

Enthalpy Changes of Adsorption of Tetrafluorocarbon (CF₄) and Hexafluoroethane (C₂F₆) on Activated Carbon

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요 약

CF₄와 C₂F₆의 압력이 20.7 kPa 이하일 경우, 활성탄에의 평형흡착량을 여러 온도(293.15-333.15 K)에서 실험적으로 조사하였다. 실험데이터가 가장 잘 맞을 수 있도록 1차층 흡착으로 Langmuir모형을 쓰고 그 다음 단계에는 Freundlich 물리흡착을 이용하는 이단계모형을 제안한다. 1단계에 대한 흡착엔탈피를 구하기 위해 실험데이터의 최초기울기를 이용하였고, Clausius-Clapeyron식을 사용함으로써 2단계에 대한 흡착엔탈피를 구하였다. CF₄의 경우 1, 2단계의 흡착엔탈피는 각각 25.9와 11.8 kJ/mol이고, C₂F₆의 경우는 38.7과 38.2 kJ/mol이다.

주제어 : 흡착엔탈피 변화, 사불화탄소, 육불화에탄, PFC

Abstract : Under low pressures of CF₄ and C₂F₆ up to 20.7 kPa, the equilibrium adsorbed quantity on activated carbon was experimentally examined using the volumetric method at various temperatures between 293.15 K and 333.15 K. To give the best fit to the experimental data curve, the two step model (i.e., Langmuir model for the first layer adsorption and then Freundlich physisorption) is suggested. The method of initial slope yielded the enthalpy of adsorption for the first step while we could apply the Clausius-Clapeyron equation to find the heat of adsorption of the second step. They are 25.9 kJ/mol and 11.8 kJ/mol, respectively, with CF₄, and 38.7 and 38.2 kJ/mol with C₂F₆.

Keywords : Enthalpy change of adsorption, Tetrafluorocarbon, Hexafluorocarbonethane, PFC

1. Introduction

Nowadays one of the popular research topics in the world is modeling the global warming process[1,2] and reducing green house gases which cause the ozone layer depletion and the global warming. These harmful phenomena come from more absorption of infrared light due to the green house gases such as carbon dioxide, methane, nitrous oxide, chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), hydrochlorofluorocarbons (HFCs), perfluorocarbons (PFCs), etc[3-5]. Among these chemicals, CFCs that had a lot of uses with refrigerators and air conditioners, have been already replaced by HFCs. PFCs are used as CFC substitutes for cleaning or printing electronic circuit boards, hybrid ICs, etc. However, PFCs which are more stable than CFCs, are not decomposed until they soar up above the stratosphere and thus are considered significant global warming compounds. Thus one needs to be concerned with the emission and life of PFCs in the atmosphere.

Among the PFCs, the light PFCs (i.e., CF₄ and C₂F₆) are the most potentially damaging due to their long atmospheric lifetime. The atmospheric lifetimes of CF₄ and C₂F₆ are estimated to be 50,000 years and 10,000 years, respectively[6]. The main usage of PFCs is the CVD chamber cleaning, dry etching, heat transfer medium and coolant in the semiconductor processing. The total amount of PFC emission is small compared to CO₂, but PFCs contribute to the global warming as much as 6,500 to 9,200 times the same amount of CO₂. Considering the long-lived contribution of PFCs to the global warming, their emissions should be treated somehow to reduce their entry into the atmosphere in the semiconductor industry[7-9].

There are many approaches to reduce and eliminate PFCs emissions from industrial processes. Potential methods are as follows: recovery/recycle of PFCs[10]; conversion of PFCs to non-PFCs[11,12]; process optimization using reconfiguration and endpoint detection[13]; replacement of PFCs with non-PFCs[14]. Among these control technologies, recovery/recycle methods are currently the most available and cost-efficient ways for treating PFCs gases from emissions of industrial processes. In general, the potential technologies are condensation, absorption, adsorption, and membrane separation[15-19].

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For recovery of volatile organic gases, adsorption is a useful method because it offers some recognized advantages. These include the possibility of recovery of raw materials for recycling and a high removal efficiency at a low concentration of adsorbates. Furthermore, this technology often demands low energy costs. It is also important to select the proper adsorbent for the development of an efficient adsorption process. Single-walled carbon nanotubes (SWNTs) can serve as good nanoscale vessels for encapsulation of tetrafluoromethane at 300 K and operating external pressure of 1 bar[20]. However, from an economic point of view, activated carbon is suitable adsorbent for commercial processes such as pressure swing adsorption[21,22].

