

# Adsorption Isotherms of Tetrafluoromethane and Hexafluoroethane on Various Adsorbents

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The amounts of tetrafluoromethane (CF<sub>4</sub>) and hexafluoroethane (C<sub>2</sub>F<sub>6</sub>) adsorbed on various adsorbents such as zeolite, activated carbon, and silica gel were measured experimentally using the volumetric method at 303 K in the pressure range from 3 kPa to 210 kPa. Experimental data for zeolite 13X, zeolite 5A, and activated carbon 20 to 40 mesh were obtained at 323 K and 343 K. Langmuir, Sips, and Toth isotherms were used to fit the experimental data. The isotherm parameters were determined, and the isosteric heats of adsorption were evaluated. Of the three isotherms tested, the Sips isotherm gave the most satisfactory fit of the experimental data. Zeolite 13X was the most favorable adsorbent showing large amounts of adsorbed CF<sub>4</sub> and C<sub>2</sub>F<sub>6</sub>.

## Introduction

PFCs (PerFluoro Compounds) are used as CFC (ChloroFluoro Carbon) substitutes for cleaning or printing electronic circuit boards, hybrid ICs, etc. PFCs are highly stable gases with long atmospheric lives and are considered significant global warming compounds.<sup>1,2</sup> The Intergovernmental Panel on Climate Change (IPCC) has adopted the use of a 100 years time horizon to express the global warming potential (GWP) of PFCs relative to CO<sub>2</sub> (i.e., GWP of CO<sub>2</sub> = 1). The GWP of PFCs was estimated to be about 7000 to 9000 times larger than that of CO<sub>2</sub>. Among the PFCs, the light PFCs (i.e., CF<sub>4</sub> and C<sub>2</sub>F<sub>6</sub>) are the most potentially damaging due to their long atmospheric lifetime. The atmospheric lifetimes of CF<sub>4</sub> and C<sub>2</sub>F<sub>6</sub> are estimated to be 50 000 yr and 10 000 yr, respectively.<sup>2</sup> Physical properties, atmospheric lifetimes, and GWP of PFCs are given in Table 1. Consequently, international organizations such as WMO, UNEP, and WSC have announced their partnership to reduce the emissions of PFCs.<sup>1,3</sup>

Although the net contribution of PFCs to the global warming may be small, reduction strategies for their emissions should be developed. There are many approaches to reduce and eliminate PFCs emissions from industrial processes. Potential methods are as follows: (1) recovery/recycle of PFCs; (2) conversion of PFCs to non-PFCs; (3) process optimization using reconfiguration and end point detection; and (4) replacement of PFCs with non-PFCs. Among these control technologies, recovery/recycle methods are currently the most available and cost-efficient ways for treating PFC gases from emissions of industrial processes. Common technologies for recovery/recycle of organic gases are condensation, absorption, adsorption, and membrane separation. Adsorption is a useful method of gas separation because it offers some recognized advantages. These include the possibility of the recovery of the raw materials for recycling and a high removal efficiency at a low concentration of adsorbates. Furthermore, this technology often demands low energy costs.<sup>3</sup>

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Table 1. Physical Properties of Selected PFCs<sup>1,3</sup>

PFC	molecular weight	boiling point K	critical point K	lifetime yr	global warming potential CO <sub>2</sub> = 1
CF <sub>4</sub>	88.005	145.13	227.65	50 000	6500
C <sub>2</sub> F <sub>6</sub>	138.01	195.05	293.15	10 000	9200
C <sub>3</sub> F <sub>8</sub>	188.020	236.5	345.15	2600	7000
C <sub>2</sub> F <sub>4</sub>	100.016	197.2	306.55	10,000	9200
C <sub>4</sub> F <sub>8</sub>	200.031	267.16	388.46	3200	8700

To design an adsorption process, adsorption equilibria must be known over a wide temperature range. It is also important to select the proper adsorbent for the development of an efficient adsorption process. In this study, the adsorption isotherms of CF<sub>4</sub> and C<sub>2</sub>F<sub>6</sub> on various adsorbents were obtained.<sup>4–7</sup> Experimental data were fitted to Langmuir, Sips, and Toth equations. The isosteric heats of adsorption on zeolite 13X, zeolite 5A, and activated carbon (20 to 40 mesh) were evaluated.

## Experimental Section

**Materials.** The adsorbents used in the experiments were activated carbon, zeolite 5A, zeolite 13X, and silica gel. Zeolite 13X and silica gel were supplied by Aldrich Co. Zeolite 5A and the activated carbons were supplied by Alltech Co. and Darco Co., respectively. Their physical properties were measured using an automatic volumetric sorption analyzer (ASAP2010, Micromeritics Instrument Co.) and pycnometer (Accupyc2375, Micromeritics Instrument Co.). These physical properties are given in Table 2. CF<sub>4</sub> and C<sub>2</sub>F<sub>6</sub> were provided by Dae-Han Gas Co. and Daikin Industry Co. The gas purity was 99.99 % and 99.999 %, respectively.

**Method.** A volumetric type apparatus was used to determine the equilibrium isotherms for the single-component systems.<sup>8,9</sup> 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, a water bath with temperature controller, a pressure transducer (PT), a thermocouple (TC), and displays.

