

V-t 도식 결과에 의한 각종 물리 흡착 등온식의 평가

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The Estimation of Standard Physisorption Isotherms based on the V-t Plots of Physisorption on Various Inorganic Adsorbents

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요 약. 현재까지 본인 등이 여러 흡착제물 가지고 측정한 질소 및 아르곤의 물리흡착 등온곡선을 가지고 각종 표준흡착 등온곡선에 맞추어서 V-t 도식을 하고, 이 도식 결과로부터 이들 표준흡착 등온곡선들의 타당성을 음미하여 보았다. 이 중에서 FHH식이 광범위한 종류의 흡착제에 대하여 표준 등온식으로 적합함을 확인할 수 있었다.

ABSTRACT. Adsorption isotherms of nitrogen and argon on various adsorbents measured up to present by authors are used to make the V-t plots using various numerical and the analytical standard adsorption isotherms to estimate the appropriateness of these standard isotherms. It is confirmed that the analytical FHH equation is appropriate for wide range of adsorbents as a standard isotherm.

INTRODUCTION

It has been generally accepted that the physisorption on non-porous solid surface, over the submonolayer region, is little affected by the nature of adsorbent for a given adsorbent surface area and a given adsorbate gas, and that physisorption isotherms are superposable each other provided that there is no capillary condensation of adsorbate gas. Based on these findings, number of standard adsorption isotherms have been proposed up to the present¹⁻¹¹. Linsen, Lippens and de Boer^{4,6} used the statistical thickness σ (V_{ad}/V_m) in expressing the standard isotherm, and called it universal t-curve. Here, V_{ad} and V_m stand for adsorbed volume and monolayer capacity, respectively, and σ is the average molecular layer thickness of the

adsorbed molecules.

It was realized later that a single standard isotherm was insufficient to use for all the adsorbents^{9,10,12}. It is well known that the shape of adsorption isotherm depends on the nature of adsorbent in the submonolayer region, and that this initial isotherm shape dominates the ensuing isotherm shape. Sing and his coworkers^{9,10} proposed two standard nitrogen adsorption isotherms on the basis of empirical data. The isotherms apply to the silica and alumina adsorbents, respectively. It seems quite reasonable to have a specific standard adsorption isotherm for a group of similar adsorbents considering a similar intensity of adsorbent-adsorbate interactions. The effect of this difference on the standard adsorption isotherm was taken

over by Lecloux and Pirard¹¹ by a little bit different way. They proposed a set of five different standard isotherms corresponding to certain deviated ranges of the BET constant C of the adsorbent-adsorbate system, and said that these isotherms should function as standard isotherms for the respective adsorbent-adsorbate systems with the appropriate the BET constant, irrespective of any adsorbent and adsorbate. The work of Lecloux and Pirard seems quite a progress in that the adsorbent-adsorbate interaction is taken into consideration elaborately more or less and that the isotherms are applicable to any adsorbate in addition to nitrogen. However, they did not show enough evidence to prove whether the BET constant alone can really serve as the principal criteria for the interaction between the adsorbent and adsorbate. It is found that none of these standard isotherms are appropriate for many of the isotherms used in this work. Chang *et al.*¹³ also tried to incorporate the difference of the BET constant into the standard adsorption isotherm. They proposed to use the BET equation as the standard isotherm with a minor correction by incorporating a number of adjustable parameters in addition to the two constants C and V_m . The introduction of many parameters, however, changed the original BET equation into a very complicated and difficult one for practical use.

The main purpose of determining the standard isotherm is to estimate the specific surface area and the porosity of the adsorbent with the t -plot method. The t -plot method⁵, the plot of the adsorption amount versus the statistical thickness estimated from the standard isotherm, should yield a straight line converging to the origin provided that the adsorbent has no micropores. Surface area of the adsorbent can be calculated from the slope of the plot. The nitrogen and argon adsorption isotherms on various adsorbents reported by authors up to the present are used to make the t -plots for each of the various standard isotherms put forth hitherto, and thereby estimated the appropriateness of these standard isotherms.

THE RESULTS AND DISCUSSIONS

The adsorption isotherms used in this work are tabulated in Tabel 1 and 2¹⁴⁻¹⁶, and some of them are also shown in Fig. 1, 2, and 3 for a comparison with various standard isotherms.

