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High-Pressure Adsorption Isotherms of N_2, CH_4, O_2, and Ar on Different Carbonaceous Adsorbents

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Adsorption equilibrium data for nitrogen, argon, methane, and oxygen on four activated carbons (Centaur, BPL, F30/470, WS42) and on one molecular sieve (CMS1) were obtained at 283 K, 303 K, and 323 K and at pressure up to 4 000 kPa. A completely automated volumetric apparatus was used to measure gas adsorption. The coherence of the results is checked by comparing some data at 303 K to those obtained by a gravimetric apparatus. The average discrepancy between the two sets of data is 5% over the whole measurement range.

Introduction

High-pressure adsorption measurements are of general interest in connection with different emerging technologies such as natural gas[1] and hydrogen storage[2] or high-pressure gas separation.[3] Moreover, the adsorption of supercritical gases such as nitrogen, argon, or methane is now commonly applied for the characterization of microporous materials.[4] Most of the research programs in the field of high-pressure adsorption are carried out using the direct gravimetric method[5] and the indirect volumetric one.[6−10] However, high-pressure adsorption data remain rare in the literature, whereas the development of the emerging technologies requires basic adsorption data (equilibrium and kinetics) in wide ranges of experimental conditions, that is to say generally for temperatures above the ambient temperature or/and high pressures (above the atmospheric pressure).

In our laboratory, two apparatuses were developed for the systematic acquisition of high-pressure adsorption data. The first one, using the gravimetric concept, consists of a magnetic suspension balance, which was instrumented to achieve completely automated adsorption isotherm measurements for pressure up to 10 000 kPa and for temperature ranging from 223 K to 393 K. The second one, using the volumetric concept, can provide automated adsorption isotherms measurements for pressure up to 4 000 kPa and for temperature ranging from 278 K to 323 K. The volumetric method is simple in its principle but requires the careful realization of each step of the experimental procedure in order to obtain reliable data. The uncertainties on the gas volume calibration and on the pressure measurements and the leakage are the main sources of errors, which may lead to nonrealistic adsorption data.[11−18] The gravimetric method is more reliable due to its relatively low sensitiveness to the leakage and due to the direct mass uptake measurement. As a consequence, the gravimetric method is often used as a reference to optimize the experimental procedure for the volumetric method.[18] This paper is devoted to the presentation of experimental excess adsorption isotherms for N_2, Ar, CH_4, and O_2 on four types of activated carbon and one molecular sieve at three temperatures, namely, 283 K, 303 K, and 323 K carried out using our volumetric apparatus. The experimental procedure was developed in such a way that the accuracy of the data may be proven.[11,18] For all gases and all adsorbents, the results obtained at 303 K are compared to those obtained with the gravimetric apparatus.

Generally, for such supercritical gases, the mass uptake at pressure can be low in comparison to the buoyancy effect on the system composed of the adsorbent and of the adsorbed phase. The buoyancy effect can be calculated if the volume of this system and the gas density are known with a good precision. It is commonly accepted that the volume of the matrix of the adsorbent can be determined by a classical helium procedure. However, such a procedure does not take into account the fact that the volume of the system is changing during the adsorption process as the porosity of the adsorbent is being filled by the adsorbate. This buoyancy effect on the adsorbed phase cannot be determined by direct experimental means as the evolution of the volume of the system is not known. That is the reason experimental adsorption data in the field of high pressures are always presented as excess adsorption data. A wide range of methods which aims at calculating the absolute adsorbed quantities from the excess quantities are proposed in the literature.[12,14,16,17,19−22]

Table 1. Structural Characteristics of the Adsorbents

	$V_{mp}/(m^3\ kg^{-1})$	$V_p/(m^3\ kg^{-1})$	$A_{mp}/(m^2\ kg^{-1})$
BPL	4.650×10^{-4}	5.786×10^{-4}	86.197
Centaur	3.556×10^{-4}	4.104×10^{-4}	40.128
WS42	7.905×10^{-4}	7.966×10^{-4}	40.066
CMS1	unknown	unknown	unknown
F30/470	3.841×10^{-4}	4.974×10^{-4}	70.460

Experimental Section

Materials. Four activated carbons Centaur, BPL, F30/470, and WS42 provided by CHEMVIRON CARBON Belgium and one carbon molecular sieve CMS1 provided by BERGBAU FORSCHUNG Gmbh were studied. Table 1 gives their structural characteristics (micropore volume V_{mP}, total pore volume V_P, and specific surface area of the mesopores and macropores A_{mP}). The micropore volume was determined using the t-plot method from N_2 adsorption data at 77 K. The total pore volume is determined from the N_2 mass uptake at 77 K and for a relative pressure

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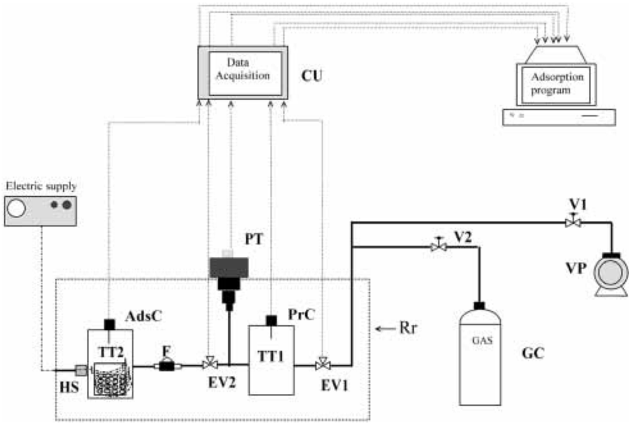

Figure 1. Volumetric apparatus: PrC, pressure cell; AdsC, adsorption cell; PT, pressure transmitter; V1 and V2, manual valves; EV1 and EV2, electrovalves 1 and 2; TT1 and TT2, Pt 100 temperatures probes; F, filter; CU, control unit; HS, in situ heating system; VP, vacuum pump; Rr, refrigerated room; GC, gas cylinder.

Table 2. Critical Parameters of the Adsorbates

adsorbate	T_c/K	P_c/kPa	ω
N_2	126.20	3 398	0.037
Ar	150.86	4 898	−0.002
CH_4	190.56	4 599	0.011
O_2	154.58	5 043	0.021

equal to 0.98. The mesopores and macropores specific surface area was determined using the t-plot method.

The gases N_2 and O_2 were provided by INDUGAS Belgium with purities equal to 99.996% vol and 99.995% vol, respectively, and Ar and CH_4 were provided by PRAXAIR Belgium with purities equal to 99.999% vol and 99.995% vol, respectively. Table 2 gives the critical temperature T_c, the critical pressure P_c, and the acentric factor ω for these adsorbates.[23]

Equipment. The volumetric apparatus is presented in Figure 1. It mainly consists of: the pressure cell (PrC); the adsorption cell (AdsC); the control unit (CU); the refrigerated room (Rr); the pressure transmitter (PT); a network of stainless steel tubes; two manual valves (V1 and V2); two electrovalves (EV1 and EV2); two Pt 100 temperature probes (TT1 and TT2); a filter (F); a vacuum pump (VP); an in situ heating system (HS) located in the adsorption cell; a gas cylinder (GC).

The apparatus is wholly automated and located in an air-refrigerated room (Rr). The tubing is made of stainless steel. Evacuation of the equipment is done with a vacuum pump (VP) (Edwards E2-M5 type) to realize a vacuum level less than 1.3 10^{-3} kPa. The heating system (HS) allows the regeneration of the sample inside the adsorption cell. Two manual valves V1 and V2 located outside the refrigerated room allow the introduction and the evacuation of the gas into and from the installation. The pressure cell (PrC) and the empty adsorption cell (AdsC) (Pyrex glass crucible included) have, respectively, a volume of 818.7 cm^3 and 323.8 cm^3. Two electrovalves EV1 and EV2 allow the progressive gas filling of (PrC) and (AdsC).

The pressure is measured by the pressure transmitter (Cerabar PMC 534 type) provided by Endress-Hauser; it allows the accurate measurement of pressure from vacuum to 4 000 kPa.

The temperatures in both PrC and AdsC are measured with two Pt 100 temperature probes (TT1 and TT2) in the temperature range 273 K ≤ T ≤ 673 K.

Table 3. N_2 Excess Adsorbed Amount on Activated Carbon CENTAUR as a Function of Pressure at 283 K, 303 K, and 323 K

T = 283 K		T = 303 K		T = 323 K	
P/kPa	n/(mmol g^{-1})	P/kPa	n/(mmol g^{-1})	P/kPa	n/(mmol g^{-1})
175	0.492	136	0.346	154	0.224
349	0.854	284	0.570	301	0.410
533	1.148	434	0.784	450	0.601
719	1.399	586	0.975	600	0.770
910	1.655	790	1.168	759	0.931
1102	1.840	998	1.388	969	1.082
1297	2.010	1153	1.561	1128	1.210
1489	2.213	1372	1.683	1343	1.384
1674	2.364	1582	1.870	1559	1.525
1852	2.502	1786	2.027	1766	1.659
2019	2.608	1985	2.148	1964	1.765
2218	2.722	2168	2.253	2153	1.784
2430	2.916	2383	2.357	2368	1.885
2628	3.001	2617	2.504	2602	2.006
2856	3.137	2828	2.617	2845	2.110
3096	3.241	3073	2.736	3086	2.190
3369	3.365	3349	2.831	3367	2.334
3737	3.513	3734	2.968	3736	2.432

Table 4. Ar Excess Adsorbed Amount on Activated Carbon CENTAUR as a Function of Pressure at 283 K, 303 K, and 323 K

T = 283 K		T = 303 K		T = 323 K	
P/kPa	n/(mmol g^{-1})	P/kPa	n/(mmol g^{-1})	P/kPa	n/(mmol g^{-1})
141	0.518	172	0.394	185	0.267
301	0.885	353	0.671	374	0.472
469	1.195	538	0.941	562	0.697
641	1.455	723	1.161	754	0.855
811	1.685	913	1.379	949	1.021
983	1.961	1102	1.583	1144	1.167
1159	2.159	1297	1.755	1290	1.293
1336	2.359	1489	1.944	1488	1.442
1510	2.520	1682	2.082	1683	1.558
1680	2.668	1867	2.220	1873	1.674
1884	2.844	2044	2.371	2053	1.785
2080	2.981	2252	2.516	2223	1.880
2297	3.131	2446	2.666	2421	1.987
2525	3.251	2660	2.765	2640	2.068
2753	3.465	2883	2.860	2865	2.183
3004	3.606	3106	2.980	3091	2.298
3301	3.832	3383	3.134	3369	2.396
3712	4.055	3736	3.320	3735	2.557

Table 5. CH_4 Excess Adsorbed Amount on Activated Carbon CENTAUR as a Function of Pressure at 283 K, 303 K, and 323 K

