Adsorption of CO_2 on Microporous Materials. 1. On Activated Carbon and Silica Gel

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Adsorption isotherms of carbon dioxide (CO_2) at temperatures ranging from 278 K to 328 K (seven temperatures) and at pressures up to 3300 kPa on activated carbon and on silica gel are presented.

Introduction

This paper is an experimental part of a general study devoted to gas adsorption on microporous media. The experimental part consists of measurements on different adsorbents such as activated carbon, silica gel, and synthetic zeolite (Berlier et al., 1995c) and using a variety of measurement methods such as gravimetric or calorimetric ones (Berlier et al., 1995b; Berlier and Frère, 1996). The present work reports adsorption isotherms of CO_2 on activated carbon and silica gel using a volumetric technique in a large range of pressure. Literature experimental studies have been made only in the low-pressure range (Valenzuela and Myers, 1989).

These experimental results are useful as they allow us to broaden the T, P domain of CO_2 adsorption. These data, together with more classical ones (obtained at low temperature and low pressure (Berlier and Frère, 1996)), will make possible the test of theoretical developments for the prediction of adsorption isotherms in a range of temperature and presure conditions never studied before.

Experimental Section

Materials. CO_2 was provided by Air Liquid Belgium with a minimum purity of 99.995 vol %. The impurities are O_2, H_2O, N_2, C_nH_m, and CO. Of these, the most important one is N_2 (≤30 ppm). Saturated pressures and enthalpies of vaporization for experimental temperatures are presented in Table 1 (Stewart et al., 1986). The critical temperature and pressure are respectively 304.21 K and 7382.5 kPa (Stewart et al., 1986).

The activated carbon F30/470 was provided by Chemviron Carbon. The BET specific surface, determined in our laboratory on a Quantasorb Sorption System, was 1150 m^2/g, and the pore volume was 0.62 cm^3/g. Other characteristics, provided by Chemviron Carbon, are listed in Table 2.

The silica gel KC-Trockenperlen Blau was provided by Kali-Chemie AG. Table 3 lists the characteristics of silica gel as an adsorbent.

Apparatus and Procedure. The wholly automated device is based on a volumetric method (Berlier et al., 1995a). The principle of this method consists of successive expansions of the gas from a buffer tank to the adsorber. From the known volume of the tanks, the adsorbed mass can be calculated using an equation of state and knowledge of the temperature and pressure in the system before and after adsorption (Berlier at al., 1995a,c).

The wholly automated apparatus enables pure gas isotherms to be determined from 273 K to 373 K and at

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Table 1. Saturated Pressure (P_s) and Enthalpy of Vaporization ($\Delta_{vap}H$) of CO_2 at Experimental Temperatures (Stewart et al., 1986)

	T/K						
	328	318	308	303	298	288	278
$P_s(T)$/kPa	$T > T_c$	$T > T_c$	$T > T_c$	7207.5	6431.1	5084.8	3968.5
$-\Delta_{vap}H(T)$/J·g^{-1}	$T > T_c$	$T > T_c$	$T > T_c$	63.407	120.00	177.83	215.74

Table 2. Main Characteristics of Activated Carbon F30/470 as an Adsorbent

apparent density/kg/m^3	460 ± 20
particle size/mm	>2.0
hardness	>98

Table 3. Main Characteristics of Silica Gel KC as an Adsorbent

specific surface/m^2/g	750
apparent density/kg/m^3	800
particle size/mm	2−5
mean diameter of pores/Å	20
volume of pores/cm^3/g	0.35

Table 4. Mass of CO_2 Adsorbed per Unit Mass of Activated Carbon F30/470 (M_r) versus Pressure (P) at 278 K and 288 K

T = 278 K		T = 288 K	
P/kPa	M_r	P/kPa	M_r
86.5	0.1396	101.9	0.1260
165.3	0.1835	188.5	0.1670
256.4	0.2214	285.3	0.1983
364.4	0.2483	393.3	0.2266
493.8	0.2721	517.0	0.2475
623.1	0.2900	649.8	0.2639
762.6	0.3068	791.5	0.2784
908.9	0.3172	953.5	0.2928
961.1	0.3182	1099.8	0.3043
1070.9	0.3294	1260.6	0.3136
1088.3	0.3288	1424.9	0.3245
1230.0	0.3367	1625.1	0.3321
1239.6	0.3375	1813.0	0.3413
1365.0	0.3404	2009.9	0.3473
1409.5	0.3457	2218.0	0.3539
1496.6	0.3472	2438.5	0.3625
1587.3	0.3525	2681.5	0.3715
1632.8	0.3523	2961.6	0.3805
1775.6	0.3560	3326.1	0.3928
1795.4	0.3599		
1919.6	0.3623		
2024.9	0.3659		
2087.3	0.3711		
2242.0	0.3735		
2243.6	0.3776		
2419.1	0.3823		
2594.6	0.3917		
2797.1	0.4030		
3028.9	0.4187		
3384.4	0.4478		