In this work, the adsorption quantity of CF₄ and C₂F₆ on activated carbon (20 to 40 mesh) were experimentally measured at various temperatures under low pressures of CF₄ and C₂F₆ up to 20.7 kPa by the constant volume method. The objective of this study is to find the heats of adsorption from the two step model which consists of Langmuir model for the first layer adsorption and then Freundlich physisorption.

2. Experimental

2.1. Materials

The adsorbents used in the experiments were activated carbon (20 to 40 mesh) supplied by Darco Co. Their physical properties were measured using an automatic volumetric sorption analyzer (ASAP2010, Micromeritics Instrument Co.) and pycnometer (Accupyc2375, Micromeritics Instrument Co.). These physical

Table 1. Physical properties of the adsorbents

Adsorbents	BET surface area m ² /g	Total pore volume cm ³ /g	Mean pore size Å	Solid density ^{a)} g/cm ³
Activated C 20 to 40 mesh	633.1	0.231	5.9	1.993
Activated C 12 to 20 mesh	549.1	0.200	5.9	2.114

^{a)} Solid density: the density crushed and compressed solid containing no pores

properties are given in Table 1. We used 20 to 40 mesh activated carbon only because smaller particles (or larger mesh) takes less time to reach equilibrium due to faster diffusion into pores. The physical data for another size range (10 to 20 mesh) are, although its activated carbon was not used for this study, presented in Table 1 for comparison. The adsorbents (CF₄ and C₂F₆) were provided by Dae-Han gas Co. and Daikin industry Co. The physical properties of their products are good enough to be used in real processes and the prices are also economical. Their purity was 99.99% and 99.999%, respectively.

2.2. Method

A volumetric type apparatus was used to determine the equilibrium isotherms for the single component systems[8,9]. A schematic diagram of the apparatus is shown in Figure 1. It was composed of an adsorption cell, a loading cell, a vacuum pump, gas cylinders, water bath with temperature controller, pressure

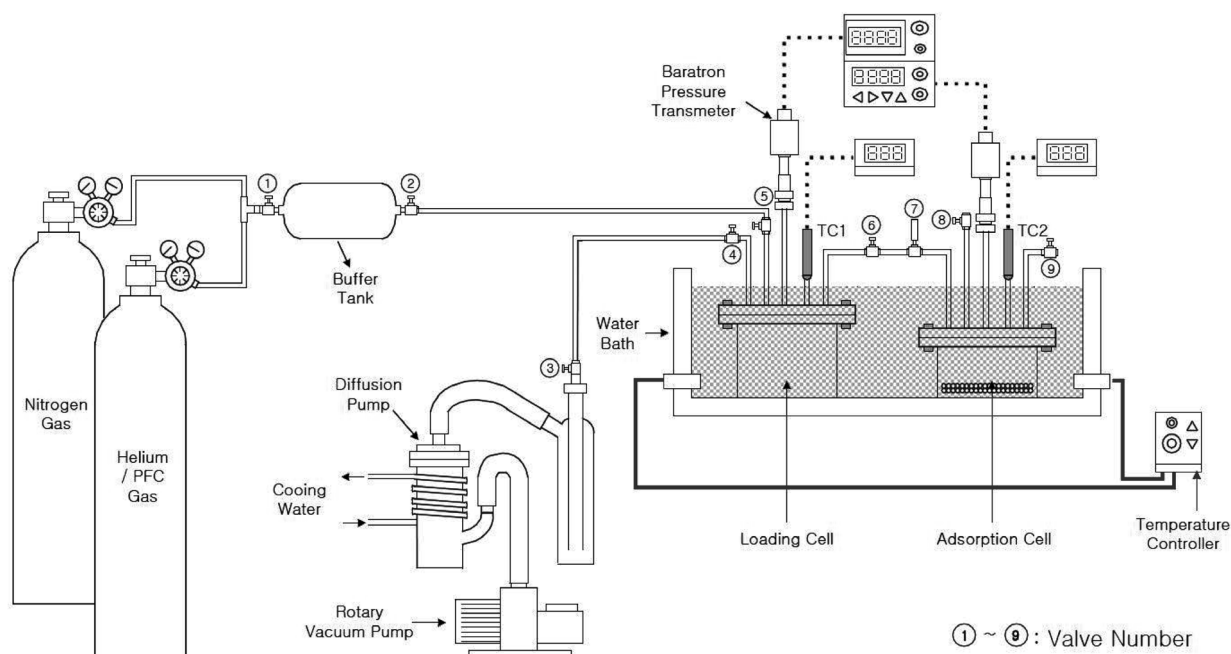


Figure 1. Volumetric apparatus used for adsorption data measurement.