T = 283 K		T = 303 K		T = 323 K	
P/kPa	n/(mmol g^{-1})	P/kPa	n/(mmol g^{-1})	P/kPa	n/(mmol g^{-1})
258	2.132	290	1.747	336	1.282
421	2.649	458	2.246	517	1.661
587	3.070	632	2.625	706	1.990
757	3.430	805	2.941	898	2.281
927	3.796	988	3.228	1093	2.556
1105	4.070	1168	3.494	1291	2.788
1282	4.316	1349	3.733	1489	2.945
1454	4.501	1519	3.862	1675	3.110
1678	4.708	1741	4.003	1854	3.277
1884	4.940	1944	4.193	2026	3.404
2084	5.063	2134	4.303	2239	3.553
2310	5.187	2353	4.447	2437	3.710
2557	5.303	2587	4.574	2662	3.833
2812	5.404	2822	4.730	2899	3.949
3063	5.484	3076	4.847	3139	4.047
3365	5.650	3359	4.976	3408	4.224
3731	5.862	3731	5.119	3754	4.389

Experimental Procedure. The adsorbent sample is initially treated by heating at 423 K during a minimum 24-h period in a drying oven (atmospheric pressure). The sample (20−30 g) is then weighed in a tight crucible using

Table 6. O_2 Excess Adsorbed Amount on Activated Carbon CENTAUR as a Function of Pressure at 283 K, 303 K, and 323 K

T = 283 K		T = 303 K		T = 323 K	
P/kPa	n/(mmol g^{-1})	P/kPa	n/(mmol g^{-1})	P/kPa	n/(mmol g^{-1})
154	0.550	181	0.432	186	0.264
330	0.925	323	0.704	330	0.433
505	1.283	469	0.937	524	0.658
688	1.518	667	1.162	721	0.836
871	1.771	866	1.365	872	0.948
1054	2.024	1018	1.512	1073	1.096
1244	2.188	1223	1.686	1276	1.252
1426	2.400	1427	1.831	1480	1.407
1611	2.573	1634	1.981	1682	1.572
1792	2.725	1831	2.185	1876	1.693
1960	2.885	2024	2.274	2059	1.836
2163	3.015	2203	2.418	2233	1.946
2383	3.197	2413	2.549	2434	2.033
2585	3.353	2609	2.628	2649	2.183
2824	3.521	2818	2.767	2875	2.317
3081	3.649	3065	2.864	3120	2.435
3370	3.758	3344	3.001	3384	2.540
3731	4.025	3722	3.199	3739	2.682

Table 7. N_2 Excess Adsorbed Amount on Activated Carbon BPL as a Function of Pressure at 283 K, 303 K, and 323 K

T = 283 K		T = 303 K		T = 323 K	
P/kPa	n/(mmol g^{-1})	P/kPa	n/(mmol g^{-1})	P/kPa	n/(mmol g^{-1})
150	0.612	159	0.411	176	0.317
311	1.018	334	0.720	344	0.565
479	1.302	514	0.955	517	0.805
647	1.550	698	1.170	688	1.002
814	1.819	884	1.345	856	1.142
990	1.973	1069	1.573	1028	1.248
1160	2.141	1261	1.737	1196	1.341
1337	2.289	1454	1.861	1390	1.512
1508	2.446	1647	1.981	1603	1.672
1711	2.595	1843	2.050	1809	1.811
1901	2.704	2039	2.181	2005	1.899
2108	2.869	2233	2.312	2183	1.989
2321	3.035	2428	2.404	2386	2.073
2538	3.102	2674	2.524	2599	2.189
2764	3.218	2899	2.647	2818	2.251
3025	3.402	3140	2.770	3071	2.310
3332	3.520	3389	2.887	3361	2.425
3724	3.791	3746	3.002	3740	2.528

Table 8. Ar Excess Adsorbed Amount on Activated Carbon BPL as a Function of Pressure at 283 K, 303 K, and 323 K

T = 283 K		T = 303 K		T = 323 K	
P/kPa	n/(mmol g^{-1})	P/kPa	n/(mmol g^{-1})	P/kPa	n/(mmol g^{-1})
173	0.645	142	0.394	147	0.221
317	0.987	295	0.668	337	0.457
464	1.280	448	0.944	530	0.681
612	1.551	606	1.161	678	0.854
761	1.833	764	1.362	875	1.053
965	2.103	925	1.545	1027	1.177
1169	2.321	1087	1.694	1228	1.312
1373	2.540	1303	1.863	1430	1.448
1579	2.747	1519	2.060	1629	1.580
1786	2.971	1738	2.233	1826	1.702
1993	3.156	1957	2.406	2014	1.873
2198	3.294	2173	2.568	2194	1.955
2393	3.454	2383	2.771	2401	2.099
2624	3.642	2581	2.938	2628	2.225
2835	3.801	2809	3.071	2851	2.323
3082	3.916	3070	3.243	3105	2.473
3374	4.053	3358	3.396	3372	2.595
3733	4.288	3734	3.588	3741	2.746

Table 9. CH_4 Excess Adsorbed Amount on Activated Carbon BPL as a Function of Pressure at 283 K, 303 K, and 323 K

T = 283 K		T = 303 K		T = 323 K	
P/kPa	n/(mmol g^{-1})	P/kPa	n/(mmol g^{-1})	P/kPa	n/(mmol g^{-1})
262	2.216	299	1.747	341	1.309
428	2.776	471	2.246	536	1.731
598	3.240	652	2.625	729	2.038
775	3.635	835	2.941	929	2.314
955	3.955	1018	3.228	1132	2.559
1138	4.173	1204	3.494	1340	2.735
1321	4.391	1390	3.733	1544	2.929
1459	4.509	1570	3.862	1741	3.098
1684	4.711	1742	4.003	1930	3.252
1900	4.845	1953	4.193	2112	3.375
2099	4.969	2155	4.303	2284	3.475
2329	5.117	2383	4.447	2494	3.611
2542	5.223	2590	4.574	2688	3.743
2768	5.77	2809	4.730	2911	3.857
3035	5.485	3058	4.847	3145	3.970
3329	5.638	3350	4.976	3408	4.045
3722	5.846	3737	5.119	3750	4.211

Table 10. O_2 Excess Adsorbed Amount on Activated Carbon BPL as a Function of Pressure at 283 K, 303 K, and 323 K

T = 283 K		T = 303 K		T = 323 K	
P/kPa	n/(mmol g^{-1})	P/kPa	n/(mmol g^{-1})	P/kPa	n/(mmol g^{-1})
145	0.605	160	0.419	157	0.252
315	1.037	331	0.722	316	0.432
491	1.365	505	0.991	475	0.646
672	1.619	681	1.262	636	0.847
851	1.936	862	1.465	801	0.983
1037	2.159	1042	1.652	963	1.152
1223	2.405	1224	1.817	1131	1.292
1409	2.627	1408	1.955	1298	1.448
1598	2.745	1591	2.113	1470	1.556
1780	2.942	1776	2.264	1694	1.697
1955	3.102	1963	2.381	1913	1.862
2164	3.272	2152	2.498	2125	1.973
2361	3.387	2337	2.596	2326	2.115
2572	3.569	2578	2.783	2560	2.272
2798	3.730	2808	2.915	2817	2.403
3049	3.869	3066	3.029	3085	2.511
3345	4.044	3348	3.173	3376	2.709
3733	4.276	3735	3.384	3732	2.842

Table 11. N_2 Excess Adsorbed Amount on Activated Carbon F30/470 as a Function of Pressure at 283 K, 303 K, and 323 K

T = 283 K		T = 303 K		T = 323 K	
P/kPa	n/(mmol g^{-1})	P/kPa	n/(mmol g^{-1})	P/kPa	n/(mmol g^{-1})
159	0.665	137	0.354	145	0.227
344	1.046	280	0.593	296	0.404
484	1.333	449	0.873	442	0.599
676	1.613	641	1.145	650	0.757
823	1.781	830	1.346	805	0.913
1023	1.956	1014	1.529	962	1.051
1219	2.163	1200	1.661	1175	1.159
1413	2.348	1382	1.801	1340	1.299
1603	2.475	1558	1.962	1534	1.389
1783	2.597	1753	2.074	1727	1.512
1996	2.722	1940	2.177	1906	1.597
2194	2.888	2146	2.335	2104	1.694
2383	2.962	2344	2.406	2314	1.767
2594	3.052	2551	2.505	2527	1.873
2815	3.166	2776	2.628	2761	1.962
3073	3.272	3042	2.743	3028	2.055
3368	3.393	3339	2.864	3331	2.181
3734	3.551	3730	3.060	3726	2.322

an analytical balance. The sample is introduced in the adsorption cell. Prior to all operations, it is regenerated under vacuum (<1.3 × 10^{-3} kPa) at 453 K (local HS) during 8 h using the VP. We introduce by mean of the EV1 a quantity of gas in the PrC with the known volume V_{PrC}, the initial pressure P_{init}, and temperature T are measured,

Table 12. Ar Excess Adsorbed Amount on Activated Carbon F30/470 as a Function of Pressure at 283 K, 303 K, and 323 K

$T = 283$ K		$T = 303$ K		$T = 323$ K	
P/kPa	n/(mmol g^{-1})	P/kPa	n/(mmol g^{-1})	P/kPa	n/(mmol g^{-1})
157	0.597	141	0.352	154	0.235
334	0.984	295	0.614	299	0.421
511	1.317	449	0.863	493	0.667
701	1.595	606	1.102	691	0.869
884	1.872	767	1.296	886	1.039
1075	2.104	930	1.429	1039	1.165
1271	2.301	1091	1.583	1239	1.345
1466	2.466	1295	1.751	1446	1.480
1658	2.650	1493	1.920	1647	1.594
1846	2.788	1682	2.084	1845	1.696
2026	2.916	1861	2.231	2037	1.828
2200	3.035	2056	2.345	2220	1.943
2404	3.159	2284	2.486	2436	2.035
2594	3.276	2497	2.621	2636	2.141
2834	3.419	2731	2.737	2853	2.236
3077	3.550	3001	2.900	3105	2.376
3355	3.720	3309	3.115	3371	2.493
3725	3.902	3723	3.286	3741	2.640

Table 13. CH_4 Excess Adsorbed Amount on Activated Carbon F30/470 as a Function of Pressure at 283 K, 303 K, and 323 K

$T = 283$ K		$T = 303$ K		$T = 323$ K	
P/kPa	n/(mmol g^{-1})	P/kPa	n/(mmol g^{-1})	P/kPa	n/(mmol g^{-1})
273	2.152	288	1.617	342	1.303
445	2.674	459	2.082	528	1.689
621	3.106	636	2.436	722	1.985
804	3.442	816	2.707	918	2.277
983	3.767	999	2.930	1118	2.491
1172	3.989	1181	3.167	1320	2.716
1359	4.175	1364	3.366	1520	2.886
1543	4.272	1543	3.553	1713	3.048
1716	4.444	1721	3.674	1898	3.181
1938	4.624	1940	3.822	2074	3.283
2145	4.761	2142	3.982	2291	3.411
2340	4.818	2335	4.075	2495	3.492
2559	4.928	2554	4.193	2723	3.577
2796	5.065	2787	4.342	2927	3.656
3069	5.156	3055	4.506	3142	3.765
3350	5.221	3352	4.684	3412	3.832
3729	5.438	3732	4.930	3748	3.994