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Table 5. Mass of CO_2 Adsorbed per Unit Mass of Activated Carbon F30/470 (M_r) versus Pressure (P) at 298 K and 303 K

T = 298 K		T = 303 K	
P/kPa	M_r	P/kPa	M_r
93.4	0.0980	101.5	0.0971
176.6	0.1363	184.8	0.1342
271.1	0.1679	283.8	0.1639
383.6	0.1943	392.9	0.1887
507.4	0.2160	520.0	0.2101
644.6	0.2344	667.4	0.2304
785.3	0.2508	806.9	0.2441
933.8	0.2640	958.8	0.2571
1098.0	0.2763	1115.1	0.2689
1273.5	0.2849	1277.1	0.2797
1443.4	0.2962	1443.6	0.2887
1615.5	0.3031	1618.0	0.2989
1795.5	0.3120	1802.5	0.3065
1987.9	0.3190	1993.8	0.3121
2198.3	0.3241	2201.9	0.3158
2421.0	0.3332	2438.1	0.3230
2666.3	0.3390	2678.9	0.3290
2955.4	0.3458	2953.4	0.3374
3335.6	0.3572	3328.0	0.3461

Table 6. Mass of CO_2 Adsorbed per Unit Mass of Activated Carbon F30/470 (M_r) versus Pressure (P) at 308 K

P/kPa	M_r	P/kPa	M_r
104.1	0.0886	1304.4	0.2676
107.4	0.0924	1432.8	0.2713
195.3	0.1238	1484.4	0.2755
209.8	0.1306	1618.4	0.2807
297.6	0.1535	1654.3	0.2837
323.4	0.1595	1823.1	0.2899
411.3	0.1771	1866.9	0.2930
435.9	0.1822	2009.9	0.2948
530.5	0.1972	2067.1	0.2988
570.9	0.2024	2238.3	0.3014
670.0	0.2151	2293.3	0.3083
700.3	0.2188	2454.3	0.3094
815.1	0.2299	2501.4	0.3139
833.0	0.2331	2693.9	0.3155
958.0	0.2424	2719.6	0.3195
972.5	0.2457	2963.9	0.3237
1108.8	0.2537	2980.6	0.3274
1123.3	0.2557	3335.1	0.3367
1273.0	0.2644	3339.5	0.3387

pressures up to 4000 kPa. In this method, the total quantity of gas admitted into the system and the amount of gas in the vapor phase remaining after adsorption equilibrium are determined by appropriate $P-T-V$ measurements.

Details of this device and the operating procedures (including the pretreatment process of the adsorbent) are presented in previous papers (Berlier et al., 1995a,c).

Measurement Accuracy. Experimental errors are linked with temperature and pressure measurements. The temperature is measured using a Pt100 with an accuracy of 0.1 K. The pressure is measured using an Endress Hauser (Cerabar) absolute transducer with an accuracy of $\pm$0.1% of the scale. The absolute error is $\pm$3.6 kPa, giving the maximum relative error in the pressure of 7% for the first point of the CO_2 isotherm on activated carbon at 328 K. Other errors (equation of state, mass of adsorbent, ...) have been discussed in previous papers (Berlier et al., 1995c; Frère et al., 1994), and a typical value of the mean experimental error is 3%.

Results and Discussion

Adsorption isotherms for CO_2 on activated carbon and silica gel at temperatures (278, 288, 298, 303, 308, 318, and 328) K were obtained at pressure up to 3300 kPa. The results are presented in Tables 4−11 and in Figures 1 and 2. Several sets of measurements were reproduced with differences of less than 2%. An example can be observed in Figure 1 at 308 K where experiments have been conducted two times over the entire range of pressure (0−3300 kPa).

The experimental isotherms are presented in Figures 1 and 2. On each adsorbent, isotherms are similar in shape and have a classic isotherm form. The comparison between activated carbon and silica gel is more interesting. At low pressures, the adsorbed mass on activated carbon increases sharply before a slower increase in the medium- and high-pressures ranges (Figure 1). The adsorption increase on silica gel is nearly constant over the entire range of pressure (Figure 2). This difference can be used in some industrial applications such as recovery systems, heat pumps, ... (Frère et al., 1994; Cacciola and Restuccia, 1994).