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

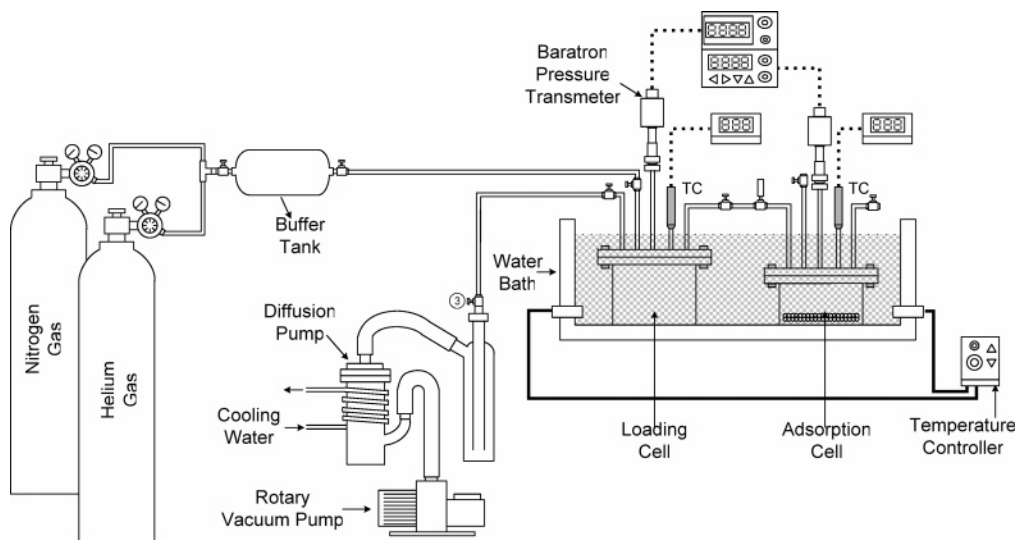


Figure 1. Volumetric apparatus used for adsorption data measurement.

Table 2. Physical Properties of the Adsorbents

adsorbents	BET surface area m <sup>2</sup> /g	total pore volume cm <sup>3</sup> /g	mean pore size Å	solid density <sup>a</sup> g/cm <sup>3</sup>
zeolite 13X 8 to 12 mesh	670.4	0.242	5.1	2.106
zeolite 5A 40 to 60 mesh	552.0	0.199	5.1	2.141
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
silica gel 30 to 60 mesh	583.7	0.215	6.5	2.021

<sup>a</sup> Solid density: the density crushed and compressed solid containing no pores.

Table 3. van der Waals Constants of Adsorbates<sup>11</sup>

adsorbates	<i>a</i>		<i>b</i>	
	kPa·cm <sup>6</sup> ·mol <sup>-2</sup>		cm <sup>3</sup> ·mol <sup>-1</sup>	
CF <sub>4</sub>	4.039 E+8		63.25	
C <sub>2</sub> F <sub>6</sub>	8.179 E+8		99.51	
N <sub>2</sub>	1.370 E+8		38.70	

at a pressure lower than 10<sup>-4</sup> kPa at 423 K. Adsorption isotherms of pure components on various adsorbents were measured at temperatures of 303 K, 323 K, and 343 K and at pressures up to 220 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 appropriate *P–V–T* relationships. The van der Waals equation was used to estimate moles of gas in the loading cell and the adsorption cell:

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT \quad (1)$$

The van der Waals constants of adsorbates used in eq 1 are shown in Table 3.<sup>11</sup>

Adsorbed phase moles are

$$n_{\text{ads}} = (n_{L1} - n_{L2}) - (n_{A2} - n_{A1}) \quad (2)$$

where *n<sub>L</sub>* and *n<sub>A</sub>* are moles of gas in the loading cell and the adsorption cell, respectively. Subscripts 1 and 2 are the before

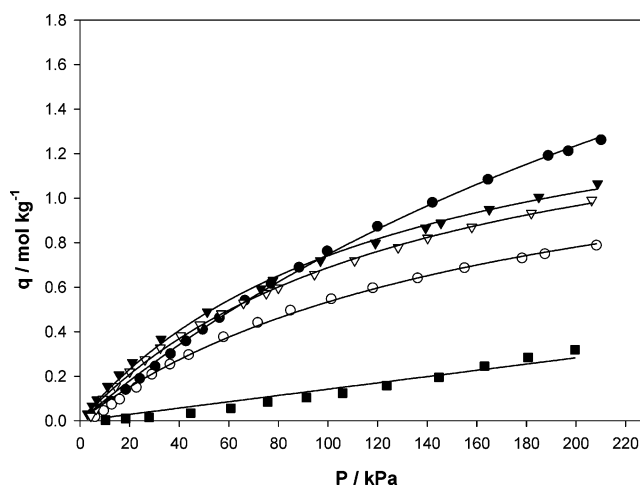


Figure 2. Adsorption isotherms of CF<sub>4</sub> on various adsorbents at 303 K: ●, zeolite 13X; ○, zeolite 5A; ▼, activated carbon 20 to 40 mesh; ▽, activated carbon 12 to 20 mesh; ■, silica gel; —, Langmuir isotherm.

and after supply of PFC gas to the adsorption cell, respectively. *n<sub>A2</sub>* was measured at adsorption equilibrium. The adsorbed amount *q* is