Table 14. O_2 Excess Adsorbed Amount on Activated Carbon F30/470 as a Function of Pressure at 283 K, 303 K, and 323 K

$T = 283$ K		$T = 303$ K		$T = 323$ K	
P/kPa	n/(mmol g^{-1})	P/kPa	n/(mmol g^{-1})	P/kPa	n/(mmol g^{-1})
142	0.557	132	0.321	146	0.227
322	0.958	275	0.588	298	0.380
505	1.331	425	0.786	451	0.577
694	1.609	575	0.983	606	0.763
886	1.875	777	1.217	763	0.872
1079	2.087	930	1.394	970	1.038
1273	2.310	1136	1.578	1180	1.217
1465	2.513	1345	1.767	1389	1.387
1656	2.717	1555	1.954	1599	1.534
1843	2.897	1765	2.120	1810	1.610
2024	3.023	1970	2.217	2007	1.740
2233	3.172	2164	2.334	2197	1.842
2426	3.318	2392	2.480	2418	1.945
2639	3.453	2604	2.633	2618	2.042
2860	3.566	2836	2.764	2838	2.123
3103	3.723	3075	2.930	3089	2.241
3370	3.861	3369	3.108	3372	2.346
3740	4.051	3730	3.294	3740	2.513

Table 15. N_2 Excess Adsorbed Amount on Activated Carbon WS42 as a Function of Pressure at 283 K, 303 K, and 323 K

$T = 283$ K		$T = 303$ K		$T = 323$ K	
P/kPa	n/(mmol g^{-1})	P/kPa	n/(mmol g^{-1})	P/kPa	n/(mmol g^{-1})
161	0.756	137	0.425	153	0.251
300	1.116	285	0.726	307	0.477
491	1.562	432	0.995	462	0.678
687	1.919	582	1.282	619	0.890
836	2.127	784	1.588	780	1.037
1037	2.397	992	1.860	939	1.197
1237	2.632	1201	2.089	1103	1.344
1439	2.838	1412	2.285	1322	1.533
1637	3.026	1618	2.469	1539	1.697
1826	3.228	1816	2.662	1748	1.910
2005	3.413	2009	2.765	1952	2.001
2215	3.581	2185	2.896	2141	2.135
2413	3.685	2392	3.034	2362	2.276
2623	3.855	2617	3.138	2564	2.383
2844	3.951	2847	3.312	2813	2.527
3085	4.118	3102	3.474	3062	2.616
3366	4.272	3375	3.626	3355	2.831
3732	4.462	3738	3.820	3733	3.006

Table 16. Ar Excess Adsorbed Amount on Activated Carbon WS42 as a Function of Pressure at 283 K, 303 K, and 323 K

$T = 283$ K		$T = 303$ K		$T = 323$ K	
P/kPa	n/(mmol g^{-1})	P/kPa	n/(mmol g^{-1})	P/kPa	n/(mmol g^{-1})
143	0.721	141	0.342	187	0.284
311	1.173	288	0.652	372	0.540
483	1.539	483	0.986	561	0.813
657	1.842	633	1.211	753	1.034
831	2.125	830	1.517	942	1.267
1007	2.457	983	1.678	1131	1.482
1184	2.704	1184	1.941	1326	1.666
1360	2.994	1385	2.135	1517	1.832
1538	3.212	1586	2.358	1709	1.995
1708	3.437	1787	2.573	1895	2.091
1914	3.641	1981	2.728	2069	2.205
2107	3.824	2170	2.882	2269	2.375
2320	4.026	2389	3.091	2460	2.433
2545	4.185	2594	3.202	2662	2.569
2769	4.422	2815	3.351	2873	2.661
3033	4.612	3070	3.566	3103	2.789
3330	4.858	3343	3.728	3370	2.932
3721	5.086	3721	3.976	3733	3.146

Table 17. CH_4 Excess Adsorbed Amount on Activated Carbon WS42 as a Function of Pressure at 283 K, 303 K, and 323 K

$T = 283$ K		$T = 303$ K		$T = 323$ K	
P/kPa	n/(mmol g^{-1})	P/kPa	n/(mmol g^{-1})	P/kPa	n/(mmol g^{-1})
272	2.539	285	1.817	348	1.451
438	3.240	447	2.390	531	1.995
608	3.804	614	2.865	720	2.410
785	4.185	784	3.283	911	2.773
962	4.600	958	3.578	1107	3.060
1141	4.952	1130	3.887	1301	3.369
1321	5.233	1304	4.120	1493	3.631
1499	5.416	1527	4.338	1682	3.814
1723	5.678	1736	4.566	1859	4.041
1933	5.915	1931	4.773	2029	4.198
2127	6.129	2112	4.984	2242	4.402
2353	6.374	2323	5.158	2441	4.528
2559	6.547	2548	5.349	2665	4.709
2782	6.701	2776	5.565	2903	4.848
3033	6.883	3045	5.790	3142	4.971
3336	7.110	3339	5.945	3415	5.200
3723	7.359	3726	6.227	3751	5.410

respectively, by the PT and the TT1 after reaching thermal and mechanical equilibria. These measurements (P_{init}, T, V_{PrC}) provide the initial mole number of gas n_1. Then, we open the EV2 and the gas expands in the whole installation (pressure cell + adsorption cell), the volume of which ($V_{\mathrm{PrC}} + V_{\mathrm{AdsC}}$) is known; adsorption occurs. As in the first step, pressure P_{f} and temperature T are measured after the achievement of equilibrium, and the mole number n_2 of

Table 18. O_2 Excess Adsorbed Amount on Activated Carbon WS42 as a Function of Pressure at 283 K, 303 K, and 323 K

T = 283 K		T = 303 K		T = 323 K	
P/kPa	n/(mmol g^{-1})	P/kPa	n/(mmol g^{-1})	P/kPa	n/(mmol g^{-1})
162	0.727	184	0.444	152	0.183
345	1.233	326	0.778	303	0.406
489	1.521	470	1.063	456	0.660
677	1.953	621	1.290	607	0.846
872	2.293	821	1.575	761	1.055
1067	2.568	1022	1.872	920	1.178
1261	2.847	1229	2.099	1128	1.382
1456	3.126	1435	2.286	1337	1.598
1652	3.338	1637	2.499	1550	1.773
1841	3.550	1835	2.675	1756	1.948
2020	3.716	2024	2.806	1955	2.065
2230	3.938	2200	3.039	2144	2.186
2425	4.104	2410	3.198	2362	2.347
2638	4.315	2634	3.444	2564	2.490
2859	4.519	2838	3.643	2783	2.624
3105	4.726	3076	3.823	3037	2.752
3375	4.917	3367	4.019	3343	2.972
3732	5.200	3736	4.254	3730	3.189

Table 19. N_2 Excess Adsorbed Amount on Activated Carbon CMS1 as a Function of Pressure at 283 K, 303 K, and 323 K

T = 283 K		T = 303 K		T = 323 K	
P/kPa	n/(mmol g^{-1})	P/kPa	n/(mmol g^{-1})	P/kPa	n/(mmol g^{-1})
169	0.605	135	0.338	163	0.229
316	0.854	281	0.545	321	0.417
469	1.023	435	0.684	484	0.516
625	1.163	590	0.819	649	0.608
785	1.253	801	0.963	817	0.690
942	1.375	962	1.076	985	0.773
1159	1.436	1177	1.175	1155	0.859
1375	1.544	1343	1.246	1326	0.926
1591	1.603	1562	1.332	1500	0.987
1798	1.676	1775	1.400	1728	1.022
1998	1.721	1979	1.477	1946	1.083
2188	1.770	2170	1.543	2154	1.139
2407	1.834	2395	1.558	2345	1.198
2611	1.858	2599	1.637	2571	1.245
2830	1.917	2823	1.675	2814	1.283
3086	1.983	3081	1.739	3059	1.349
3380	2.026	3373	1.787	3356	1.387
3742	2.129	3738	1.867	3740	1.470

Table 20. Ar Excess Adsorbed Amount on Molecular Sieve CMS1 as a Function of Pressure at 283 K, 303 K, and 323 K

T = 283 K		T = 303 K		T = 323 K	
P/kPa	n/(mmol g^{-1})	P/kPa	n/(mmol g^{-1})	P/kPa	n/(mmol g^{-1})
172	0.610	174	0.370	142	0.210
322	0.844	360	0.629	331	0.384
475	1.042	552	0.843	519	0.587
632	1.210	698	0.961	714	0.726
790	1.360	896	1.104	912	0.821
952	1.475	1097	1.217	1114	0.903
1165	1.622	1298	1.310	1263	1.004
1330	1.722	1502	1.390	1467	1.077
1549	1.814	1701	1.476	1668	1.159
1765	1.916	1897	1.516	1862	1.244
1980	1.975	2082	1.618	2051	1.312
2189	1.999	2266	1.647	2232	1.386
2383	2.100	2475	1.708	2444	1.429
2617	2.158	2671	1.766	2636	1.483
2833	2.212	2881	1.825	2849	1.539
3067	2.284	3130	1.891	3098	1.594
3344	2.336	3390	1.970	3383	1.681
3731	2.430	3745	2.065	3738	1.757

Table 21. CH_4 Excess Adsorbed Amount on Molecular Sieve CMS1 as a Function of Pressure at 283 K, 303 K, and 323 K

T = 283 K		T = 303 K		T = 323 K	
P/kPa	n/(mmol g^{-1})	P/kPa	n/(mmol g^{-1})	P/kPa	n/(mmol g^{-1})
276	1.605	309	1.257	331	1.011
455	1.866	494	1.515	519	1.241
642	2.028	687	1.640	714	1.384
829	2.159	878	1.772	906	1.519
1018	2.255	1074	1.849	1107	1.581
1211	2.323	1268	1.948	1308	1.648
1400	2.362	1463	2.000	1503	1.731
1579	2.430	1649	2.019	1692	1.778
1753	2.482	1825	2.075	1872	1.808
1972	2.511	2044	2.141	2094	1.873
2172	2.566	2251	2.144	2300	1.939
2400	2.632	2437	2.209	2492	2.015
2610	2.640	2653	2.243	2711	2.036
2832	2.736	2881	2.304	2939	2.090
3090	2.798	3111	2.321	3171	2.131
3373	2.831	3399	2.398	3435	2.192
3741	2.977	3751	2.451	3755	2.319

Table 22. O_2 Excess Adsorbed Amount on Molecular Sieve CMS1 as a Function of Pressure at 283 K, 303 K, and 323 K

T = 283 K		T = 303 K		T = 323 K	
P/kPa	n/(mmol g^{-1})	P/kPa	n/(mmol g^{-1})	P/kPa	n/(mmol g^{-1})
166	0.580	167	0.369	140	0.215
314	0.867	356	0.631	327	0.397
470	1.077	503	0.814	519	0.562
627	1.261	653	0.944	715	0.697
789	1.405	806	1.063	869	0.758
949	1.506	1010	1.205	1067	0.876
1112	1.623	1220	1.286	1270	0.989
1334	1.775	1427	1.418	1474	1.065
1555	1.860	1637	1.473	1675	1.146
1774	1.951	1837	1.565	1871	1.214
1990	2.030	2032	1.615	2059	1.298
2195	2.097	2215	1.686	2233	1.373
2389	2.170	2428	1.771	2437	1.445
2614	2.240	2626	1.823	2658	1.515
2859	2.323	2838	1.907	2886	1.598
3115	2.435	3091	1.951	3111	1.696
3399	2.494	3373	2.045	3388	1.740
3744	2.644	3738	2.163	3742	1.851

adsorbate remaining in the gas phase is calculated in the new conditions (P_f, T, $V_{PrC} + V_{AdsC}$). The adsorbed mole number n is calculated by the difference ($n_1 - n_2$). The same set of operations is repeated to cover the whole pressure range at constant temperature.