Table 7. Mass of CO_2 Adsorbed per Unit Mass of Activated Carbon F30/470 (M_r) versus Pressure (P) at 318 K and 328 K

T = 318 K		T = 328 K	
P/kPa	M_r	P/kPa	M_r
116.6	0.0780	50.0	0.0375
224.6	0.1108	150.1	0.0769
337.1	0.1373	243.5	0.1023
453.0	0.1587	345.9	0.1240
593.6	0.1783	457.3	0.1428
739.9	0.1956	578.8	0.1575
881.6	0.2077	707.0	0.1717
1041.4	0.2207	842.0	0.1845
1202.3	0.2298	984.9	0.1960
1356.4	0.2402	1133.4	0.2057
1553.3	0.2483	1289.8	0.2151
1733.3	0.2561	1456.3	0.2230
1918.9	0.2641	1627.3	0.2299
2100.0	0.2712	1807.3	0.2373
2291.3	0.2787	2014.3	0.2452
2501.6	0.2856	2232.5	0.2540
2762.6	0.2915	2448.5	0.2592
3005.6	0.3000	2693.8	0.2662
3345.4	0.3085	2993.0	0.2740
		3348.5	0.2834

Table 8. Mass of CO_2 Adsorbed per Unit Mass of Silica Gel KC (M_r) versus Pressure (P) at 278 K and 328 K

T = 278 K		T = 328 K	
P/kPa	M_r	P/kPa	M_r
56.3	0.0468	81.0	0.0171
122.6	0.0721	172.1	0.0291
198.0	0.0937	266.6	0.0402
276.8	0.1134	363.4	0.0500
363.4	0.1293	460.1	0.0588
453.4	0.1430	554.6	0.0661
541.1	0.1568	643.5	0.0735
626.6	0.1685	757.1	0.0808
738.0	0.1809	852.8	0.0879
840.4	0.1920	959.6	0.0936
952.9	0.2040	1072.1	0.1007
1066.5	0.2149	1180.1	0.1064
1174.5	0.2253	1292.6	0.1121
1287.0	0.2353	1408.5	0.1174
1406.3	0.2454	1543.5	0.1233
1540.1	0.2562	1662.8	0.1285
1669.5	0.2681	1794.4	0.1355
1818.0	0.2786	1935.0	0.1410
1963.1	0.2910	2082.4	0.1469
2113.9	0.3031	2246.6	0.1536
2284.9	0.3163	2400.8	0.1604
2472.8	0.3304	2581.9	0.1670
2692.1	0.3465	2800.1	0.1742
2953.1	0.3660	3034.1	0.1833
3322.1	0.3892	3344.6	0.1925