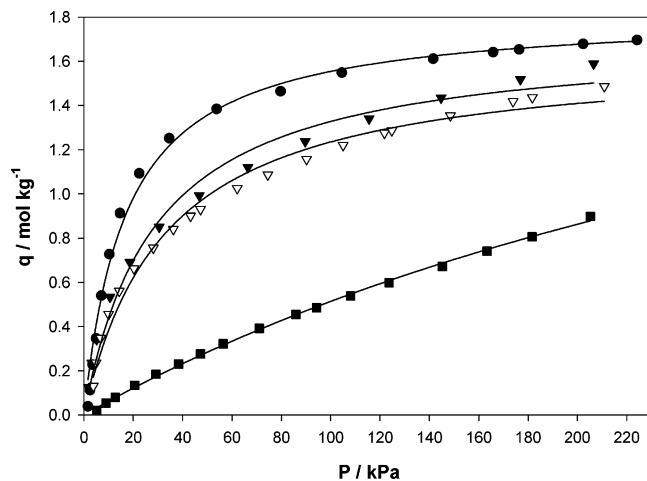
$$q = n_{\text{ads}}/w \quad (3)$$

where *w* is mass of adsorbent.

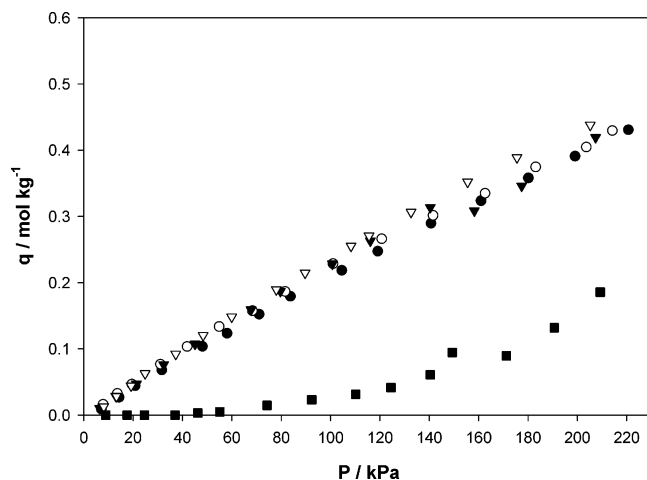
## Results and Discussion

The adsorption isotherms of the pure gases CF<sub>4</sub>, C<sub>2</sub>F<sub>6</sub>, and N<sub>2</sub> on various adsorbents were measured at 303 K and at pressures up to 220 kPa. The time to reach an adsorption equilibrium state was typically 30 min. These experimental data are presented in Figures 2, 3, and 4. The marks and lines indicate experimental data and fitting of data to the Langmuir isotherm, respectively. It is seen from Figures 2 and 3 that zeolite 13X and activated carbon (20 to 40 mesh) adsorb larger amounts of CF<sub>4</sub> and C<sub>2</sub>F<sub>6</sub> than the other adsorbents. Adsorption amounts of C<sub>2</sub>F<sub>6</sub> on zeolite 5A were not measured because it took too much time to reach an adsorption equilibrium. This may have been caused by a molecular sieving effect. PFCs are usually diluted with N<sub>2</sub> in the exhausts of the semiconductor production processes.

To evaluate its influence, the amounts of adsorbed N<sub>2</sub> were compared with those of CF<sub>4</sub> and C<sub>2</sub>F<sub>6</sub>. As shown in Figure 4,



**Figure 3.** Adsorption isotherms of  $C_2F_6$  on various adsorbents at 303 K: ●, zeolite 13X; ▼, activated carbon 20 to 40 mesh; ▽, activated carbon 12 to 20 mesh; ■, silica gel; —, Langmuir isotherm.



**Figure 4.** Adsorption isotherms of  $N_2$  on various adsorbents at 303 K: ●, zeolite 13X; ○, zeolite 5A; ▼, activated carbon 20 to 40 mesh; ▽, activated carbon 12 to 20 mesh; ■, silica gel.

the amounts of  $N_2$  adsorbed on each adsorbent were smaller than those of  $CF_4$  and  $C_2F_6$  at the same pressure. Since PFCs are strong adsorbates and  $N_2$  is a weak adsorbate, enrichment or removal of PFCs from and  $N_2$  would be possible.

To obtain more useful data, it was necessary to measure the adsorption isotherms at various temperatures. Adsorption experiments on zeolite 13X, zeolite 5A, and activated carbon (20 to 40 mesh) were also carried out at 323 K and 343 K. All experimental data were fitted to Langmuir, Sips, and Toth isotherms:<sup>9,10</sup>