A preliminary adsorption cell volume V_{AdsC} determination using the helium expansion method is required for the final adsorbed amount calculation. The Redlich−Kwong equation of state is used for the gas density calculations. The maximum deviation between calculated and experimental (from literature)[24] densities was reported to be less than 0.4% for the temperature and pressure conditions concerned by the adsorption experiments. The complete description of both the experimental device and procedure may be found elsewhere.[10,11,18]

Measurement Uncertainties. The pressure is measured using an Endress−Hausser pressure transmitter with an announced uncertainty of 0.2% of the full scale ($0 \leq P \leq 4\,000$ kPa) that is to say an absolute uncertainty of 8 kPa. The uncertainty on the pressure measurement is thus a function of the point of the isotherm. It varies from 6% for low-pressure data points to 0.1% for high-pressure data points using the maximum full scale. A recalibration procedure has allowed to perform pressure measurements with a reduced uncertainty in comparison to what is announced in the technical notice of the pressure transmitter (1 kPa − 0.025% of the full scale). As a consequence,

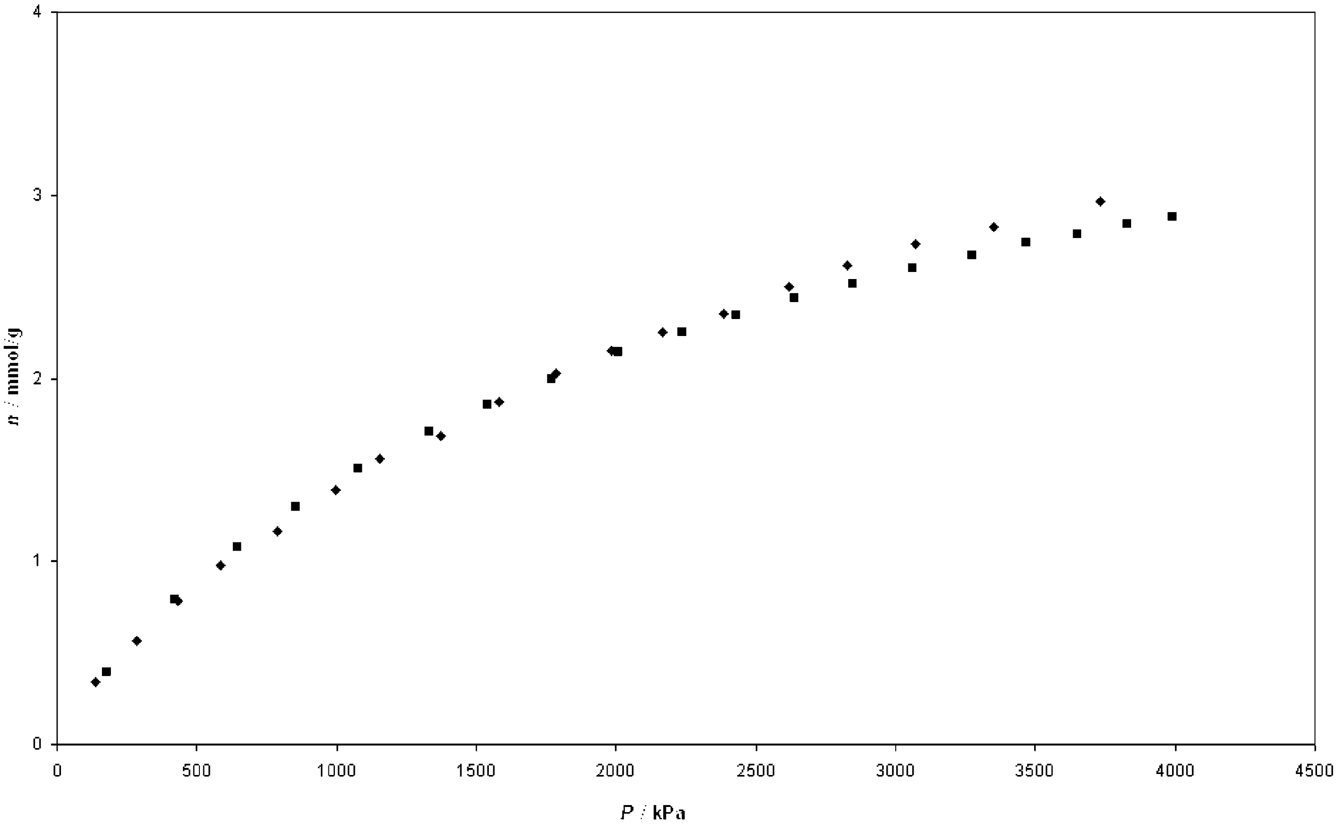

Figure 2. Excess adsorption isotherms of N_2 on CENTAUR at 303 K: ◆, volumetric; ■, gravimetric.

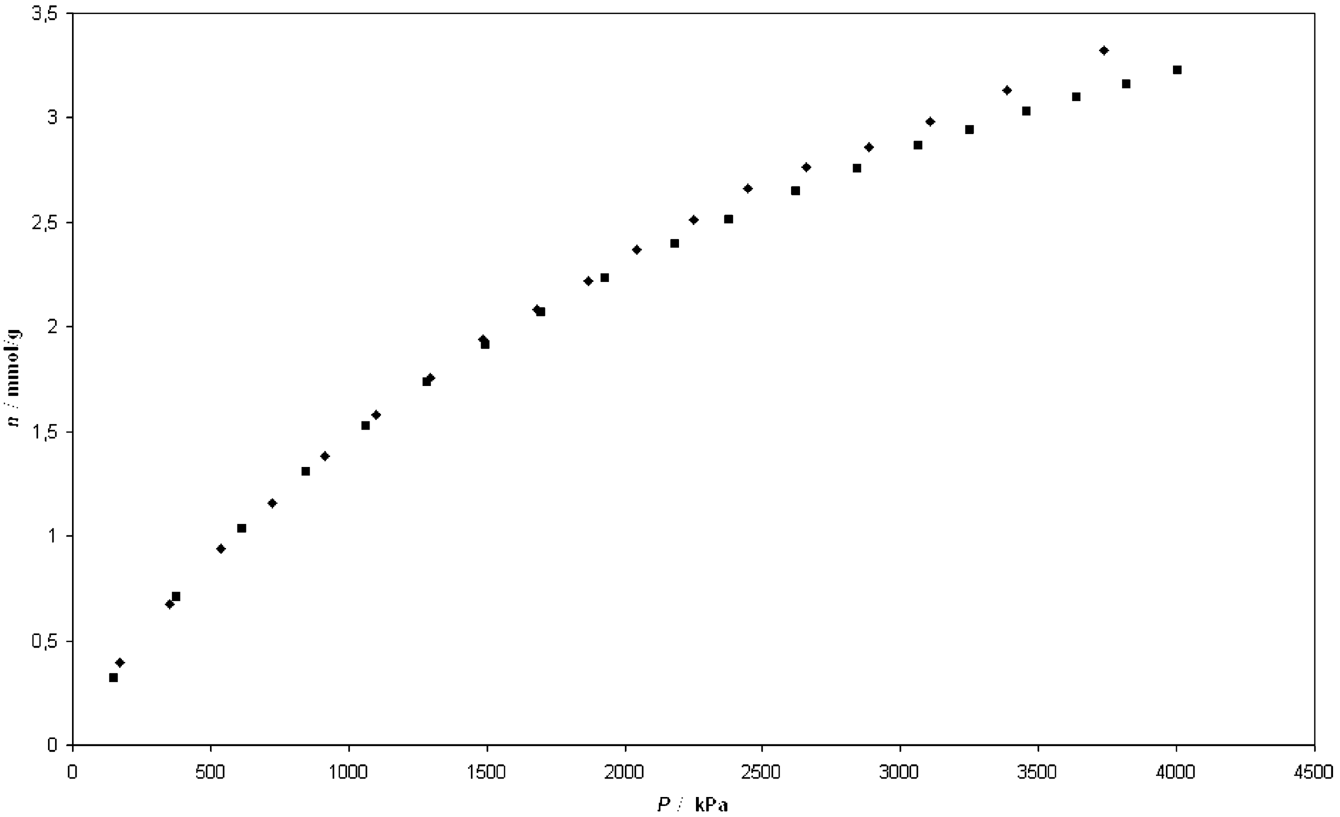

Figure 3. Excess adsorption isotherms of Ar on CENTAUR at 303 K: ◆, volumetric; ■, gravimetric.

the uncertainty on the pressure measurement ranges from 0.75% for low-pressure data points to 0.01% for high-pressure data points. For temperature measurements, the Pt 100 probes are characterized by an uncertainty equal to 0.15 K. The pressure cell volume and the adsorption cell volume were determined by helium expansion using a calibrated reference cell volume. The estimated uncertainties on the pressure cell and the adsorption cell volumes are, respectively, equal to 1.7% and 3.5%. The measurements errors on the adsorbed quantities may be calculated