All the BET plots of the adsorption data show a good linearity in the pressure range of $0.05 < P/P_0 < 0.30$. The BET surface area and the BET constant C determined with these plots are given in Table 3 and 4.

The t -plot is obtained by plotting the adsorption V_{ad} at a given temperature against the statistical thickness t using the equation

$$V_{ad} = \frac{V_0 A}{N_A a_m \sigma} t = k A t \quad (1)$$

where, V_0 is the molar volume of the adsorbate gas at 0°C and 1 atm, A the surface area of adsorbent, N_A the Avogadro number, and a_m the average molecular cross section of adsorbed molecules. The currently used values of a_m and σ are used in this work, viz $16.2 \text{ \AA}^2/\text{molecule}$ and 3.54 \AA for nitrogen, and $16.65 \text{ \AA}^2/\text{molecule}$ and 3.82 \AA for argon, respectively. The numerical values of constant k corresponding to units of A in square meter, t in angstrom, and V_{ad} in ml of STP volume are $1/15.47$ and $1/12.71$ for nitrogen and argon, respectively. The statistical thickness is calculated from various standard isotherms. For non-porous adsorbent which causes no capillary condensation, the t -plot should yield a straight line passing through the origin, and the slope of the plot will give the surface area of the adsorbent. For porous adsorbents, the same argument should apply at least in the initial region where no capillary condensation takes place.

The t -plots of nitrogen adsorption on various adsorbents are made using standard isotherms of de Boer *et al.*^{7,8}, and Sing^{9,10}, and FHH equation¹⁷⁻¹⁹. The results are shown in Fig. 4 through 7. The surface areas of various adsorbents estimated from the slope of these plots are also shown in Table 3 and 4.

In the relatively lower vapor pressure region ($P/P_0 < 0.3$), where there is no indication of the capillary condensation, various standard adsorption isotherms cited in Fig. 1 through 3 fit fairly