Langmuir isotherm

$$q = \frac{bq_{\max}P}{1 + bP} \quad (4)$$

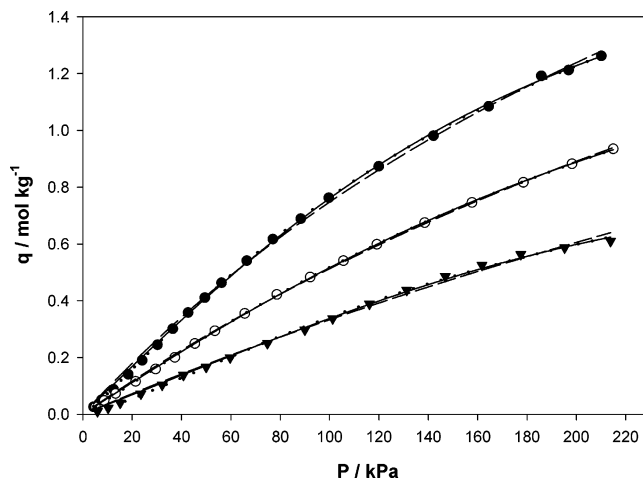
Sips isotherm

$$q = \frac{bq_{\max}P^n}{1 + bP^n} \quad (5)$$

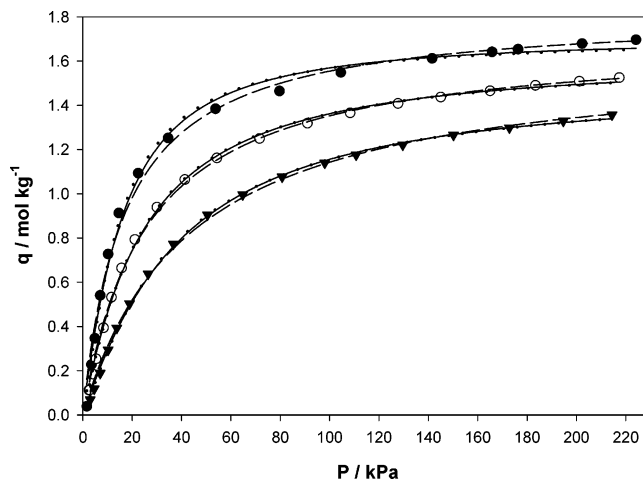
Toth isotherm

$$q = \frac{q_{\max}P}{(b + P^n)^{1/n}} \quad (6)$$

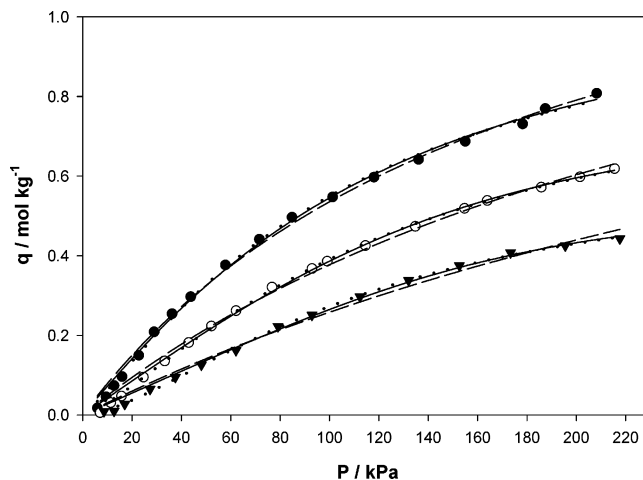
The amounts of PFC adsorbed on zeolite 13X, zeolite 5A, and activated carbon (20 to 40 mesh) at 303 K, 323 K, and 343 K



**Figure 5.** Adsorption isotherms of  $CF_4$  on zeolite 13X: ●, 303.15 K; ○, 323.15 K; ▼, 343.15 K; — —, Langmuir isotherm; - - -, Sips isotherm; —, Toth isotherm.



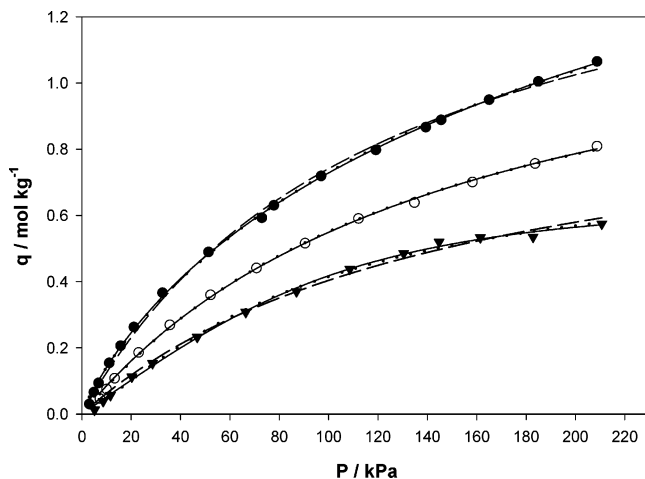
**Figure 6.** Adsorption isotherms of  $C_2F_6$  on zeolite 13X: ●, 303.15 K; ○, 323.15 K; ▼, 343.15 K; — —, Langmuir isotherm; - - -, Sips isotherm; —, Toth isotherm.