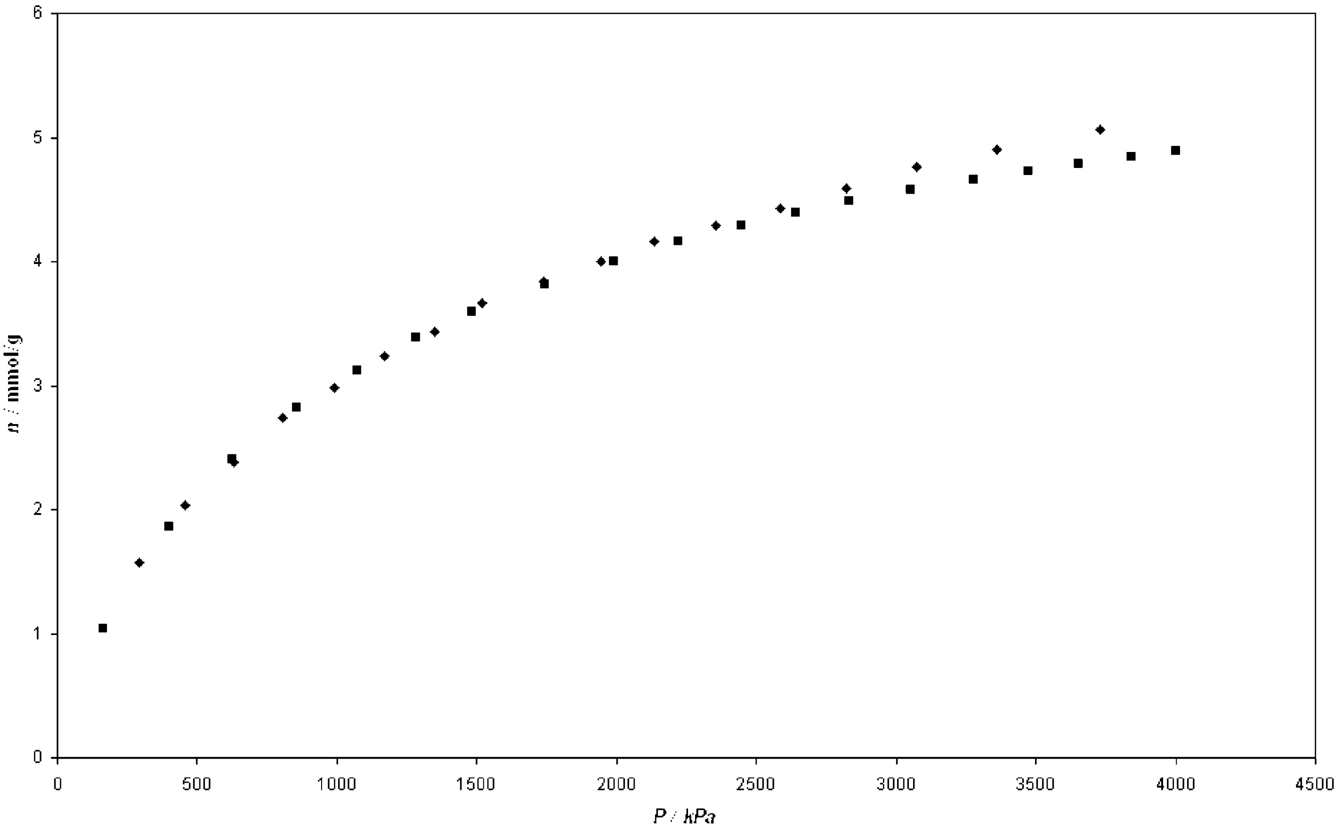

Figure 4. Excess adsorption isotherms of CH_4 on CENTAUR at 303 K: ◆, volumetric; ■, gravimetric.

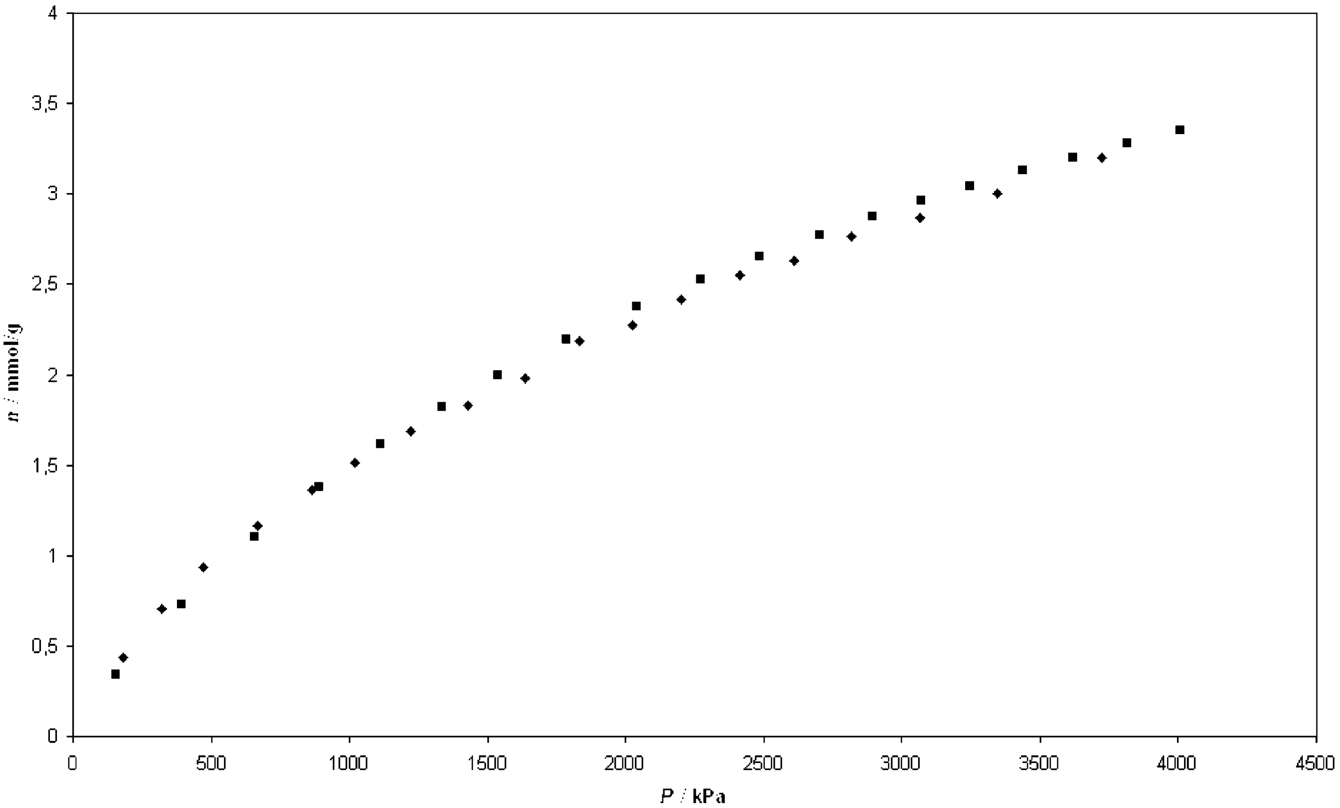

Figure 5. Excess adsorption isotherms of O_2 on CENTAUR at 303 K: ◆, volumetric; ■, gravimetric.

from the errors on the $P-V-T$ measurements taking into account the calculation procedure. The estimated effects on the adsorbed quantities may be computed for each kind of error separately (pressure, temperature, volumes, gas densities calculated from the equation of state). Such an analysis can be found elsewhere.[18] The main source of error comes from the pressure measurement uncertainty. For example, the computed uncertainty on the adsorbed amount related to the error on the pressure ranges from 51.7% for the first point (low pressure) to 6% for the last point (high

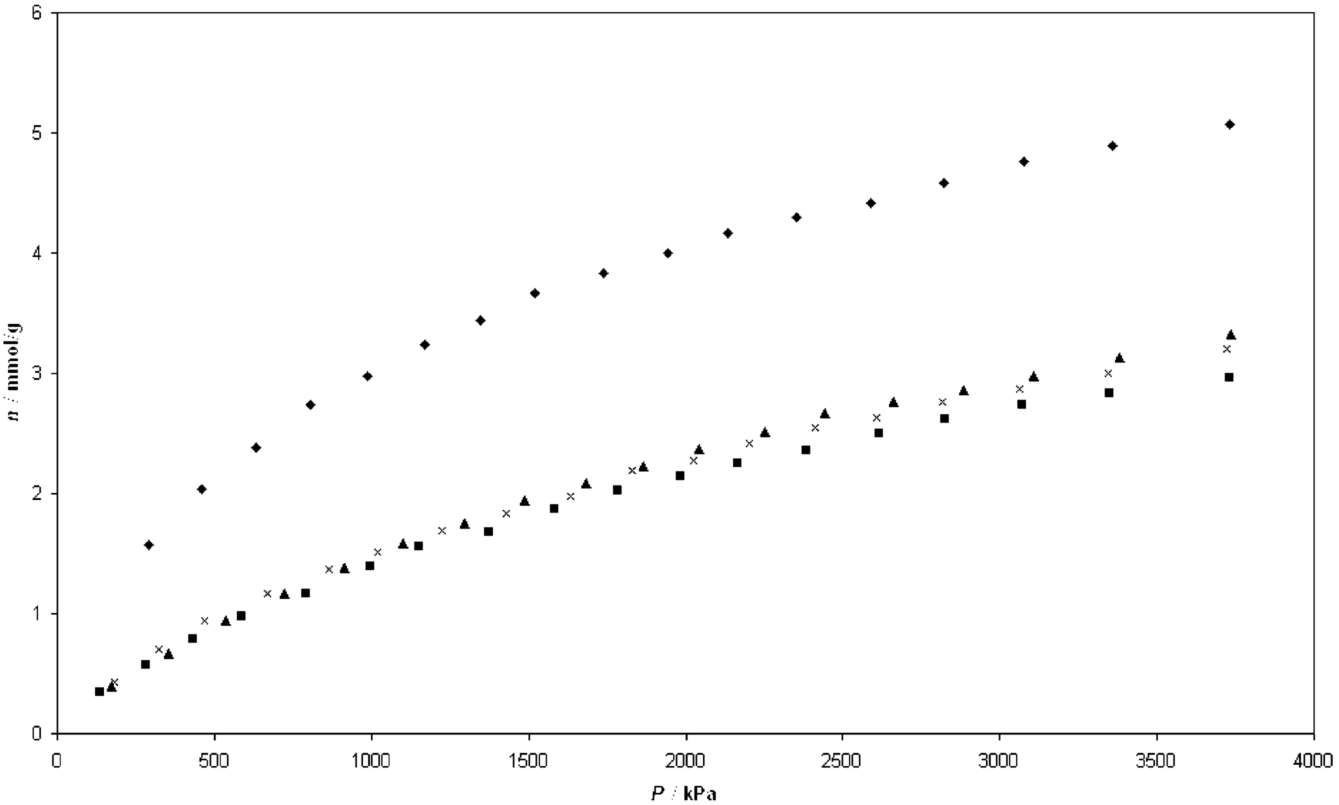

Figure 6. Excess adsorption isotherms of all adsorbates on CENTAUR at 303 K: ◆, CH_4; ■, N_2; ▲, Ar; ×, O_2.

