expanded to the Taylor series and the terms of higher order were discarded, and linear isotherms shown in Figure 5 were formed with the data that remained. The ordinate of Figure 5 is the double logarithm of the 10 times enlarged amount adsorbed, n, expressed in millimoles per gram, that is, $y = \ln[\ln(10n/\mathrm{mmol{\cdot}g^{-1}})]$. The linear plots must satisfy the constraint for $n = n^{\mathrm{s}}$. Because of linearity, the formulation of the absolute adsorption contains only two parameters:

$$\ln[\ln(n^{\mathrm{s}}/\mathrm{mmol{\cdot}g^{-1}})] = \alpha + \frac{\beta}{\ln P} \tag{5}$$

where the units of P are 10^3Pa and n^{s} is in millimoles per gram but 10 times enlarged in order to facilitate the mathematical operations. The values of the parameters α and β could be correlated with temperature by polynomial functions:

$$\alpha = -0.6899 + 0.056\,19(T/K) - 4.6554 \times 10^{-4}(T/K)^2 + 1.7357 \times 10^{-6}(T/K)^3 - 2.2588 \times 10^{-9}(T/K)^4 \tag{6.1}$$

$$\beta = 15.8848 - 0.3572(T/K) + 2.9700 \times 10^{-3}(T/K)^2 - 1.1551 \times 10^{-5}(T/K)^3 + 1.5310 \times 10^{-8}(T/K)^4 \tag{6.2}$$

The quantity of the absolute adsorption corresponding to the value of the excess adsorption at a given set of temperature and pressure can, therefore, be evaluated with eq 5.

It is known from eq 3 that both the volume, V_{a}, and density, ρ_{a}, of the adsorbed phase can be evaluated presently, since the values of n, n^{s}, and ρ_{g} have been known. Therefore, eq 3 deserves to be the model of describing the adsorption isotherms even for supercritical temperatures. The volume of the adsorbed phase, V_{a}, has to be evaluated beforehand:

$$V_{\mathrm{a}} = \frac{n^{\mathrm{s}} - n}{\rho_{\mathrm{g}}} \tag{7}$$

The second term of the right-hand side of eq 3 was omitted for modeling the adsorption isotherms at subcritical temperatures, and all the isotherm equations were presented for the absolute adsorption. On the basis of the mechanism of monomolecular coverage, an isotherm equation was proposed by the authors.[24] The new isotherm equation works well for the supercritical adsorption isotherms till today:

$$n^{\mathrm{s}} = n_0^{\mathrm{s}}[1 - \exp(-bP^{q})] \tag{8}$$

Both values of the adsorbed phase volume and the gas phase density can be expressed by polynomial functions to facilitate the calculations in the subsequent nonlinear regression. Therefore, the expression for the excess adsorption isotherms becomes

$$n = n_0^{\mathrm{s}}[1 - \exp(-bp^{q})] - (\sum_{i=0}^{4} c_i p^i)(\sum_{j=0}^{4} c_j p^j) \tag{9}$$

There are three parameters to be evaluated from the experimental isotherms: the saturation quantity of the absolute adsorption, n_0^{s}, in millimoles per gram; parameter b in inverted megapascals relating to the adsorption affinity; and numeric parameter q relating to the surface heterogeneity. Fitting eq 9 to the 12 isotherms aforementioned, values of the three parameters were evaluated, as shown in Table 1 for different temperatures. A satisfactory fit of the model to the experimental data was obtained, as shown in Figure 1, by the consistency between the dots

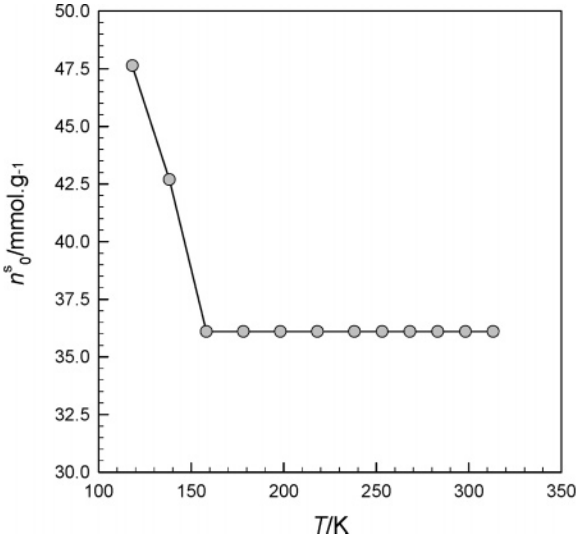

Figure 6. Variation of the parameter n_0^{s} with temperature.