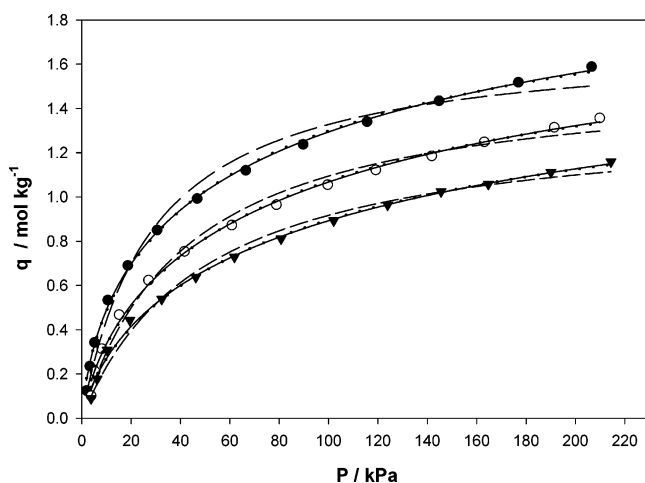
**Figure 7.** Adsorption isotherms of  $CF_4$  on zeolite 5A: ●, 303.15 K; ○, 323.15 K; ▼, 343.15 K; — —, Langmuir isotherm; - - -, Sips isotherm; —, Toth isotherm.

are shown in Figures 5 to 9 and Tables 4 to 8. The adsorption amounts of  $CF_4$  and  $C_2F_6$  increased with increasing pressure and decreased with increasing temperature.

All the isotherms (Langmuir, Sips, and Toth isotherms) fit the experimental data for  $CF_4$  and  $C_2F_6$  in the pressure range



**Figure 8.** Adsorption isotherms of  $\text{CF}_4$  on activated carbon 20 to 40 mesh: ●, 303.15 K; ○, 323.15 K; ▼, 343.15 K; ---, Langmuir isotherm; ···, Sips isotherm; -·-, Toth isotherm.



**Figure 9.** Adsorption isotherms of  $\text{C}_2\text{F}_6$  on activated carbon 20 to 40 mesh: ●, 303.15 K; ○, 323.15 K; ▼, 343.15 K; ---, Langmuir isotherm; ···, Sips isotherm; -·-, Toth isotherm.

**Table 4.** Adsorption Data for  $\text{CF}_4$  on Zeolite 13X

$T = 303.15 \text{ K}$		$T = 323.15 \text{ K}$		$T = 343.15 \text{ K}$	
$P$	$q$	$P$	$q$	$P$	$q$
kPa	mol/kg	kPa	mol/kg	kPa	mol/kg
4.346	0.026	5.156	0.026	5.966	0.010
7.586	0.051	8.666	0.049	10.29	0.022
12.45	0.088	13.26	0.073	15.15	0.040
18.39	0.141	21.36	0.116	23.52	0.072
24.06	0.190	29.46	0.159	32.16	0.103
30.27	0.245	37.29	0.200	40.80	0.138
36.48	0.301	45.39	0.249	49.98	0.166
42.69	0.358	53.49	0.294	59.70	0.199
49.44	0.411	65.64	0.355	74.82	0.250
56.19	0.463	78.60	0.422	89.94	0.297
66.45	0.541	92.10	0.483	101.3	0.337
76.98	0.617	105.6	0.541	116.1	0.389
88.32	0.689	119.1	0.598	131.3	0.437
99.66	0.762	138.5	0.675	146.9	0.486
119.9	0.873	157.7	0.746	161.8	0.525
142.1	0.981	178.5	0.817	177.4	0.563
164.5	1.084	198.2	0.882	195.2	0.587
185.8	1.192	215.0	0.935	213.9	0.610
196.9	1.212				
210.1	1.262				

between 3 kPa and 210 kPa. The Langmuir isotherm, which has a simpler form, is good enough to predict the adsorbed amounts.

**Table 5.** Adsorption Data for  $\text{C}_2\text{F}_6$  on Zeolite 13X

$T = 303.15 \text{ K}$		$T = 323.15 \text{ K}$		$T = 343.15 \text{ K}$	
$P$	$q$	$P$	$q$	$P$	$q$
kPa	mol/kg	kPa	mol/kg	kPa	mol/kg
1.646	0.039	2.725	0.112	2.996	0.068
2.456	0.112	4.076	0.184	4.616	0.118
3.536	0.227	5.426	0.253	7.046	0.189
4.886	0.346	8.396	0.394	10.29	0.294
7.046	0.540	11.64	0.532	13.80	0.393
10.29	0.728	15.69	0.664	18.93	0.503
14.61	0.913	21.09	0.793	26.49	0.637
22.44	1.093	30.00	0.939	36.75	0.773
34.59	1.252	41.34	1.064	50.52	0.904
53.76	1.384	54.30	1.162	64.83	0.996
79.68	1.464	71.58	1.250	80.76	1.077
104.5	1.549	91.02	1.319	98.04	1.139
141.5	1.612	108.3	1.366	110.7	1.176
165.8	1.642	127.7	1.409	129.6	1.221
176.3	1.654	145.0	1.437	150.2	1.265
202.3	1.679	165.0	1.466	172.8	1.298
224.1	1.697	183.4	1.490	194.7	1.329
		201.2	1.508	214.4	1.357
		217.4	1.525		