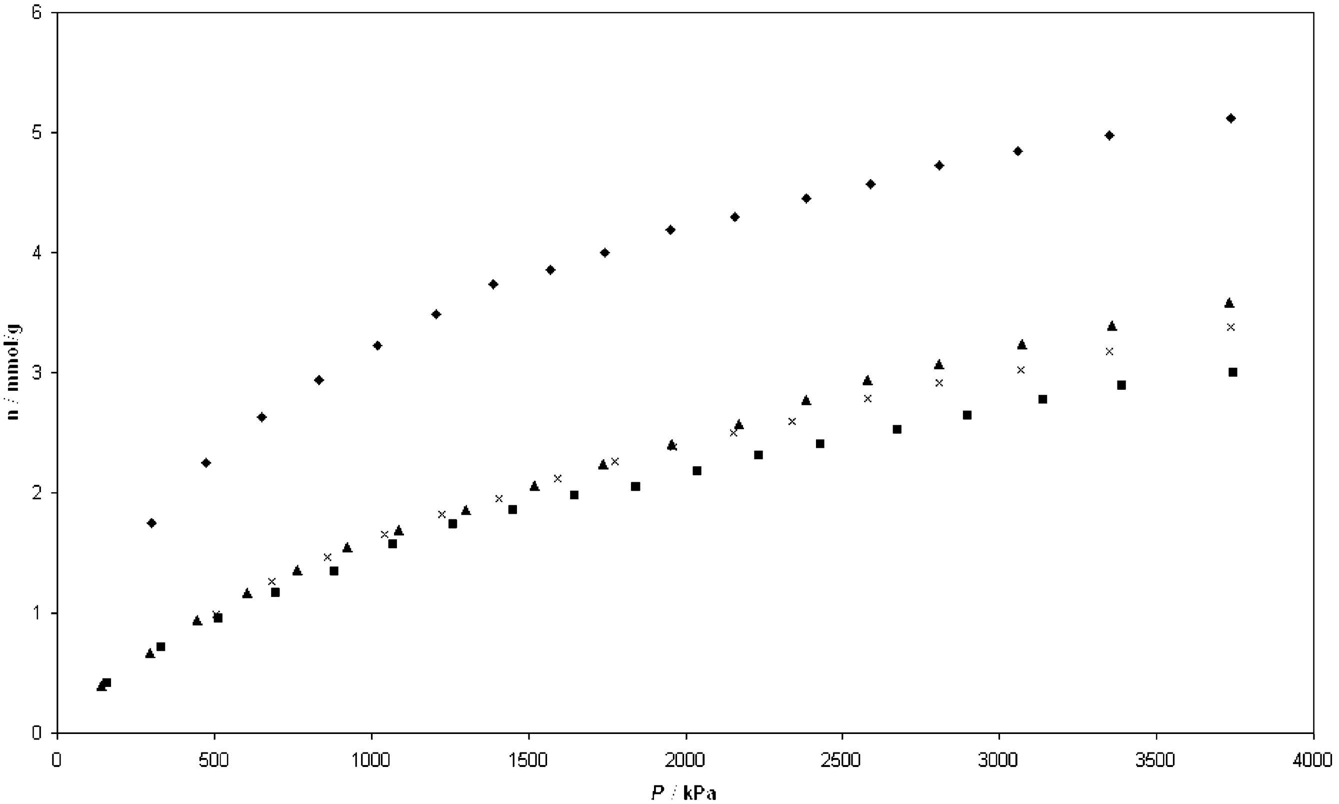

Figure 7. Excess adsorption isotherms of all adsorbates on BPL at 303 K: ◆, CH_4; ■, N_2; ▲, Ar; ×, O_2.

pressure) for the N_2–Centaur system at 303 K if we use the maximum full scale (0–4 000 kPa) and an uncertainty of 8 kPa on the pressure measurements. If we consider an uncertainty of 1 kPa on the pressure measurements, the computed uncertainty on the adsorbed quantities ranges from 6.2% to 1.2%. The observed discrepancy between the gravimetric and the volumetric data for the same system ranges from 1.46% to 6.24%.

Experimental Results. Tables 3–22 present the experimental excess adsorbed amount as a function of pres-

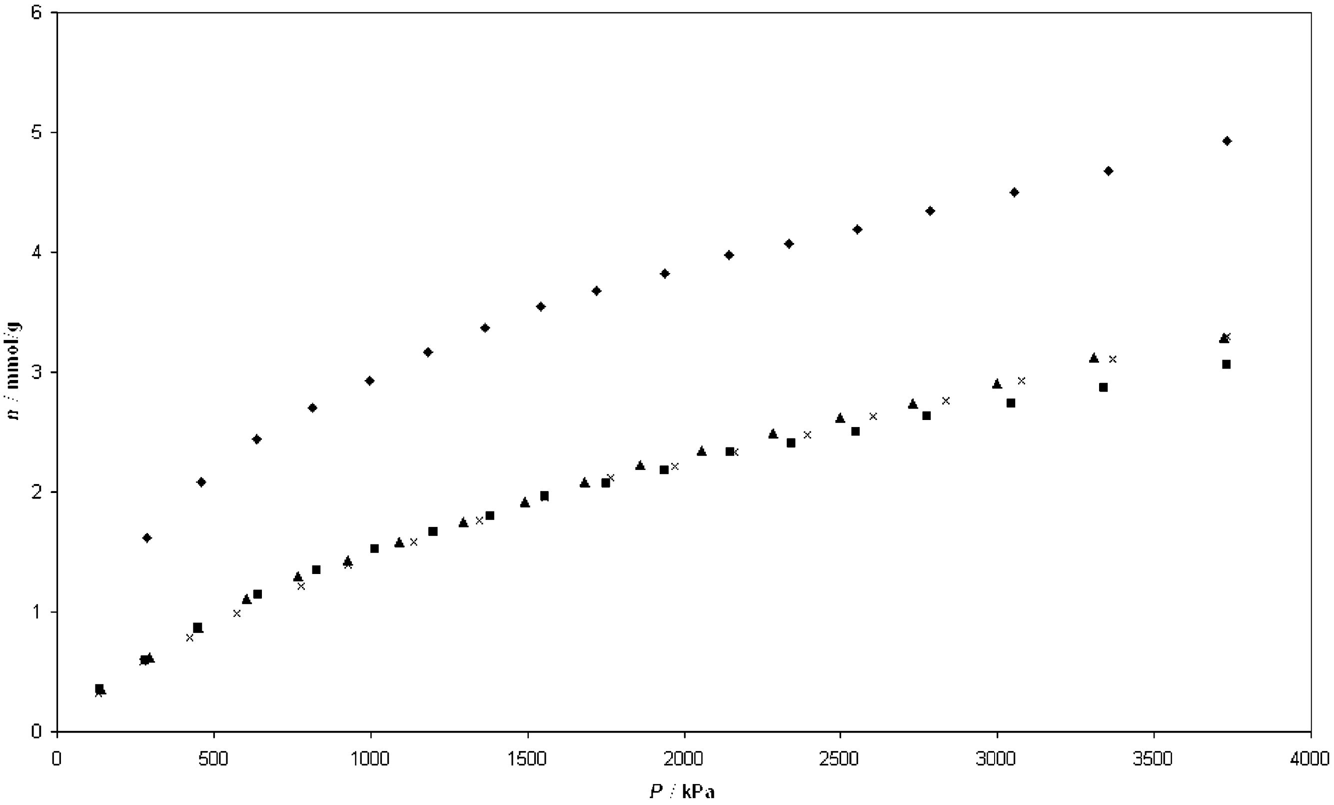

Figure 8. Excess adsorption isotherms of all adsorbates on F30/470 at 303 K: ◆, CH_4; ■, N_2; ▲, Ar; ×, O_2.

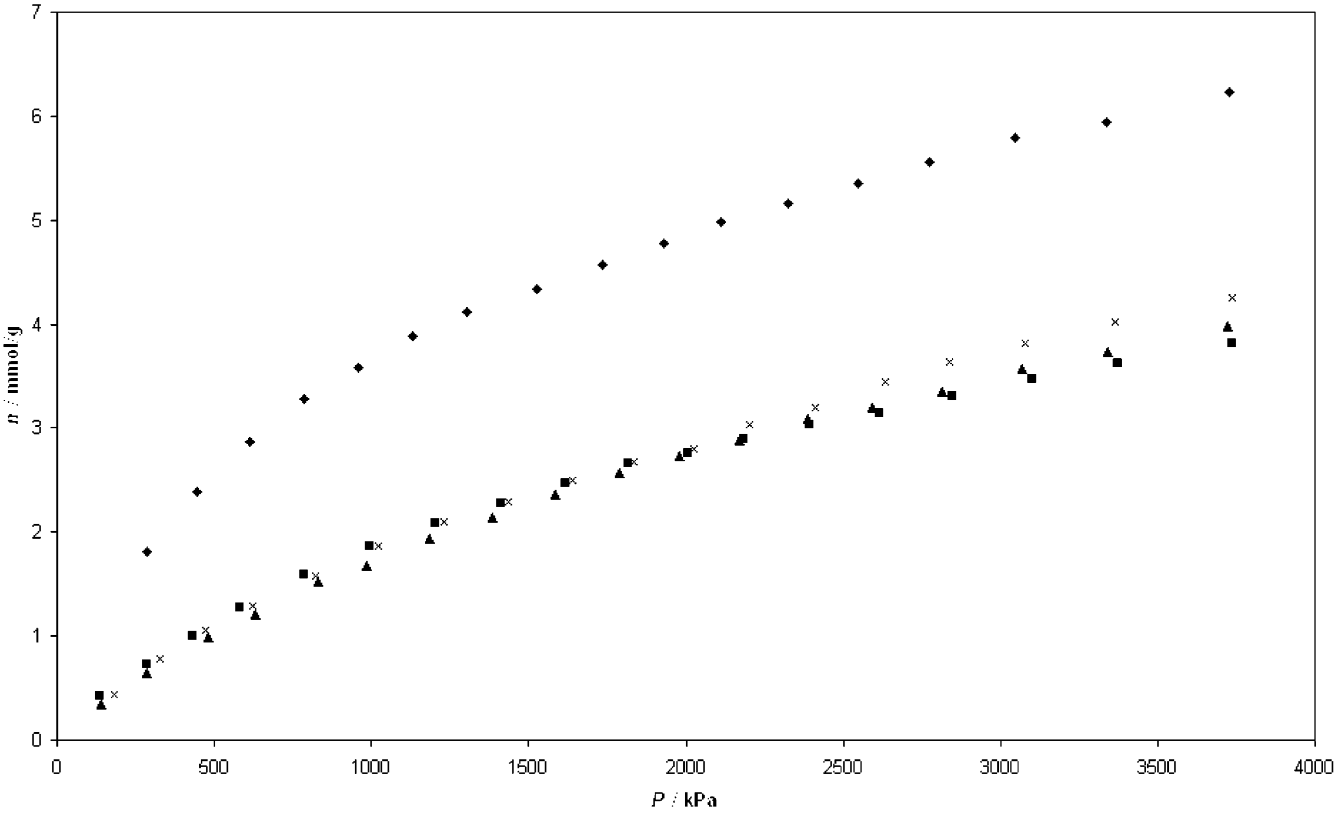

Figure 9. Excess adsorption isotherms of all adsorbates on WS 42 at 303 K: ◆, CH_4; ■, N_2; ▲, Ar; ×, O_2.

sure at temperatures of 283 K, 303 K, and 323 K for N_2, Ar, CH_4, and O_2 on activated carbons CENTAUR, BPL, F30/470, and WS42 and on carbon molecular sieve CMS1. As we noticed previously, these data were compared with those obtained by the gravimetric apparatus for all our adsorbent−adsorbate systems at 303 K. Examples of the comparison of the isotherms for activated carbon CENTAUR obtained by using these two methods are presented in Figures 2−5. Generally, the average deviation between these two sets of results is less than 5%.