Table 1. Adsorption of nitrogen on various adsorbents at 77.36 K

BN P/P ₀	Y-Alumina		Silica-gel (A)		Silica-gel (B)		Y-Alumina		LaNiO ₃		La _{0.98} St _{0.02} NiO ₃		La _{0.96} St _{0.04} NiO ₃		LaFeO ₃		La _{0.93} St _{0.07} FeO ₃		
	V _{ad}	P/P ₀	V _{ad}	P/P ₀	V _{ad}	P/P ₀	V _{ad}	P/P ₀	V _{ad}	P/P ₀	V _{ad}	P/P ₀	V _{ad}	P/P ₀	V _{ad}	P/P ₀	V _{ad}	P/P ₀	V _{ad}
.0013	1.60	.0014	23.12	.0014	27.63	.0013	6.98	.0014	.24	.0014	.42	.0049	.48	.0013	.50	.0012	1.68	.0014	.98
.0061	2.32	.0113	33.42	.0436	58.05	.0375	12.85	.0133	.33	.0490	.52	.0168	.58	.0105	.58	.0135	2.14	.0176	1.14
.0246	2.76	.0239	35.51	.0937	66.68	.0640	15.53	.0337	.39	.0667	.55	.0636	.66	.0267	.62	.0271	2.27	.0407	1.59
.0554	3.09	.0357	37.61	.1481	73.51	.0948	15.58	.0528	.43	.0880	.59	.0810	.70	.0471	.66	.0520	2.49	.0661	1.75
.0923	3.32	.0526	40.24	.2229	84.30	.1243	17.46	.0739	.48	.1007	.61	.1046	.74	.0670	.69	.0788	2.69	.0947	1.91
.1178	3.42	.0642	41.53	.2758	88.15	.1544	18.22	.0925	.51	.1232	.65	.1363	.78	.0879	.73	.1048	2.86	.1186	2.02
.1402	3.85	.0752	42.81	.3275	94.50	.1813	19.37	.1185	.54	.1503	.69	.1595	.81	.1059	.75	.1319	3.06	.1484	2.15
.1734	3.83	.0867	44.17	.3806	99.94	.2150	20.36	.1450	.58	.1754	.72	.1833	.85	.1238	.77	.1590	3.22	.1710	2.26
.2071	3.92	.0975	45.24	.4168	105.20	.2485	21.68	.1720	.62	.1976	.76	.2118	.83	.1450	.80	.1851	3.40	.2009	2.39
.2411	4.06	.1156	47.00	.4466	107.43	.2868	22.94	.1958	.64	.2259	.79	.2342	.90	.1711	.84	.2009	3.57	.2271	2.49
.2740	4.32	.1360	49.00	.4738	111.46	.3192	23.67	.2246	.68	.2511	.82	.2724	.96	.1989	.88	.2374	3.73	.2509	2.58
.3008	4.42	.1594	50.99	.5014	116.94	.3660	25.05	.2501	.70	.2871	.87	.3080	1.00	.2249	.91	.2647	3.92	.2791	2.66
.3418	4.53	.1850	53.30	.5236	121.28	.4145	26.45	.2837	.74	.3216	.91	.3420	1.04	.2478	.94	.2913	4.08	.3108	2.79
.3731	4.74	.2106	55.37	.5503	128.60	.4626	27.89	.3283	.79	.3597	.96	.3754	1.09	.2911	.99	.3295	4.30	.3570	2.93
.3984	4.91	.2375	57.59	.5741	139.46	.5034	29.20	.3691	.82	.4039	1.01	.4082	1.13	.3297	1.04	.3703	4.49	.3912	3.04
.4286	5.14	.2634	59.40	.6036	150.45	.5475	30.59	.4072	.86	.4355	1.05	.4416	1.18	.3701	1.09	.4084	4.68	.4379	3.21
.4639	5.33	.2875	61.24	.6370	161.02	.5877	31.81	.4458	.89	.4687	1.09	.4792	1.23	.4107	1.15	.4660	4.97	.4758	3.34
.5120	5.50	.3251	63.54	.6605	172.20	.6314	33.25	.4992	.94	.5007	1.13	.5225	1.28	.4542	1.20	.5261	5.22	.5216	3.48
.5561	5.67	.3539	65.83	.6863	183.63	.6779	35.29	.5500	1.00	.5386	1.18	.5574	1.33	.4975	1.26	.5930	5.57	.5690	3.66
.5825	5.79	.3822	67.64	.7158	195.15	.7145	36.82	.6020	1.05	.5778	1.23	.6073	1.41	.5528	1.33	.7038	6.26	.6176	3.83
		.4111	69.43	.7405	208.94	.7741	39.83	.6591	1.12	.6138	1.28	.6588	1.49	.6051	1.40	.7912	6.98	.6758	4.10
		.4377	70.78	.7650	225.21	.8190	42.36	.7097	1.17	.6547	1.35	.7062	1.57	.6586	1.48	.8917	8.25	.7324	4.38
		.4834	73.78	.7889	241.49	.8696	46.74	.7634	1.25	.6929	1.43	.7641	1.69	.7104	1.57	.9413	9.75	.7980	4.80
		.5110	75.36	.8142	266.08	.9242	53.58	.8164	1.33	.7379	1.51	.8132	1.81	.7639	1.68			.8604	5.31
		.5432	76.80	.8371	283.53	.9825	64.55	.8650	1.42	.7886	1.61	.8714	1.97	.8120	1.79			.9301	6.26
		.5803	79.00	.8607	309.15			.9202	1.55	.8271	1.70	.9261	2.18	.8713	1.96			.9788	7.59
		.6191	81.04	.8896	340.15			.9740	1.72	.8657	1.81	.9767	2.47	.9133	2.12				
		.6548	83.57	.9134	369.84					.9192	1.99			.9763	2.51				
		.7226	86.88	.9427	394.19					.9713	2.28								
		.7529	89.33	.9657	402.66														
		.8036	92.19																
		.8570	95.07																
		.9083	98.91																
		.9555	103.32																

Table 2. Adsorption of argon on various adsorbents at 77.36 K (ml/g adsorbent)