**Table 6.** Adsorption Data for  $\text{CF}_4$  on Zeolite 5A

$T = 303.15 \text{ K}$		$T = 323.15 \text{ K}$		$T = 343.15 \text{ K}$	
$P$	$q$	$P$	$q$	$P$	$q$
kPa	mol/kg	kPa	mol/kg	kPa	mol/kg
5.966	0.018	7.046	0.006	8.666	0.009
9.476	0.046	11.37	0.031	12.72	0.010
12.72	0.074	15.69	0.048	17.04	0.027
15.96	0.096	24.60	0.095	27.30	0.065
22.71	0.150	33.24	0.136	37.56	0.095
28.92	0.209	42.96	0.182	48.09	0.126
36.21	0.254	52.14	0.223	62.13	0.162
43.77	0.297	62.13	0.262	79.14	0.222
57.81	0.377	76.71	0.321	92.91	0.251
71.58	0.441	92.91	0.368	112.4	0.297
84.81	0.497	99.12	0.386	132.1	0.338
101.3	0.548	114.5	0.426	152.6	0.375
118.0	0.597	134.8	0.474	173.4	0.408
136.1	0.642	154.7	0.519	195.5	0.425
155.0	0.687	163.9	0.539	217.7	0.443
178.2	0.731	185.8	0.572		
187.4	0.769	201.5	0.598		
208.2	0.808	215.5	0.619		

**Table 7.** Adsorption Data for  $\text{CF}_4$  on Activated Carbon (20 to 40 mesh)

$T = 303.15 \text{ K}$		$T = 323.15 \text{ K}$		$T = 343.15 \text{ K}$	
$P$	$q$	$P$	$q$	$P$	$q$
kPa	mol/kg	kPa	mol/kg	kPa	mol/kg
2.996	0.030	7.316	0.047	5.156	0.012
4.886	0.066	10.02	0.076	8.666	0.039
6.776	0.094	13.26	0.108	11.64	0.057
11.10	0.155	22.98	0.186	20.28	0.113
15.69	0.206	35.67	0.269	28.65	0.154
21.09	0.263	52.14	0.360	46.74	0.233
32.70	0.366	70.77	0.441	66.45	0.308
51.33	0.490	90.48	0.516	86.97	0.370
72.93	0.593	112.1	0.591	108.6	0.438
77.79	0.631	134.8	0.639	130.4	0.486
96.96	0.719	158.3	0.701	144.8	0.520
119.1	0.798	183.6	0.757	161.5	0.533
139.4	0.867	208.7	0.809	182.8	0.535
145.6	0.889			210.6	0.575
165.0	0.949				
185.0	1.005				
208.7	1.065				

The parameters obtained from the best fit for the experimental data are summarized in Tables 9 to 11 with the 95 % confidence

**Table 8. Adsorption Data for C<sub>2</sub>F<sub>6</sub> on Activated Carbon (20 to 40 mesh)**

T = 303.15 K		T = 323.15 K		T = 343.15 K	
P	q	P	q	P	q
kPa	mol/kg	kPa	mol/kg	kPa	mol/kg
1.916	0.125	3.806	0.102	3.806	0.089
3.266	0.235	5.426	0.211	6.236	0.177
5.156	0.342	8.126	0.314	10.29	0.308
10.56	0.534	15.15	0.468	19.47	0.443
18.66	0.690	27.03	0.624	32.43	0.538
30.54	0.851	41.61	0.754	46.20	0.637
46.74	0.993	60.78	0.873	61.86	0.728
66.45	1.120	78.87	0.965	80.76	0.811
89.67	1.238	99.66	1.056	102.1	0.893
115.6	1.341	119.1	1.122	124.0	0.963
144.8	1.435	141.8	1.186	145.6	1.024
176.9	1.518	163.1	1.249	164.7	1.058
206.6	1.589	191.5	1.315	190.1	1.112
		209.8	1.357	214.4	1.159

**Table 9. Langmuir Isotherm Parameters Estimated for CF<sub>4</sub> and C<sub>2</sub>F<sub>6</sub> on Various Adsorbents<sup>a</sup>**

	T	q <sub>max</sub>	b	Δq
	K	mol/kg	1/kPa·10 <sup>3</sup>	%
Zeolite 13X				
CF <sub>4</sub>	303	3.609 ± 0.350	2.612 ± 0.420	6.5
	323	3.412 ± 0.252	1.800 ± 0.212	2.3
	343	3.345 ± 1.448	1.100 ± 0.636	10.3
C <sub>2</sub> F <sub>6</sub>	303	1.820 ± 0.070	58.50 ± 9.38	11.7
	323	1.702 ± 0.032	38.70 ± 2.74	3.5
	343	1.633 ± 0.042	23.30 ± 1.91	4.6
Zeolite 5A				
CF <sub>4</sub>	303	1.511 ± 0.145	5.500 ± 0.848	9.2
	323	1.506 ± 0.242	3.300 ± 0.848	11.3
	343	1.483 ± 0.629	2.100 ± 1.080	13.2
Activated Carbon				
CF <sub>4</sub>	303	1.658 ± 0.092	8.100 ± 0.852	3.9
	323	1.386 ± 0.069	6.600 ± 0.660	2.2
	343	1.028 ± 0.132	6.500 ± 1.530	7.7
C <sub>2</sub> F <sub>6</sub>	303	1.712 ± 0.121	34.60 ± 8.58	8.3
	323	1.563 ± 0.099	23.40 ± 4.79	6.2
	343	1.371 ± 0.094	20.20 ± 4.14	5.8

<sup>a</sup> ±, 95 % confidence intervals.

intervals and the average percent deviations Δq, calculated using the following equation:

$$\Delta q = \frac{100}{k} \sum_{j=1}^k \left| \frac{q_j^{\text{exp}} - q_j^{\text{cal}}}{q_j^{\text{exp}}} \right| \quad (7)$$

where  $k$ ,  $q^{\text{exp}}$ , and  $q^{\text{cal}}$  are the number of data points at a given temperature, the experimental adsorbed amount, and the estimated adsorbed amount, respectively.