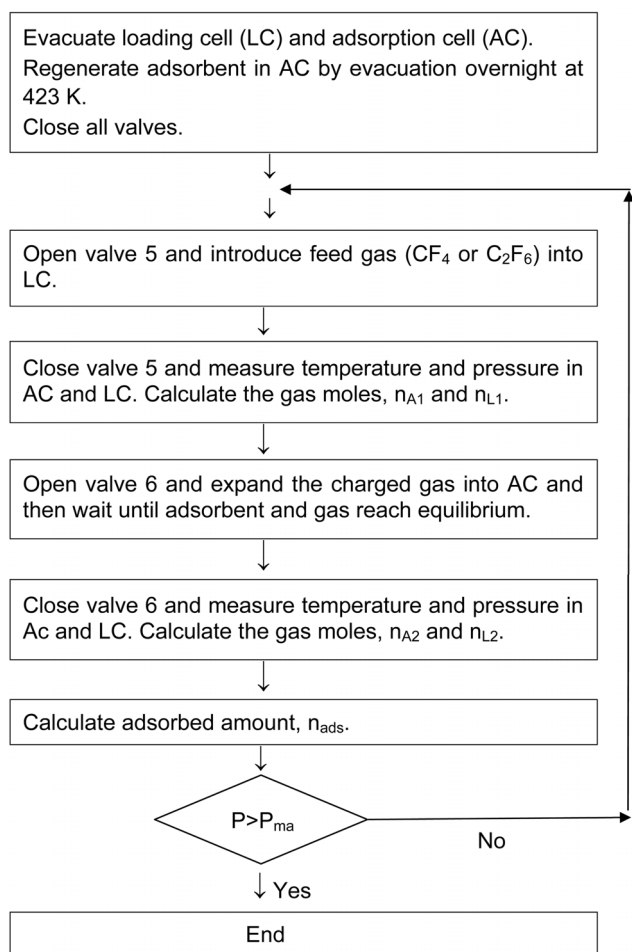


Figure 2. Flow diagram of experiment procedure.

transducer (PT), thermocouple (TC), and displays. Figure 2 displays a flow diagram of the experiment procedure.

The internal volume of the various parts of the system was accurately measured by expanding helium gas. Before each experiment, the adsorbent was outgassed overnight in a vacuum at a pressure lower than 10^{-4} kPa at 423 K. Adsorption isotherms of pure components on various adsorbents were measured at temperatures; 303 K, 323 K, 343 K and pressures up to 20.7 kPa. A static equilibrium technique was used for the measurement of the pure gas adsorption isotherms. The sample gas was introduced into the adsorption cell containing the weighed adsorbent sample. The amount of gas adsorbed was hence determined by performing a material balance on the number of moles present in the gas and the adsorbed phase before and after the addition of a new dose of gas to the adsorption cell using the ideal gas P-V-T relationships.

Adsorbed phase moles are

$$n_{ads} = (n_{L1} - n_{L2}) - (n_{A2} - n_{A1}) \quad (1)$$

where n_L and n_A are moles of gas in the loading cell and the

adsorption cell, respectively. Subscripts 1 and 2 are the before and after supply of PFC gas to the adsorption cell, respectively. The moles of gas (n_{A2}) was measured at adsorption equilibrium.

The adsorbed amount q is

$$q = n_{ads} / w \quad (2)$$

where w is mass of adsorbent.

3. Results and Discussion

We employ the two step model of adsorption for data analysis of the present adsorption experiments. This model applies Langmuir isotherm model until the first layer of adsorbate is covered. Thus this first step is a sort of chemical reaction between the gas phase adsorbent and the solid phase adsorbate. After all the possible spots of adsorbate are covered, the gas phase adsorbent may deposit right on the already-adsorbed spots. This second step may be taken as Freundlich physisorption. Another way of interpretation of the second step is the phase change to a condensed phase. Although most isotherms (for instance, Langmuir, Sips, and Toth isotherms) would fit the experimental data for CF_4 and C_2F_6 in the experimental pressure range (under 20.7 kPa), the two step model is theoretically more reasonable and good enough to predict the adsorbed amounts.

For the second step of physisorption or condensation, the enthalpy change of adsorption ($-\Delta H_2$) can be calculated by the Clausius-Clapeyron equation

$$\left(\frac{\partial \ln P}{\partial T} \right)_q = \frac{-\Delta H_2}{RT^2} \quad (3)$$

where P is the pressure, T is the temperature, and R is the gas constant.