LaNiO ₃		La _{0.98} Sr _{0.02} NiO ₃		La _{0.96} Sr _{0.04} NiO ₃		LaFeO ₃		La _{0.9} Sr _{0.1} FeO ₃	
P/P ₀	V _{ad}	P/P ₀	V _{ad}	P/P ₀	V _{ad}	P/P ₀	V _{ad}	P/P ₀	V _{ad}
2.475 × 10 ⁻³	.34	2.548 × 10 ⁻³	.42	2.341 × 10 ⁻³	.23	1.854 × 10 ⁻³	.86	2.290 × 10 ⁻³	.59
5.269 × 10 ⁻³	.42	5.517 × 10 ⁻³	.49	5.349 × 10 ⁻³	.30	5.085 × 10 ⁻³	1.27	5.307 × 10 ⁻³	.82
.0273	.58	.0154	.60	.0273	.46	.0171	1.76	.0159	1.18
.0532	.64	.0357	.68	.0542	.52	.0516	2.14	.0356	1.41
.1016	.71	.0595	.72	.0996	.58	.0985	2.40	.0566	1.54
.1499	.77	.0987	.77	.1484	.62	.1463	2.60	.0984	1.71
.1963	.83	.1388	.80	.1963	.66	.1958	2.79	.1458	1.86
.2466	.89	.1757	.84	.2461	.70	.2448	2.98	.1890	1.98
.2959	.94	.2144	.87	.3003	.75	.2937	3.18	.2306	2.09
.3452	.99	.2540	.90	.3476	.79	.3447	3.39	.2750	2.21
.3950	1.04	.2937	.93	.4004	.84	.3882	3.59	.3203	2.34
.4434	1.06	.3333	.96	.4429	.89	.4412	3.83	.3676	2.47
.4922	1.14	.3714	1.00	.4902	.93	.4901	4.04	.4158	2.62
.5415	1.19	.4074	1.04	.5649	1.02	.5415	4.28	.4689	2.78
.5903	1.24	.4462	1.07	.6421	1.09	.6123	4.60	.5117	2.93
.6611	1.32	.4883	1.12	.7412	1.19	.6855	4.93	.5996	3.19
.7466	1.40	.5557	1.19	.8139	1.27	.7622	5.29	.6582	3.40
.8105	1.48	.6343	1.28	.8769	1.36	.8320	5.69	.7617	3.74
.8833	1.59	.7075	1.37	.9658	1.46	.8877	6.02	.8364	4.03
.9790	1.76	.7959	1.46					.9009	4.29
		.8823	1.56					.9751	4.70
		.9624	1.69						

P₀ = 204.8 torr

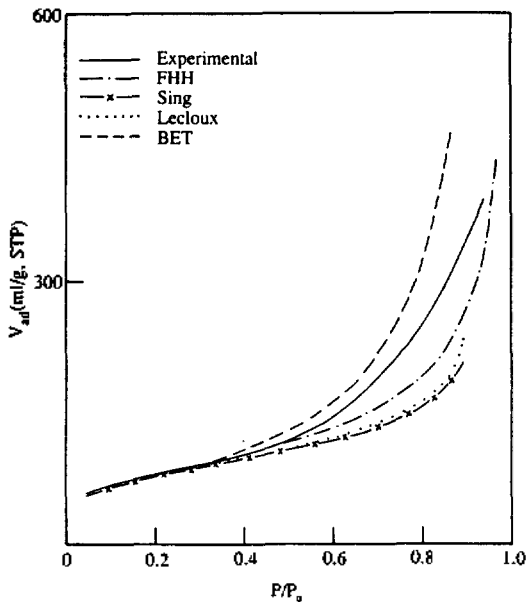


Fig. 1. Nitrogen adsorption on silica-gel (A) compared with various standard isotherms.

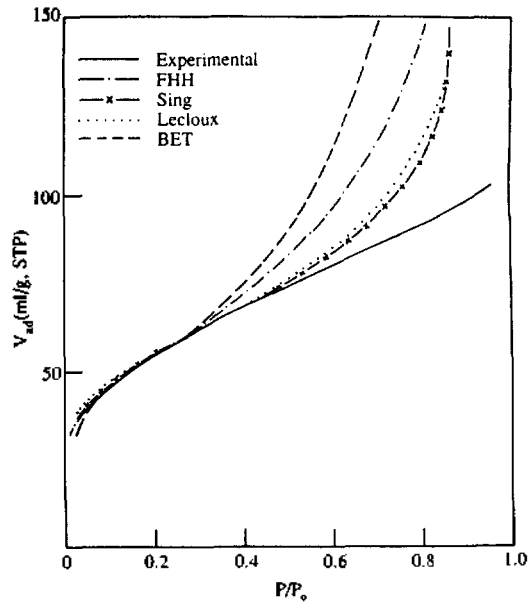


Fig. 2. Nitrogen adsorption on γ -alumina compared with various standard isotherms.