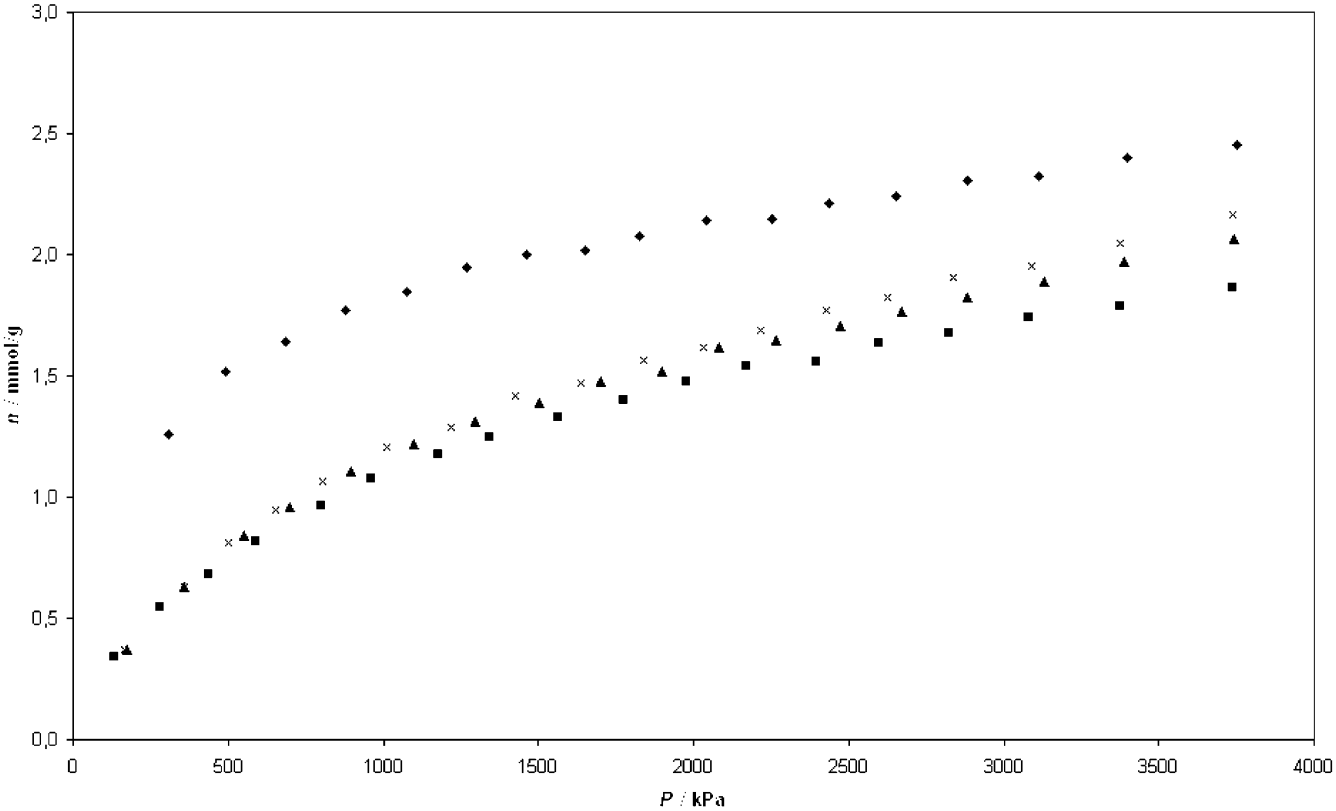

Figure 10. Excess adsorption isotherms of all adsorbates on CMS1 at 303 K: ◆, CH_4; ■, N_2; ▲, Ar; ×, O_2.

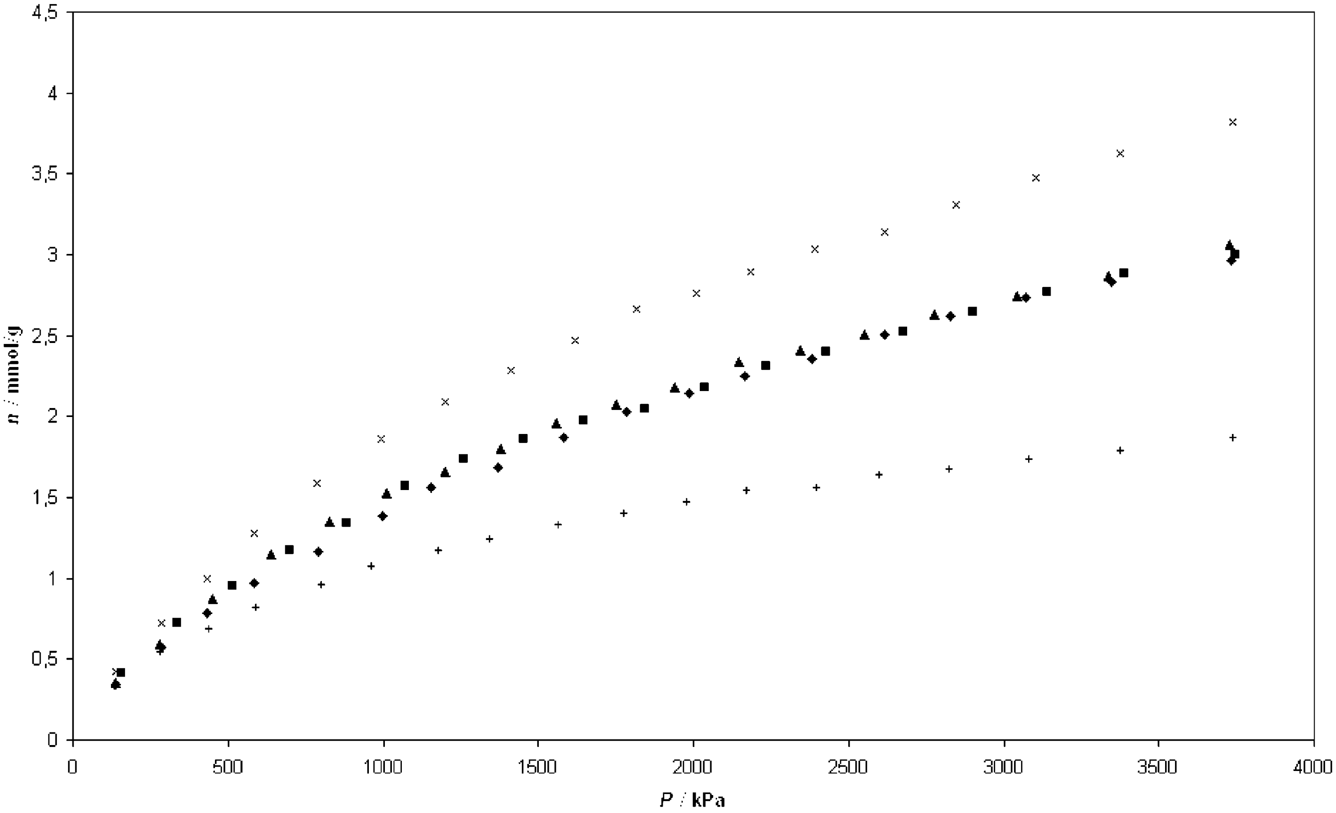

Figure 11. Excess adsorption isotherms of N_2 on all adsorbents at 303 K: ◆, CENTAUR; ■, BPL; ▲, F30/470; ×, WS42; +, CMS1.

The maximum discrepancies are observed for the high-pressure data ($P > 3\,000$ kPa). At such high pressures, the volumetric method may lead to overestimated adsorbed amounts due to microleakage, whereas the gravimetric method may lead to underestimated adsorbed quantities due to the buoyancy effect.

Figures 6−10 present the adsorption isotherms at 303 K for all the adsorbates on a given adsorbent.

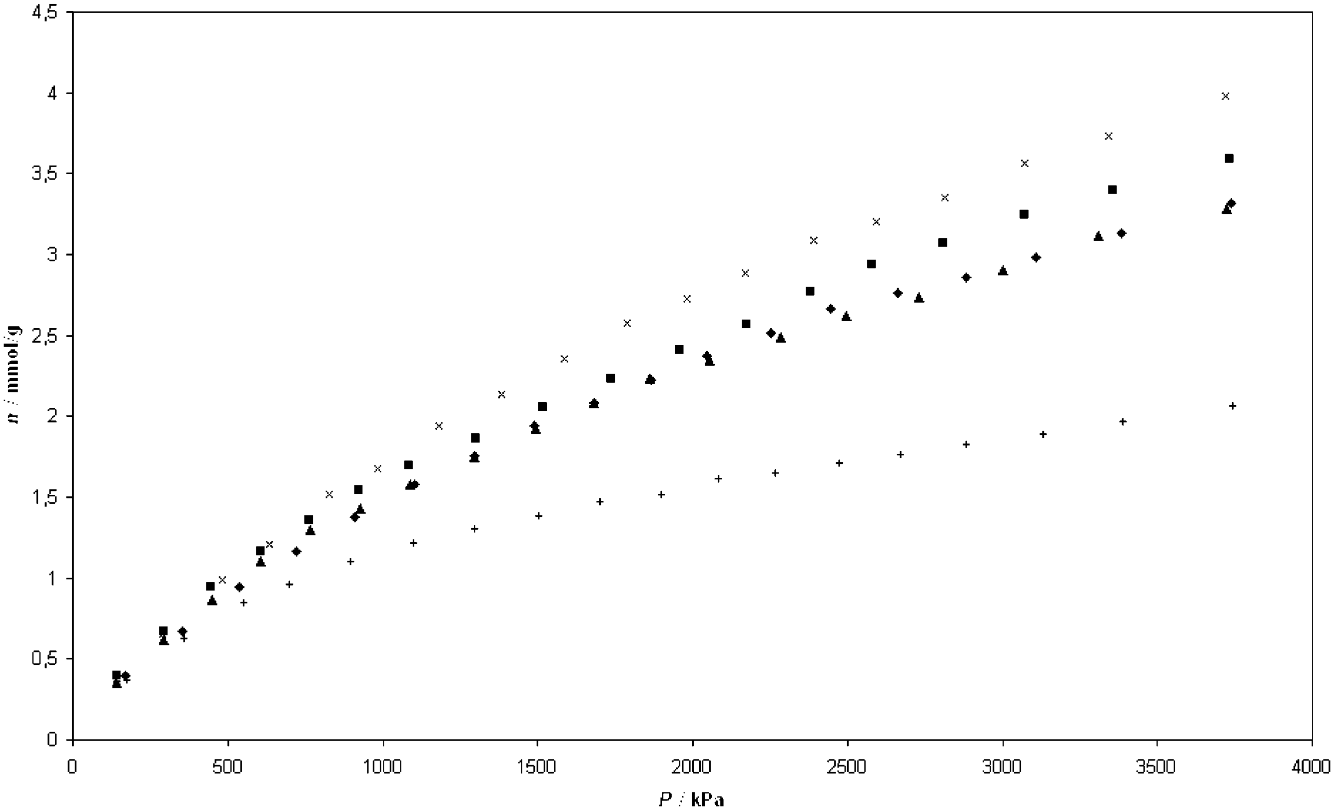

Figure 12. Excess adsorption isotherms of Ar on all adsorbents at 303 K: ◆, CENTAUR; ■, BPL; ▲, F30/470; ×, WS42; +, CMS1.