If the difference in the heat capacity of the adsorbate in adsorbed and vapor phases can be neglected,

$-\Delta H_2$ is independent of temperature and Eq. (3) may be integrated directly to yield.

$$\ln P = const + \frac{\Delta H_2}{RT} \quad (4)$$

Assuming that the above approximation concerning the heat capacity is valid, a plot of $\ln P$ versus $1/T$ should yield a linear plot with slope $(\Delta H_2)/R$. This provides a simple and useful method for the determination of the heat of adsorption for CF_4 and C_2F_6 .

As for the first step of the two step model, one can derive the Langmuir isotherm by considering the reaction between empty active surface spots and the gas phase molecules. Langmuir

isotherm is derived as

$$q = \frac{Kq_{\max}P}{1 + KP} \quad (5)$$

where K is the equilibrium constant for the reaction of the second step and q_{\max} is the maximum amount of the first layer adsorption.

One cannot determine from the experimental adsorption isotherms when the first step is finished and when the adsorption process evolves to the second step because this change of adsorption mechanism is not clearly being made. While the first step is still going on, the second step may move in. Rather than using the general form of Langmuir isotherm, Eq. (5), one can calculate the asymptotic slope of the adsorption isotherm curve at zero pressure and obtain the heat of adsorption from the simplified form of Eq. (5) at zero pressure. At zero pressure the adsorbed amount (q) is proportional to the pressure. These initial slopes are listed in Table 2 for the present investigation.

Adsorption experiments of CF₄ and C₂F₆ were performed on activated carbon in the pressure lower than 21 kPa, maintaining the temperature at 293.15 K, 303.15 K, 313.15 K, 323.15 K, and 333.15 K. The adsorption amounts of CF₄ and C₂F₆ increased with increasing pressure and decreased with increasing temperature. These experiments are a typical gas solid reaction and thus samples of solid should be variant from each other when they are newly prepared, which causes experimental data very difficult to reproduce. We should admit that data spread is inevitable in the present research and that every data point should be taken as entailing an error. Figure 3 is a typical data set of experiments with error bars. The solid line going through the data points were carefully drawn. Other isotherm figures that will appear later are results similarly obtained and should be understood to have error bars with them, which were left out for clarity of lines and points. Figures 4 and 5 are displays of the equilibrium amounts adsorbed with respect to the pressure at the above-mentioned temperatures. One can see that adsorption is more favorable with lower temperature and higher pressure, which is a typical adsorption characteristic. Figures 4 and 5 allow us to determine the equilibrium pressure at any selected adsorbed quantity. In the present investigation four values (0.05, 0.10, 0.15, 0.20 mol/kg) of adsorbed quantity (q) were picked out and then the corresponding pressures were read from Figures

Table 2. Initial slopes of adsorption isotherms for CF₄ and C₂F₆ at various temperatures

Temperature (K)	293.15	303.15	313.15	323.15	333.15
$K \text{ [mol/kg/kPa]} \times 10^2 \text{ for CF}_4$	2.82	1.92	1.35	1.05	0.781
$K \text{ [mol/kg/kPa]} \times 10^2 \text{ for C}_2\text{F}_6$	16.1	11.2	6.31	4.34	2.39

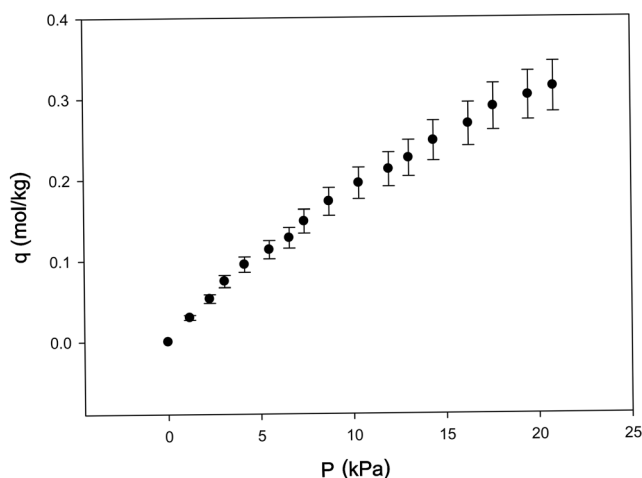


Figure 3. A typical data set of adsorbed amounts with respect to pressure. The error bars are used to imply that the data are scattered and that data reproduction is very hard to accomplish with a new setup of adsorbates.