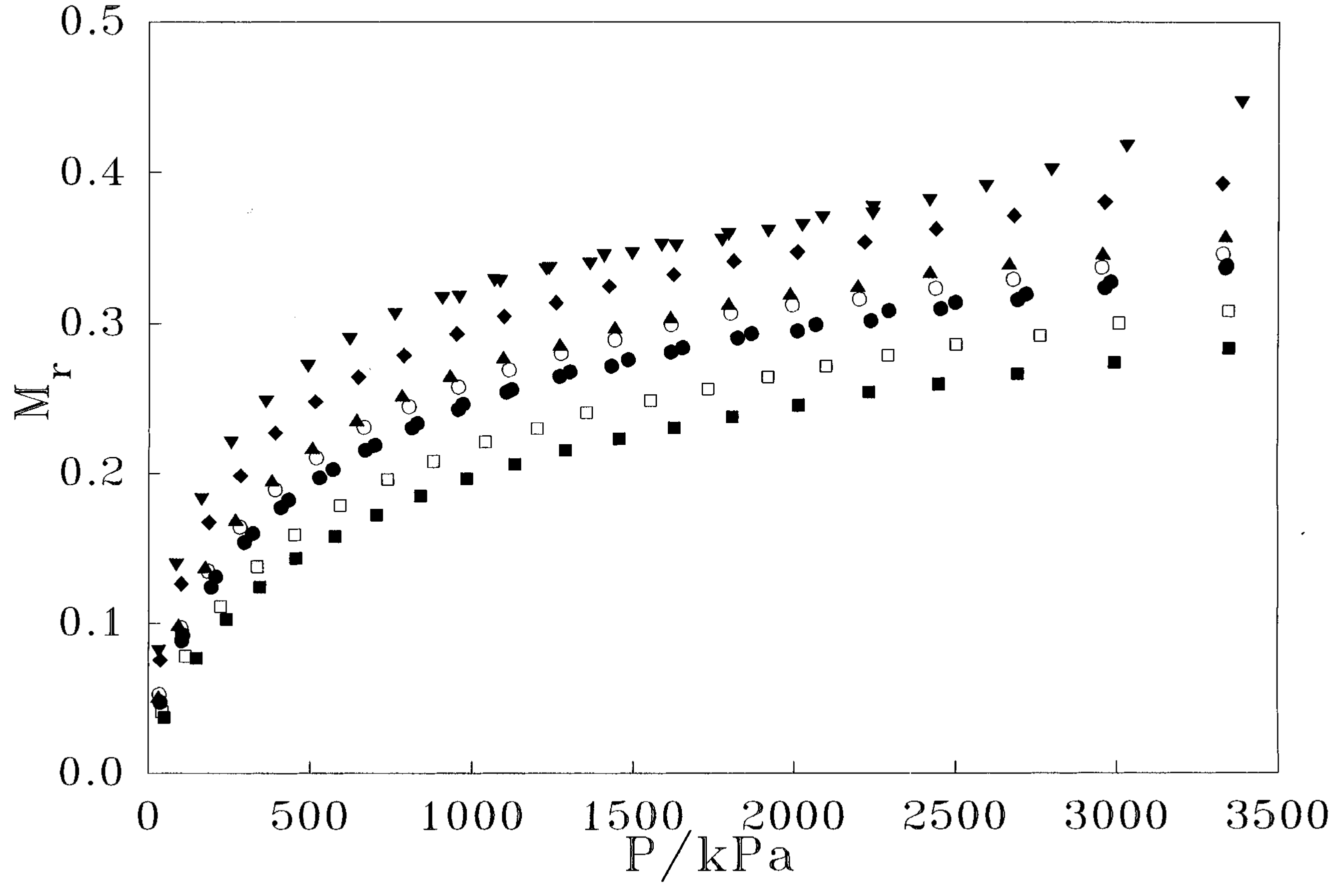

Figure 1. Isotherms of adsorption of CO_2 on activated carbon at 278 (▼), 288 (♦), 298 (▲), 303 (○), 308 (●), 318 (□), and 328 K (■).