Isosteric heat of adsorption ( $-\Delta H_s$ ) can be calculated by the Clausis–Clapeyron equation:

$$\left( \frac{\partial \ln P}{\partial T} \right)_q = \frac{-\Delta H_s}{RT^2} \quad (8)$$

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,  $-\Delta H_s$  is independent of temperature and eq 8 may be integrated directly to yield

$$\ln P = \left( \ln P_0 - \frac{\Delta H_s}{T_0} \right) + \frac{\Delta H_s}{RT} \quad (9)$$

**Table 10. Sips Isotherm Parameters Estimated for CF<sub>4</sub> and C<sub>2</sub>F<sub>6</sub> on Various Adsorbents**

	T	q <sub>max</sub>	b	N	Δq
	K	mol/kg	1/kPa·10 <sup>3</sup>	(-)	%
Zeolite 13X					
CF <sub>4</sub>	303	2.364 ± 0.144	2.100 ± 0.210	1.178 ± 0.036	1.3
	323	2.463 ± 0.166	1.800 ± 0.000	1.086 ± 0.022	1.1
	343	1.217 ± 0.237	0.900 ± 0.212	1.310 ± 0.119	2.7
C <sub>2</sub> F <sub>6</sub>	303	1.706 ± 0.062	36.70 ± 2.74	1.244 ± 0.150	6.6
	323	1.626 ± 0.038	30.00 ± 4.43	1.117 ± 0.061	2.1
	343	1.513 ± 0.036	16.80 ± 2.12	1.142 ± 0.048	2.0
Zeolite 5A					
CF <sub>4</sub>	303	1.140 ± 0.123	4.000 ± 1.000	1.208 ± 0.106	4.5
	323	0.899 ± 0.062	1.600 ± 0.424	1.342 ± 0.076	2.6
	343	0.613 ± 0.051	0.600 ± 0.216	1.564 ± 0.121	2.8
Activated Carbon					
CF <sub>4</sub>	303	2.108 ± 0.315	9.600 ± 0.852	0.870 ± 0.058	2.8
	323	1.330 ± 0.174	6.300 ± 1.101	1.027 ± 0.084	1.9
	343	0.775 ± 0.094	3.500 ± 1.525	1.262 ± 0.151	2.5
C <sub>2</sub> F <sub>6</sub>	303	2.288 ± 0.352	54.60 ± 7.48	0.691 ± 0.089	2.4
	323	1.961 ± 0.388	34.70 ± 7.63	0.770 ± 0.127	2.7
	343	1.789 ± 0.401	30.90 ± 6.32	0.755 ± 0.126	2.9

<sup>a</sup> ±, 95 % confidence intervals.**Table 11. Toth Isotherm Parameters Estimated for CF<sub>4</sub> and C<sub>2</sub>F<sub>6</sub> on Various Adsorbents**

	T	q <sub>max</sub>	b	n	Δq
	K	mol/kg	kPa <sup>n</sup> ·10 <sup>3</sup>	(-)	%
Zeolite 13X					
CF <sub>4</sub>	303	1.856 ± 0.338	382.9 ± 50.95	1.899 ± 0.498	6.5
	323	1.793 ± 0.311	565.8 ± 52.88	1.623 ± 0.280	2.3
	343	0.844 ± 0.081	904.5 ± 456.2	3.060 ± 0.072	10.3
C <sub>2</sub> F <sub>6</sub>	303	1.709 ± 0.094	17.10 ± 2.716	1.319 ± 0.362	11.7
	323	1.622 ± 0.058	25.87 ± 1.818	1.170 ± 0.144	3.6
	343	1.493 ± 0.065	42.91 ± 3.357	1.251 ± 0.152	4.6
Zeolite 5A					
CF <sub>4</sub>	303	1.078 ± 0.265	182.2 ± 29.83	1.520 ± 0.601	9.2
	323	0.766 ± 0.164	299.2 ± 71.55	2.284 ± 1.043	11.3
	343	0.532 ± 0.053	474.9 ± 266.0	3.099 ± 0.099	13.3
Activated Carbon					
CF <sub>4</sub>	303	2.916 ± 0.909	123.7 ± 13.81	0.600 ± 0.126	3.9
	323	1.374 ± 0.363	152.4 ± 14.03	1.010 ± 0.294	2.2
	343	0.646 ± 0.077	154.6 ± 36.76	2.229 ± 0.787	7.7
C <sub>2</sub> F <sub>6</sub>	303	2.864 ± 0.711	28.92 ± 7.170	0.452 ± 0.110	8.3
	323	2.343 ± 0.801	42.74 ± 8.610	0.548 ± 0.196	6.2
	343	2.244 ± 0.938	49.52 ± 10.07	0.513 ± 0.199	5.8