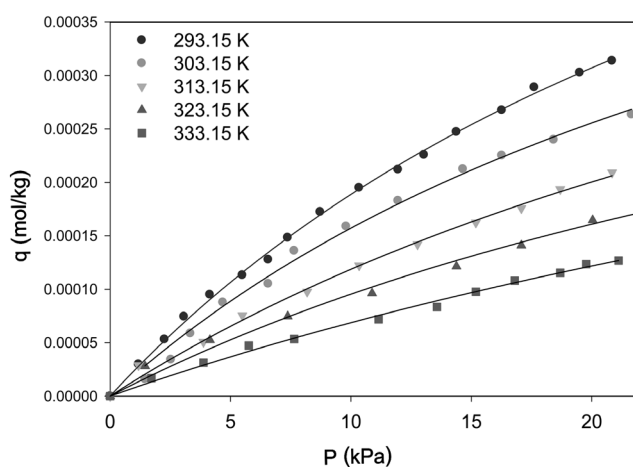


Figure 4. Adsorption isotherms of CF₄ on activated carbon at various temperatures with respect to pressure.

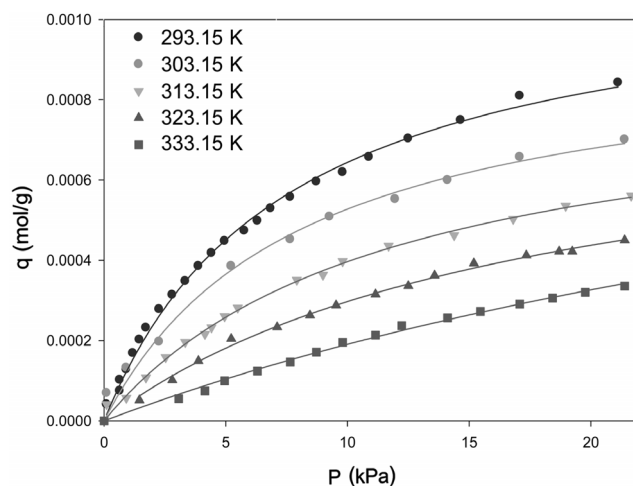


Figure 5. Adsorption isotherms of C₂F₆ on activated carbon at various temperatures with respect to pressure.

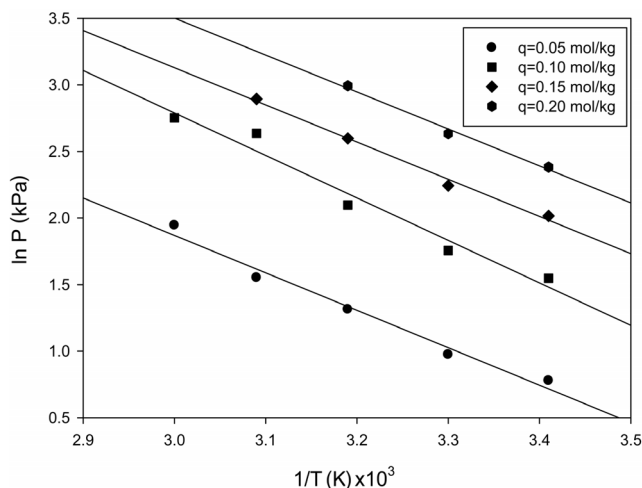


Figure 6. Logarithm of pressure (kPa) versus $1/T$ (K) for CF_4 . The heat of adsorption can be calculated from the slope.

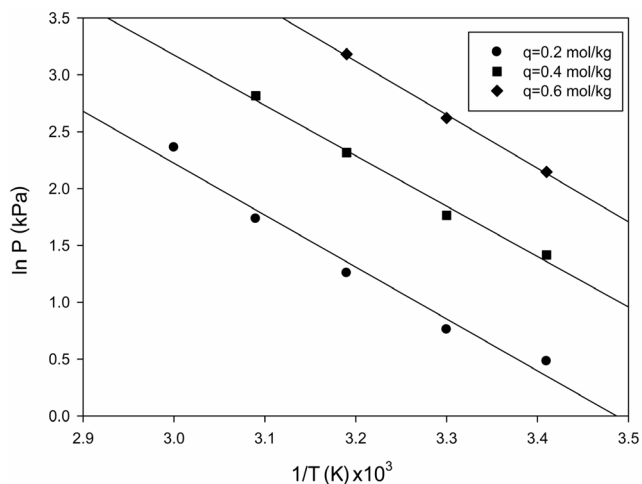


Figure 7. Logarithm of pressure (kPa) versus $1/T$ (K) for C_2F_6 . The heat of adsorption can be calculated from the slope.