well with the experimental isotherms, showing that all of these standard isotherms are appropriate at least in this vapor pressure region. The theoretically derived isotherms of BET and FHH also fit well with experimental isotherms. At high pressure region ($P/P_0 > 0.4$) however, the experimental isotherms deviate considerably from stan-

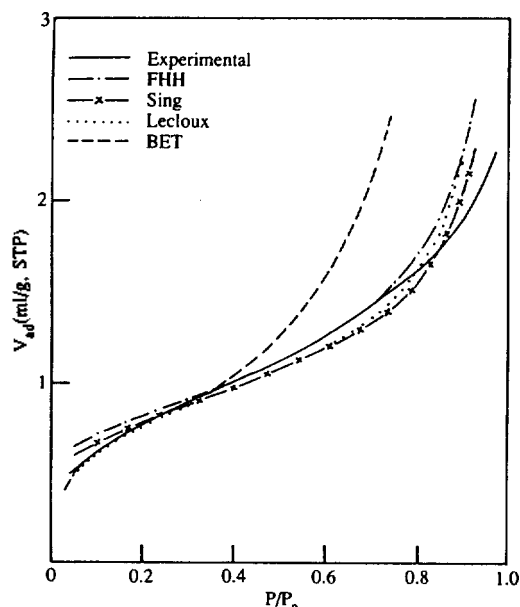


Fig. 3. Nitrogen adsorption on LaNiO_3 compared with various standard isotherms.

dard isotherms. The deviations result largely from the Kelvin condensation in the pore of adsorbents. The degree of deviation differs, however, depending on which standard isotherms is used. This reflects the uncertainty as well as the difficulty in estimating the adsorption isotherm exclusive of capillary condensation at high pressure region either experimentally or theoretically. It is noted that the BET equation given largest positive-ward deviations.

The BET equation is known to overestimate the adsorption at high vapor pressure region. Chang *et al.* assumed that the multilayer adsorption could

Table 4. Surface area determined with argon adsorption

Adsorbent	Surface area (m^2/g)		
	BET (C) ^a	t-method	
		FHH (s, b) ^b	Lecloux
LaNiO_3	3.01 (215)	2.25 (2.29, 2.59)	2.32
$\text{La}_{0.98}\text{Sr}_{0.02}\text{NiO}_3$	3.12 (237)	2.35 (3.10, 3.04)	2.30
$\text{La}_{0.96}\text{Sr}_{0.04}\text{NiO}_3$	2.40 (262)	1.81 (2.38, 2.68)	1.86
LaFeO_3	10.19 (333)	7.68 (2.25, 2.54)	7.23
$\text{La}_{0.9}\text{Sr}_{0.1}\text{FeO}_3$	7.35 (309)	5.51 (2.28, 2.54)	5.13

^aC in the bracket is the value of BET constant used in this work, ^bs and b in the bracket are values of the parameters used in this work.

Table 3. Surface area determined with nitrogen adsorption

Adsorbent	Surface area (m^2/g)				
	BET (C) ^a	t-method			
		FHH (s, b) ^b	Lecloux	de Boer	Sing
BN	14 (469)	14 (2.30, 2.65)	14	14	14
γ -Alumina	199 (79)	200 (2.00, 2.29)	213	191	198
Silica-gel (A)	283 (154)	283 (2.24, 2.25)	324	283	289
Silica-gel (B)	74 (93)	74 (1.83, 2.17)	77	71	76
γ' -Alumina	16.91 (72)	16.65 (2.16, 2.30)	14.76	16.07	19.17
LaNiO_3	2.81 (54)	2.81 (1.64, 2.07)	2.80	2.66	3.06
$\text{La}_{0.98}\text{Sr}_{0.02}\text{NiO}_3$	3.09 (127)	3.14 (2.21, 2.48)	3.29	3.00	3.15
$\text{La}_{0.96}\text{Sr}_{0.04}\text{NiO}_3$	3.16 (110)	3.15 (2.17, 2.41)	3.29	2.92	3.04
LaFeO_3	13.07 (54)	13.39 (2.34, 2.52)	12.85	12.86	10.60
$\text{La}_{0.9}\text{Sr}_{0.1}\text{FeO}_3$	8.71 (66)	8.73 (2.79, 3.02)	8.75	8.52	7.30

^aC in the bracket is the value of BET constant used in this work, ^bs and b in the bracket are values of the parameters used in this work.

take place through the adsorption of adsorbate molecules on the center of a square or a triangular array of molecules which in turn were formed by random adsorption and desorption on the adsorbent surface. With this lattice gas model and the additional introduction of as many as 4 adjustable parameters, they modified the BET equation and reduced the diverging tendency at high vapor pressure region. Persistent use of lattice gas model to the top region of the multi-adsorbed-layer is hardly persuasive. In addition, the modified equation is of no practical use since the adjustment of the parameters is impossible without recourse to some other standard isotherm.