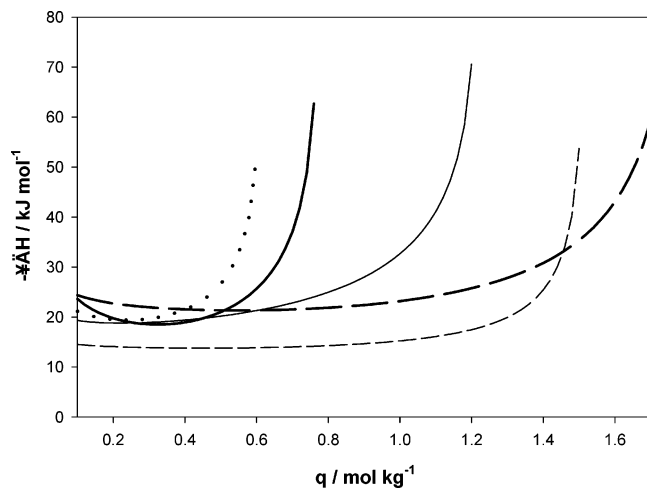
<sup>a</sup> ±, 95 % confidence intervals.

Assuming that the above approximation concerning the heat capacity is valid, a plot of  $\ln P$  versus  $1/RT$  should yield a linear plot with slope ( $-\Delta H_s$ ). This provides a simple and useful method for the determination of the isosteric heat. Isosteric heats of adsorption for CF<sub>4</sub> and C<sub>2</sub>F<sub>6</sub> are shown in Figure 10.

## Conclusions

The amounts of CF<sub>4</sub> and C<sub>2</sub>F<sub>6</sub> adsorbed on zeolite 13X, zeolite 5A, activated carbons (12 to 20 mesh and 20 to 40 mesh), and silica gel were measured experimentally using a volumetric method at 303 K in the pressure range up to 220 kPa. In this study, zeolite 13X and activated carbon (20 to 40 mesh) were shown to have a larger adsorbed amount of CF<sub>4</sub> and C<sub>2</sub>F<sub>6</sub> than the other adsorbents. Additionally the same experiments on zeolite 13X, zeolite 5A, and activated carbon (20 to 40 mesh) were carried out at 323 K and 343 K. Experimental data were reasonably fitted to Langmuir, Sips, and Toth isotherms. The Sips isotherm showed the most satisfactory agreement with the





**Figure 10.** Isothermic heats of adsorption for  $\text{CF}_4$  and  $\text{C}_2\text{F}_6$  on various adsorbents: —,  $\text{CF}_4$  on zeolite 13X; - - -,  $\text{C}_2\text{F}_6$  on zeolite 13X; - · - ·,  $\text{CF}_4$  on zeolite 5A; — — —,  $\text{CF}_4$  on activated carbon 20 to 40 mesh; · · ·,  $\text{C}_2\text{F}_6$  on activated carbon 20 to 40 mesh.

experimental data. Furthermore, the isosteric heats of adsorption were determined for each adsorbent.

### Literature Cited

- (1) Van Hoeymissen, J. A. B.; Daniels, M.; Anderson, N.; Fyen, W.; Heyns, M. Gas stream analysis and PFC recovery in a semiconductor process. *Mater. Res. Soc. Symp. Proc.* **1997**, No. 447, 55–60.

- (2) Tanada, S.; Kawasaki, N.; Nakamura, T.; Ohue, T.; Abe, I. Adsorbability of 1,1,1,2-tetrafluoroethane (HFC134a) onto plasma-treated activated carbon in  $\text{CF}_4$  and  $\text{CCl}_4$ . *J. Colloid Interface Sci.* **1997**, *191*, 337–340.
- (3) Tsai, W. T.; Chen, H. P.; Hsien, W. Y. A review of uses, environmental hazards and recovery/recycle technologies of perfluorocarbons (PFCs) emissions from the semiconductor manufacturing processes. *J. Loss Prev. Process Ind.* **2002**, *15*, 65–75.
- (4) Moon, D. J.; Chung, M. J.; Kim, H.; Lee, B. G.; Lee, S. D.; Park, K. Y. Adsorption equilibria of chloropentafluoroethane on activated carbon powder. *Korean J. Chem. Eng.* **1998**, *15* (6), 619–624.
- (5) Yun, J. H.; Choi, D. K.; Lee, Y. W. Adsorption equilibria of hexafluoropropene and 1,1,1,2,3,3,3-heptafluoropropane on activated carbon at 283, 303, 333, and 363 K. *J. Chem. Eng. Data* **2000**, *45*, 136–139.
- (6) Cho, S. Y.; Kim, S. J. Adsorption equilibria of two halogenated carbons on a carbon fiber. *Korean J. Chem. Eng.* **1996**, *13* (3), 225–229.
- (7) Buss, E.; Heuchel, M. Adsorption equilibria of methane and tetrafluoromethane and their binary mixture on silicalite. *J. Chem. Soc., Faraday Trans.* **1997**, *93* (1), 1621–1628.
- (8) Ruthven, D. M. *Principles of Adsorption and Adsorption Processes*; John Wiley and Sons: New York, 1984.
- (9) Wankat, P. C. *Rate-Controlled Separation*; Elsevier Applied Science: London, 1990.
- (10) Yang, R. T. *Adsorbents: Fundamentals and Applications*; John Wiley and Sons: New York, 2003.
- (11) Lide, D. R. *CRC Handbook of Chemistry and Physics*; CRC Press: Boca Raton, FL, 2000.

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