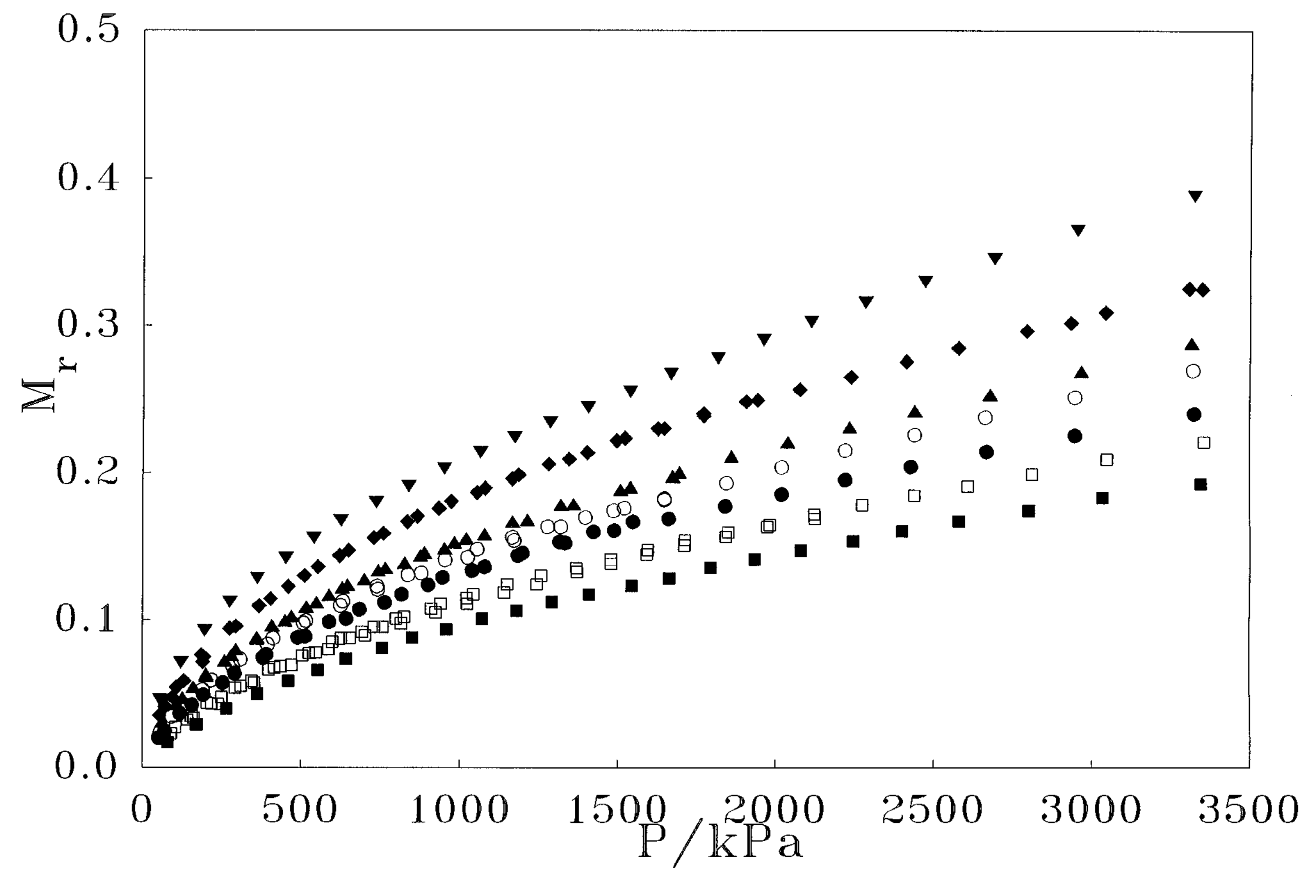

Figure 2. Isotherms of adsorption of CO_2 on silica gel at 278 (▼), 288 (♦), 298 (▲), 303 (○), 308 (●), 318 (□), and 328 K (■).

Even if the adsorbed mass at a fixed pressure is more important on activated carbon, if the application consists of pressure swing adsorption, the cycled mass is more important with silica gel.

Table 9. Mass of CO_2 Adsorbed per Unit Mass of Silica Gel KC (M_r) versus Pressure (P) at 288 K and 298 K

T = 288 K		T = 298 K	
P/kPa	M_r	P/kPa	M_r
53.9	0.0353	63.3	0.0300
72.9	0.0414	109.3	0.0423
95.3	0.0476	128.5	0.0462
107.9	0.0543	162.1	0.0534
132.5	0.0587	201.5	0.0622
187.8	0.0761	201.6	0.0612
190.9	0.0714	261.1	0.0713
194.4	0.0747	281.5	0.0751
276.6	0.0942	296.0	0.0791
296.8	0.0957	361.3	0.0862
368.9	0.1095	362.5	0.0869
404.8	0.1144	409.6	0.0950
461.1	0.1228	451.4	0.0987
511.6	0.1302	471.5	0.1014
554.5	0.1361	517.6	0.1080
623.0	0.1435	549.3	0.1110
651.3	0.1472	589.6	0.1159
731.0	0.1557	631.3	0.1211
761.5	0.1586	648.3	0.1227
835.6	0.1666	701.0	0.1266
867.3	0.1705	745.0	0.1326
935.8	0.1758	767.4	0.1343
975.3	0.1806	827.0	0.1376
1056.1	0.1866	877.8	0.1427
1082.1	0.1896	890.0	0.1447
1167.5	0.1959	954.1	0.1477
1187.9	0.1986	984.6	0.1518
1282.3	0.2058	1021.6	0.1544
1346.5	0.2093	1080.1	0.1573
1403.8	0.2137	1167.9	0.1659
1497.3	0.2219	1215.1	0.1670
1523.0	0.2235	1320.9	0.1772
1626.6	0.2299	1360.3	0.1778
1646.8	0.2301	1508.8	0.1877
1771.8	0.2402	1539.1	0.1894
1772.8	0.2388	1674.1	0.1966
1906.8	0.2483	1695.5	0.1992
1942.6	0.2492	1859.8	0.2103
2077.6	0.2564	2039.8	0.2199
2239.6	0.2649	2234.4	0.2300
2415.1	0.2753	2441.4	0.2411
2579.4	0.2845	2678.8	0.2522
2794.3	0.2959	2966.8	0.2680
2933.6	0.3015	3314.4	0.2868
3042.9	0.3085		
3304.9	0.3250		
3347.8	0.3246		

The adsorption isotherm on activated carbon at 278 K shows an increase of adsorption at high pressures (2797–3384 kPa), i.e. where relative pressure $p/p_s > 0.7$ and $p/p_s = 0.85$ for the last point. This phenomenon can be explained as multilayer adsorption in mesopores linked with capillary condensation. This phenomenon is not observed at 288 K because the maximum relative pressure reached is $p/p_s = 0.65$.