The FHH equation, is an improved version of the BET equation in which a liquid-like properties of the adsorbed layer is taken into consideration, agrees with the experimental isotherms quite well as shown in Fig. 1~3. This agreement is considered to be a favorable endorsement to the appropriateness of the equation to be used as a standard isotherm.

The comparison of the adsorption isotherm with

standard isotherms alone cannot be a principal norm in estimating the appropriateness of the standard isotherm. The analysis of the V-t plot, a plot of adsorption versus the statistical thickness, is used in this work to estimate further the appropriateness of various standard isotherms. The V-t plot should give straight lines converging to the origin provided that there are no capillary condensation, and that the plot is based on the proper standard isotherm. The standard isotherms of Sing, de Boer *et al.*, and FHH especially among others are considered proper in this regard as can be seen in Fig. 4, 5, and 6. However, somewhat unsatisfactory results are obtained with the nitrogen adsorptions on some of the adsorbents when the standard isotherms proposed by Lecloux and Pirard are used as shown in Fig. 7. It seems that the standard isotherms are not appropriate for the nitrogen adsorption on these adsorbents. The BET plots of the adsorptions which give these undesirable results of V-t plots show satisfactory straight lines in the vapor pressure ranges used for the purpose usually. It can be said that the BET con-

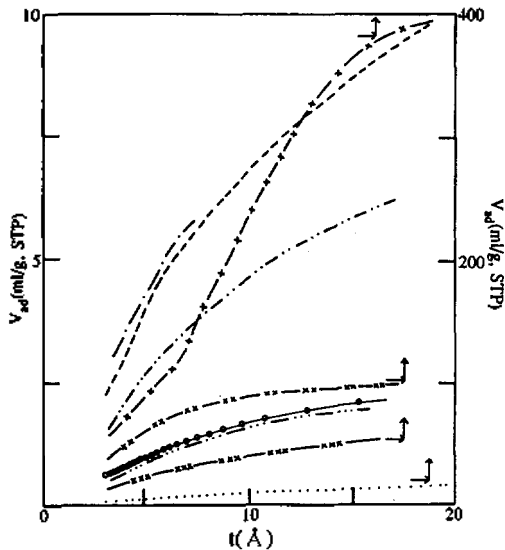


Fig. 4. The V-t plots for nitrogen adsorptions based on the standard isotherm of de Boer and Broekhoff; ---, BN; -x-x-, γ -Alumina; ·····, γ' -Alumina; -x-x-, Silica-gel (A); -x-x-x-, Silica-gel (B); -·-·-·-, LaNiO₃; ———, La_{0.98}Sr_{0.02}NiO₃; ·····, La_{0.98}Sr_{0.04}NiO₃; -·-·-·-, LaFeO₃; -·-·-·-, La_{0.9}Sr_{0.1}FeO₃.

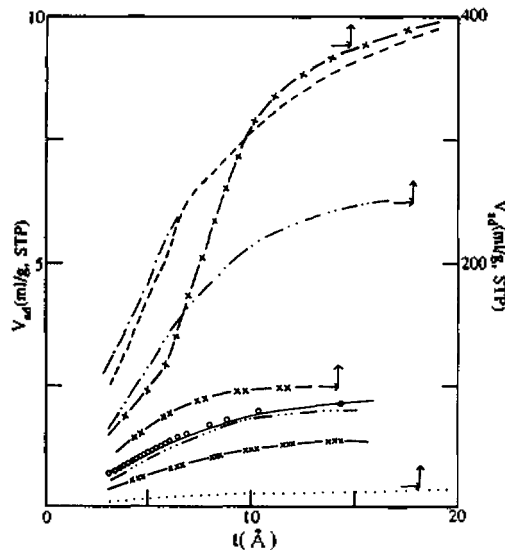


Fig. 5. The V-t plots of nitrogen adsorptions based on Sing's standard isotherm; ---, BN; -x-x-, γ -Alumina; ·····, γ' -Alumina; -x-x-, Silica-gel (A); -x-x-x-, Silica-gel (B); -·-·-·-, LaNiO₃; ———, La_{0.98}Sr_{0.02}NiO₃; ·····, La_{0.98}Sr_{0.04}NiO₃; -·-·-·-, LaFeO₃; -·-·-·-, La_{0.9}Sr_{0.1}FeO₃.