Table 3. Heats of adsorption [kJ/mol] derived with the two step model for CF_4 and C_2F_6

	The 1 st step	The 2 nd step
Heat of adsorption [kJ/mol] for CF_4	25.9	11.8
Heat of adsorption [kJ/mol] for C_2F_6	38.7	38.2

4 and 5. Those results of (P, T) in Figure 4 for CF_4 are displayed in Figure 6. The straight line fitting the data points in Figure 6 gave us the slope to find the heat of adsorption ($-\Delta H_2$) for CF_4 .

Similarly we could choose three different values (0.2, 0.4, 0.6 mol/kg) of adsorbed quantity and produce Figure 7 using the results of (P, T) in Figure 5 for C_2F_6 . In the same way as with CF_4 the slope was measured and we could find the heat of adsorption ($-\Delta H_2$) for C_2F_6 . These enthalpy changes for the second

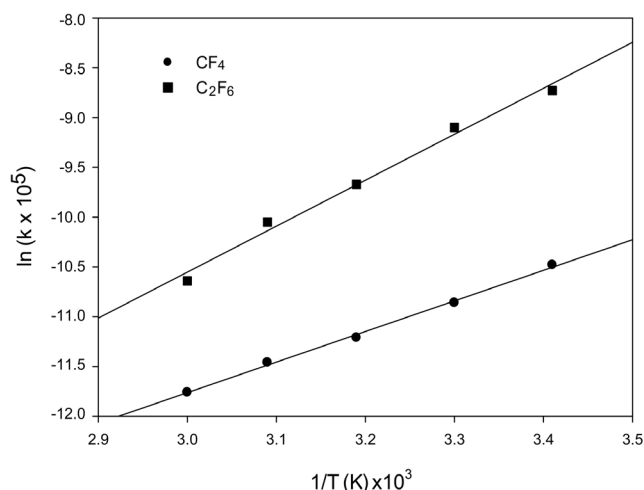


Figure 8. Logarithm of the initial slope (k) versus $1/T$ (K).

step of the two step model are listed in Table 3.

We could measure the initial slope of each curve in Figures 4 and 5 and have them listed in Table 2. The equilibrium constant, K , in Eq. (5) is the ratio of adsorption coefficient to desorption coefficient, and has the relationship with temperature as

$$K = K_0 \exp\left(\frac{-\Delta H_1}{RT}\right) \quad (6)$$

At very low pressure Eq. (5) reduces to a straight line with the initial slope of Kq_{\max} . We assume the maximum amount of the first layer, q_{\max} , is independent of temperature. Then the logarithm of the initial slope versus $1/T$ should give a straight line as long as the heat of adsorption, $-\Delta H_1$, is constant over the range of experimental temperature. We produced Figure 8 for this purpose and measured the slopes of the data points in Figure 8. Consequently, the heats of adsorption for the first step are 25.9 kJ/mol for CF_4 and 38.7 kJ/mol for C_2F_6 .

When we compare the heats of adsorption of the first step and the second in Table 3, we see that $-\Delta H_1$ is about 3 times as large as $-\Delta H_2$ for CF_4 . This is very reasonable in the sense that the first step of the present adsorption model is a kind of chemical reaction between the active solid surface and the gas phase molecule while the second step is a physisorption. It is a well-known fact that condensation requires a lot less heat release than chemical reaction. However, this reasoning breaks down with C_2F_6 because $-\Delta H_1$ is practically the same as $-\Delta H_2$ for C_2F_6 . Thus the two step model is totally agreeable with CF_4 . The first step for C_2F_6 may be interpreted as just a physical condensation and could not be differentiated from the second step.

4. Conclusions

Static equilibrium adsorption experiments were performed to

measure the amounts of CF₄ and C₂F₆ adsorbed on activated carbons, using a volumetric method at various temperatures between 293.15 K and 323.15 K in the low pressure range up to 21 kPa. From these data we could calculate the heats of adsorption of CF₄ and C₂F₆ on activated carbon using the two-step model which employs the Langmuir-type chemisorption in the first step and the next step of Freundlich physisorption. With CF₄ the heats of adsorption are 25.9 kJ/mol for the first step and 11.8 kJ/mol for the second step. The heats of adsorption of C₂F₆ were obtained in the same way and they are 38.7 and 38.2 kJ/mol.

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