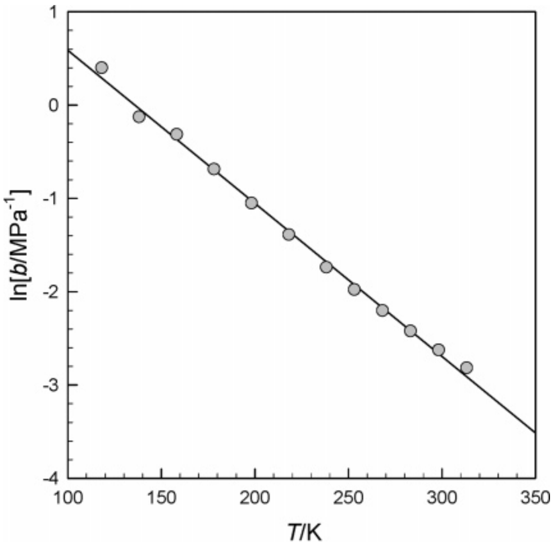

Figure 7. Variation of the parameter b with temperature.

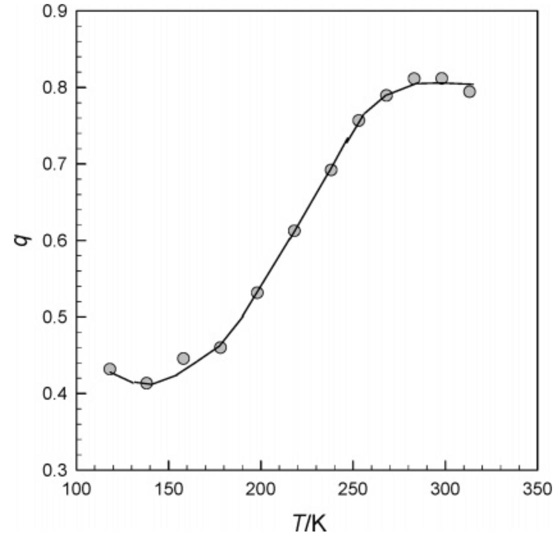

Figure 8. Variation of the parameter q with temperature.

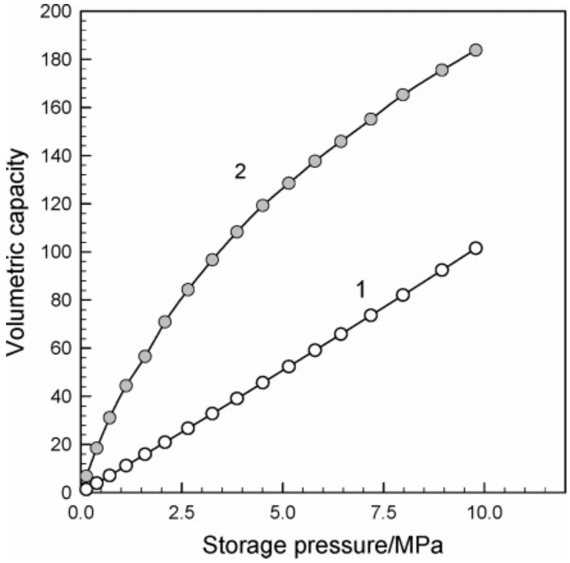

Figure 9. Storage enhancement of filling carbon pellets in containers at 25 °C. Curve 1, empty; curve 2, filled with carbon pellets.