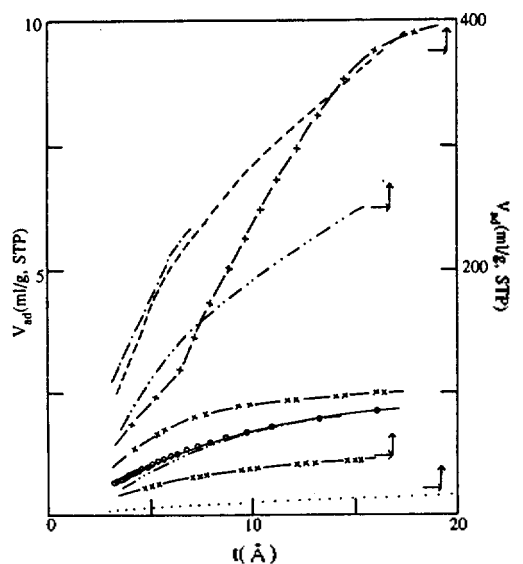


Fig. 6. The V-t plots of nitrogen adsorptions based on FHH's isotherm equation; ---, BN; -x-x-, γ -Alumina; ·····, γ -Alumina; -x-x-, Silica-gel (A); -x-x-x-, Silica-gel (B); -·-·-·-, LaNiO_3 ; —, $\text{La}_{0.96}\text{Sr}_{0.02}\text{NiO}_3$; ·····, $\text{La}_{0.96}\text{Sr}_{0.04}\text{NiO}_3$; -·-·-·-, LaFeO_3 ; -·-·-·-, $\text{La}_{0.9}\text{Sr}_{0.1}\text{FeO}_3$.

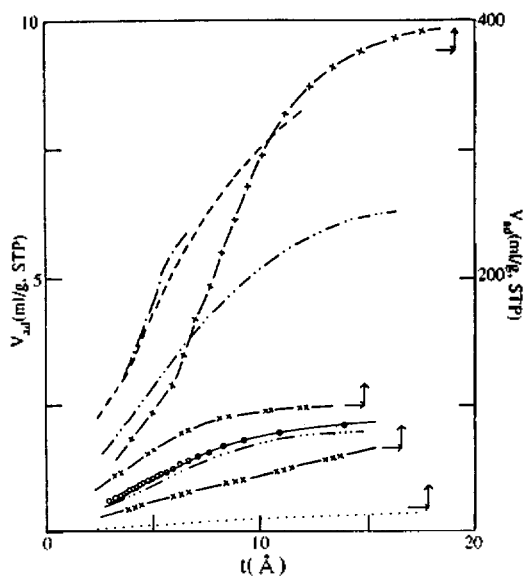


Fig. 7. The V-t plots for nitrogen adsorptions based on the standard isotherms of Lecloux and Pirard; ---, BN; -x-x-, γ -Alumina; ·····, γ -Alumina; -x-x-, Silica-gel (A); -x-x-x-, silica-gel (B); -·-·-·-, LaNiO_3 ; —, $\text{La}_{0.96}\text{Sr}_{0.02}\text{NiO}_3$; ·····, $\text{La}_{0.96}\text{Sr}_{0.04}\text{NiO}_3$; -·-·-·-, LaFeO_3 ; -·-·-·-, $\text{La}_{0.9}\text{Sr}_{0.1}\text{FeO}_3$.