Conclusion

The automated apparatus allows us to determine adsorption isotherms at pressures up to 3350 kPa. At 278 K, this maximum absolute pressure corresponds to a relative pressure of $p/p_s = 0.85$ where capillary condensation has been observed. This range of high relative pressure has not been studied much in the literature.

Part 2 will be devoted to adsorption of CO_2 on four synthetic zeolites in the same ranges of temperature and pressure.

Table 10. Mass of CO_2 Adsorbed per Unit Mass of Silica Gel KC (M_r) versus Pressure (P) at 303 K and 308 K

T = 303 K		T = 308 K	
P/kPa	M_r	P/kPa	M_r
57.8	0.0241	52.4	0.0201
93.6	0.0346	71.5	0.0248
133.1	0.0426	119.9	0.0364
190.4	0.0528	158.1	0.0427
218.6	0.0593	193.0	0.0494
287.1	0.0686	254.9	0.0572
310.9	0.0730	292.0	0.0638
395.1	0.0835	380.9	0.0744
413.3	0.0876	392.1	0.0768
508.8	0.0977	491.1	0.0881
516.8	0.0997	513.6	0.0888
624.6	0.1098	589.0	0.0985
633.8	0.1126	643.0	0.1009
741.8	0.1227	685.8	0.1073
742.8	0.1206	764.5	0.1118
837.4	0.1307	817.4	0.1173
880.0	0.1319	901.8	0.1235
954.4	0.1408	946.8	0.1286
1026.3	0.1423	1041.3	0.1337
1056.8	0.1480	1079.5	0.1362
1167.0	0.1561	1184.1	0.1436
1173.6	0.1537	1199.9	0.1454
1278.4	0.1632	1316.9	0.1531
1321.0	0.1633	1334.9	0.1523
1396.5	0.1698	1423.8	0.1600
1486.4	0.1743	1489.0	0.1608
1520.3	0.1759	1547.5	0.1669
1647.4	0.1825	1661.1	0.1691
1648.4	0.1815	1838.9	0.1775
1843.0	0.1930	2020.0	0.1856
2019.6	0.2037	2221.4	0.1953
2219.9	0.2150	2429.5	0.2042
2440.4	0.2256	2668.0	0.2144
2664.3	0.2376	2947.0	0.2255
2946.6	0.2515	3323.9	0.2404
3320.1	0.2697		

Table 11. Mass of CO_2 Adsorbed per Unit Mass of Silica Gel KC (M_r) versus Pressure (P) at 318 K

P/kPa	M_r	P/kPa	M_r
67.5	0.0190	826.9	0.1021
67.5	0.0196	911.3	0.1077
92.3	0.0229	924.8	0.1049
105.8	0.0271	941.6	0.1110
142.9	0.0325	1021.5	0.1149
156.4	0.0350	1023.8	0.1110
164.3	0.0335	1045.1	0.1175
204.8	0.0437	1141.9	0.1185
218.3	0.0435	1152.0	0.1242
240.8	0.0431	1245.4	0.1243
250.9	0.0478	1257.8	0.1300
293.6	0.0540	1369.1	0.1352
312.8	0.0554	1371.4	0.1328
345.4	0.0587	1479.4	0.1383
353.3	0.0573	1479.4	0.1412
398.3	0.0664	1591.9	0.1444
417.4	0.0675	1595.3	0.1476
436.5	0.0686	1711.1	0.1505
471.4	0.0692	1713.4	0.1542
504.0	0.0759	1842.8	0.1566
525.4	0.0775	1850.6	0.1597
547.9	0.0780	1975.5	0.1632
587.3	0.0800	1983.4	0.1647
600.8	0.0848	2122.9	0.1717
627.8	0.0874	2126.3	0.1689
654.8	0.0876	2274.8	0.1782
693.0	0.0919	2440.1	0.1848
703.1	0.0894	2608.9	0.1910
730.1	0.0951	2810.3	0.1989
759.4	0.0953	3047.6	0.2093
799.9	0.1007	3354.8	0.2211
816.8	0.0976		

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