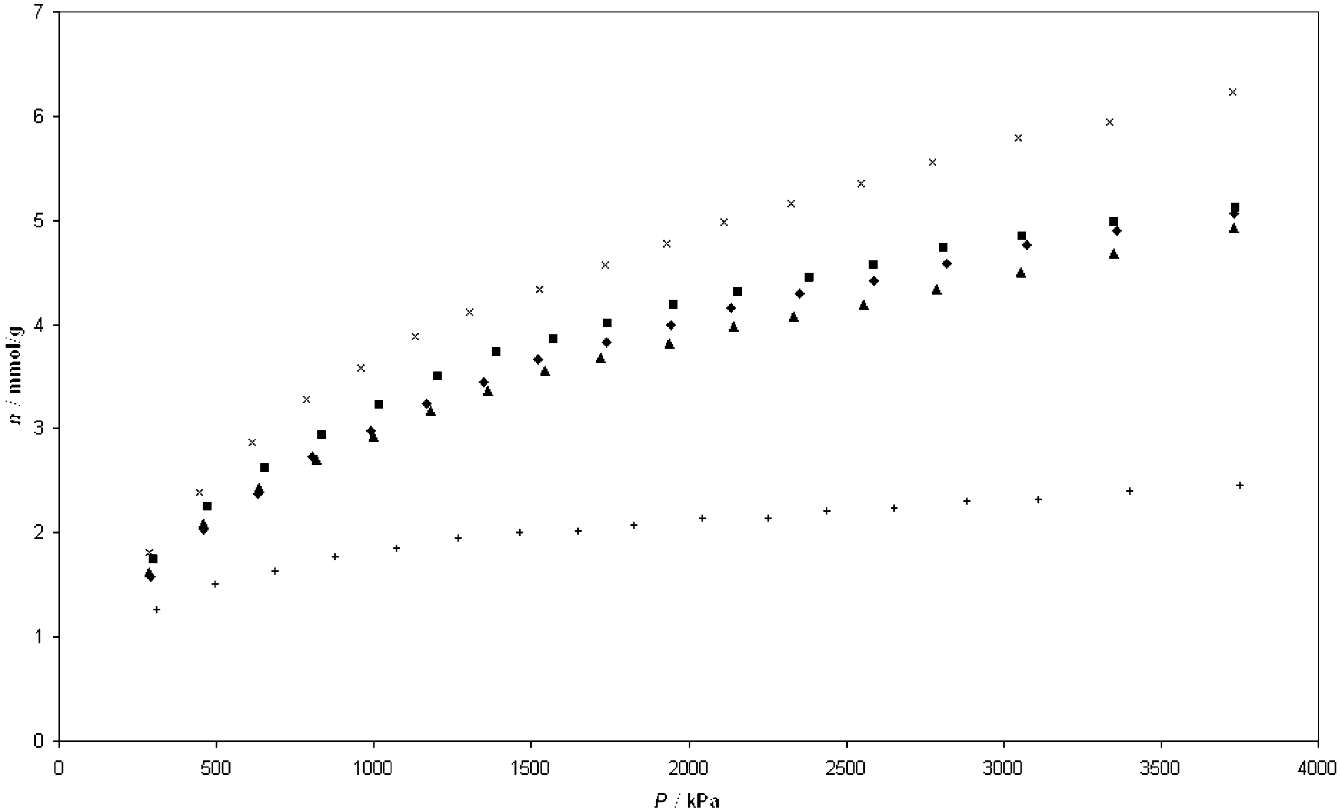

Figure 13. Excess adsorption isotherms of CH_4 on all adsorbents at 303 K: ◆, CENTAUR; ■, BPL; ▲, F30/470; ×, WS42; +, CMS1.

Figures 11−14 present the adsorption isotherms at 303 K for a given adsorbate on all the adsorbents.

Results and Comments

First of all, it should be reminded that the provided data are excess data. They do not take into account the buoyancy effect on the adsorbed phase. For supercritical temperatures, it has been established that the deviations between the absolute and excess data do not exceed the experimental error as far as carbonaceous are concerned.[22] Theoretical methods for the calculation of the buoyancy effect on the adsorbed phase are proposed in the litera-

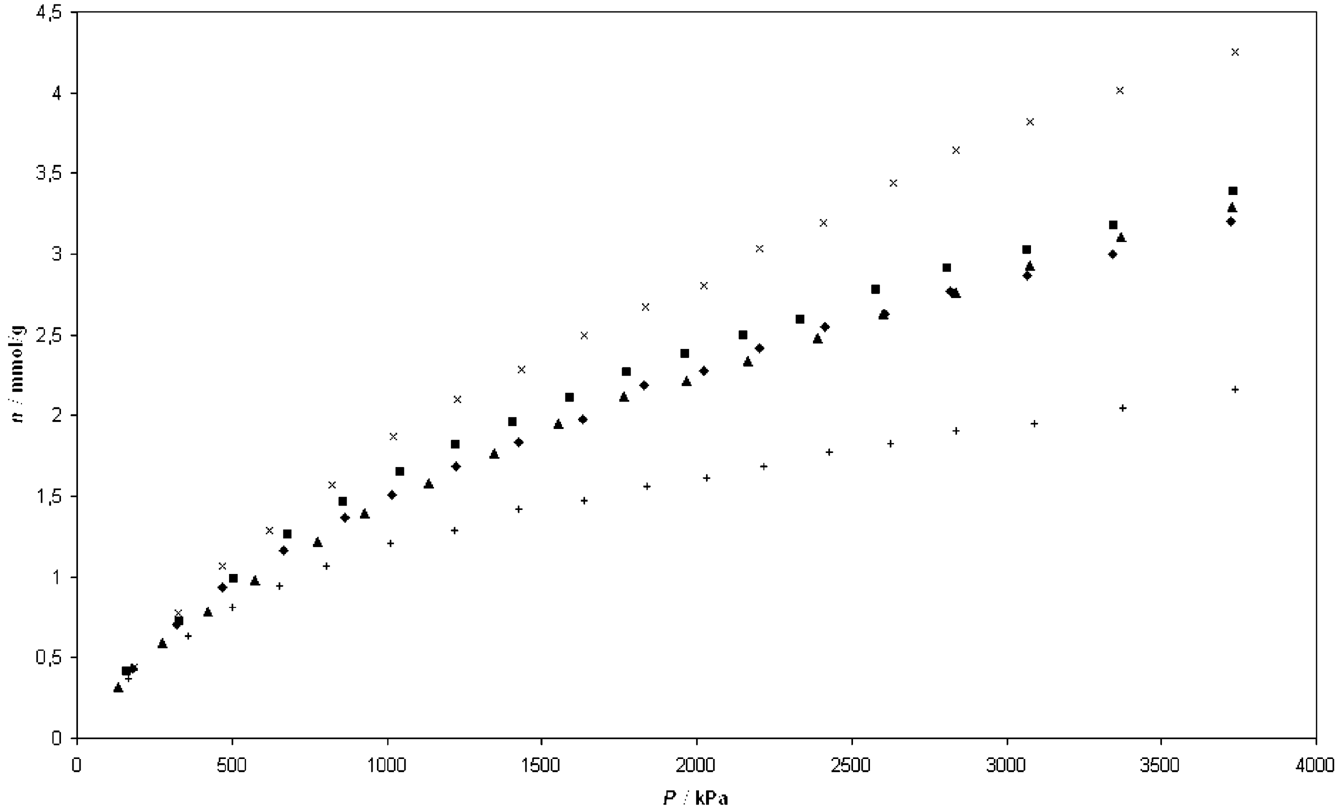

Figure 14. Excess adsorption isotherms of O_2 on all adsorbents at 303 K: ◆, CENTAUR; ■, BPL; ▲, F30/470; ×, WS42; +, CMS1.

ture,[12,14,16,17,19−22] but none of them can be validated by experimental means.

A brief analysis of the data shows generally almost the same structural picture of each adsorbent independently of the adsorbate. From Figures 11−14, it appears that the maximum adsorbed amounts are obtained for WS42 due to the fact that this adsorbent is characterized by a high total pore volume (Table 1). The slope of the isotherms is high in the whole pressure range, which may be due to multilayer adsorption: this adsorbent seems to have a relatively wide pore size distribution. The lowest adsorbed amounts are obtained for CMS1. CMS1 isotherms exhibit a steep initial slope but the micropores seem to be completely filled at 1 000−1 500 kPa. It is the typical behavior of molecular sieve materials characterized by a narrow micropore size distribution. BPL, CENTAUR, and F30/470 show a relatively intermediate behavior. This first qualitative analysis of these data agrees perfectly with the values of the structural characteristics presented in Table 1 obtained by the t-plot method.

From Figures 6−10, it appears that CH_4 is always preferably adsorbed. The other adsorbates are generally adsorbed in the same way. This could be due to the fact that these adsorbates have relatively low polarizabilities compared to CH_4 (Ar, 1.64×10^{-3} nm^3; O_2, 1.60×10^{-3} nm^3; N_2, 1.74×10^{-3} nm^3; CH_4, 2.59×10^{-3} nm^3)[25] and to the higher nonspecific interactions between the surface and the CH_4 molecule.

Conclusions

In this paper, we present excess adsorption isotherms for N_2, Ar, CH_4, and O_2 on activated carbons (CENTAUR, BPL, F30/470, WS42) and on one molecular sieve CMS1 for pressures ranging from 0 to 4 000 kPa and for temperatures ranging from 283 to 323 K.

These measurements have been obtained using a volumetric apparatus, and the comparison at 303 K with gravimetric measurements for one activated carbon proves their good precision.

Some comments relating these results to the structural characteristics of the adsorbent are provided.

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