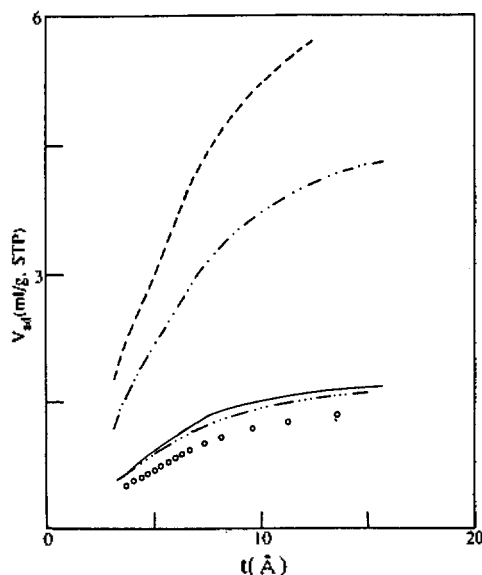


Fig. 8. The V-t plots of argon adsorptions based on FHH's isotherm equation; ---, LaNiO_3 ; —, $\text{La}_{0.96}\text{Sr}_{0.02}\text{NiO}_3$; ·····, $\text{La}_{0.96}\text{Sr}_{0.04}\text{NiO}_3$; -·-·-·-, LaFeO_3 ; -·-·-·-, $\text{La}_{0.9}\text{Sr}_{0.1}\text{FeO}_3$.

tant cannot alone be a criteria for the subdivision of the standard isotherm, and more refined criteria is desirable.

The V-t plot method was put forward by Lipens and de Boer in order to estimate the surface area of adsorbents based on their standard isotherms and also to detect any indication of capillary condensation in the pore of adsorbents. The deviations of the V-t plot from the straight line caused by the use of improper standard isotherm may lead to the erroneous interpretation of capillary condensation. On the other hand, the diverging of the V-t plot from the origin may lead to the erroneous interpretation of micro pore condensation.

One of the strong merits of the FHH equation as well as the standard isotherms of Lecloux and Pirard is that they are valid for isotherms with adsorbate gases other than nitrogen. The V-t plots of argon adsorption is impossible with numerical standard isotherms of Sing, or de Boer *et al.* All the V-t plots of argon adsorption of this work based on the standard isotherms of FHH are quite satisfactory as shown in Fig. 8. The V-t plots based

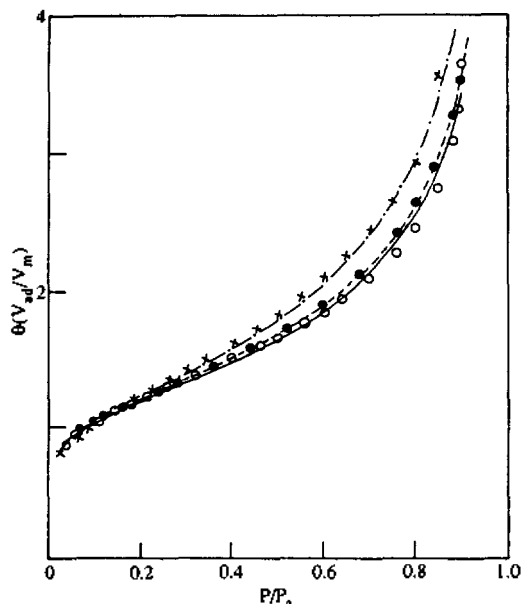


Fig. 9. The representation of various standard isotherms in terms of the FHH equation; O, Sing (silica); ●, Sing (alumina); ×, de Boer and Broekhoff. The connecting lines are the results of FHH equation with the parameters (2.58, 2.53) for Sing (silica), (2.54, 2.57) for Sing (alumina), and (2.23, 2.56) for de Boer.

on the standard isotherms of Lecloux and Pirard also give straight lines passing through the origin in contrast to the case of nitrogen adsorption.

The t -method areas obtained with the nitrogen adsorption based on various standard isotherms are quite close to the BET area, although they are completely independent of the latter one as shown in Table 3. The t -method areas obtained with the argon adsorption do not in general agree with those obtained from the nitrogen adsorption. This kind of discrepancy is a familiar occurrence in the BET areas also.

In conclusion it is confirmed that the characteristics of the V - t plot which shows a straight converging curve to the origin can be used to estimate the appropriateness of the standard isotherm. It is found also that the FHH equation, with the 2 parameters adjusted properly, can represent various standard adsorption isotherms very satisfactorily as shown in Fig. 9. The equation can serve as a standard isotherm of any adsorbate gas in

addition to nitrogen unlike any other numerical standard isotherms put forth hitherto.

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