(experimental) and the curves (model predicted). Because the isotherms in both sides of the critical temperature belong to the same type, eq 9 successfully modeled all the isotherms collected. The variation trend of the parameters with temperature, shown respectively in Figures 6−8, is reasonable. The parameter n_0^{s} takes higher values below the critical temperature, since the adsorption mechanism is different, and the possibility of liquefaction allows higher saturation quantity. However, the mechanism of monomolecular coverage functions for all supercritical temperatures; therefore, the saturation quantity of absolute adsorption stays constant. The value of parameter b varies exponentially with temperature. Parameter q is a numeric index of the surface energetic heterogeneity recognized by the adsorptive molecules. The surface is uniform if $q = 1$. The value of q exponentially increases with temperature and shows a minimum near the critical temperature.

Enhanced Storage of Oxygen with Adsorption. Oxygen is usually stored in high pressure cylinders or sacks of normal pressure. Because the density of the adsorbed oxygen is much higher than the oxygen in free state, adsorption can be applied to enhance the storage. Superactivated carbon with a high surface area was developed initially for the adsorptive storage of natural gas. The higher the specific surface area, the less the bulk density of activated carbon. To increase the amount adsorbed in a given volume, more mass of carbon is preferred to fill in; therefore, carbon powder was pressed into pellets. The amount adsorbed on unit mass of activated carbon pellets was decreased for about 20−30% due to the blockage of micropores during pressing.[29] However, the total gas stored in the volume still increased because the bulk density of carbon increased for more than two times. The total quantity of gas stored in unit volume is the sum of the gas adsorbed on the carbon surface and that compressed in the void space of the container. For example, the density of carbon pellets is 0.72 kg/dm^3, the density of graphite is 2.27 kg/dm^3, and the volume of the void space in 1 L is $(1 - 0.72/2.27) = 0.683$ L. The total volumetric storage capacity was expressed in the standard volumes of oxygen per unit volume of container (*V/V*) that filled with carbon pellets and is shown in Figure 9 in comparison with compression only. Apparently, filling active carbon pellets considerably enhances the storage capacity of oxygen. However, the enhancement factor, defined as the ratio of storage capacity with activated carbon to that without carbon, decreases with the increasing storage pressure, as shown in Figure 10 because the adsorption of oxygen reaches gradually

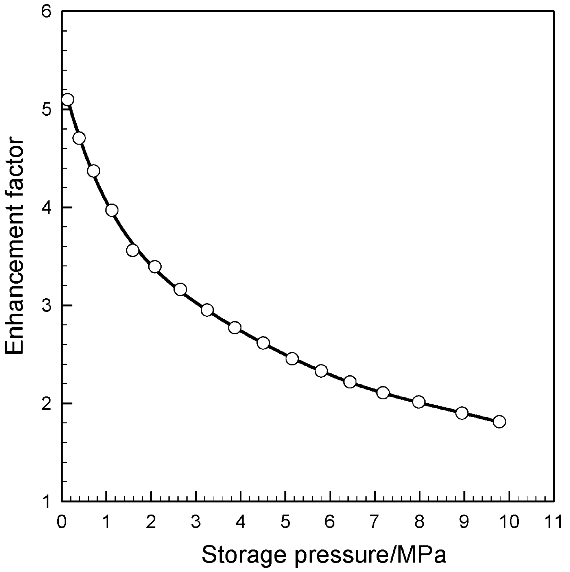

Figure 10. Variation of the enhancement factor with storage pressure at 298 K.

saturation as pressure increases. The enhancement effect can also be applied to reduce the storage pressure and the weight of cylinders. The total cost of canned oxygen will thus be decreased.

Conclusion

The adsorption data of oxygen on active carbon of high surface area were presented for the range (118−313) K and (0−10) MPa. Although the condition covers the critical temperature, this set of isotherms was well modeled with the common model for supercritical adsorption because the isotherms below and above the critical temperature belong to the same type. On the basis of the set of data, adsorptive storage of oxygen was suggested and the enhancement factor of adsorption was calculated.

Supporting Information Available:

Table showing tabulated experimental data. This material is available free of charge via the Internet at http://pubs.acs.org.

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