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# Gibbs Dividing Surface and Helium Adsorption

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**Abstract.** All adsorption data is based on the definition of Gibbs dividing surface, which is a purely mathematical transformation. Adsorption measurements in microporous solids necessitate experimental determination of the dividing surface. An international protocol does not exist on how to perform this important measurement. Commonly, helium is assumed not to adsorb and used as a probe molecule for this measurement. Each experimentalist chooses an arbitrary set of conditions, often without even disclosing them, which adds to the confusion in adsorption literature. Here, a self-consistent method for the analysis of helium data is proposed which does not assume non-adsorbing helium. The method is compared to others using the extensive set of helium/silicalite data. The Gibbs dividing surface and hence the helium isotherms at all temperatures are determined.

**Keywords:** adsorption equilibrium, helium adsorption, Gibbs dividing surface, silicalite, pore volume measurement

## Introduction

Adsorption is a widely used separation process. The design of adsorption processes requires equilibrium data. Simplest form of adsorption equilibrium data is pure component isotherms. Most of the isotherms are measured based on the concept of Gibbs surface excesses (GSE) (Gibbs, 1928). Although the idea by Gibbs is elegant involving a simple mathematical transformation, it is difficult to implement experimentally especially for microporous solids. Almost all applications of adsorption involve microporous solids to maximize surface area per volume of contacting equipment. The implementation of GSE usually involves the so called “helium isotherm” experiments with the assumption that helium adsorption is negligible around room temperature and at low pressure. Such an assumption is questionable since the solid atoms attract helium just like other molecules. Therefore, helium may have a net increase in density near a solid. By definition this implies

that helium is adsorbed (Sing et al., 1985; Roquerol et al., 1999). There have been some articles in the literature trying to explore ways to measure the helium amount adsorbed based on certain other assumptions (Maggs et al., 1960; Springer et al., 1969; Sircar, 2001b; Suzuki et al., 1987). These results are subject to the validity of the assumptions involved therein, which are somewhat arbitrary. It is the purpose of this work to estimate the amount adsorbed for helium with a realistic model and with as little assumptions as possible. This estimation involves determination of true GSE. Towards this goal, helium “adsorption” in silicalite was measured gravimetrically over a wide range of temperature and pressure. The data is used to deduce the impenetrable solid volume, the GSE and thus the amount of helium adsorbed.

## Gibbs Definition of Adsorption

The adsorbed phase properties can only be measured as differences much like other thermodynamic

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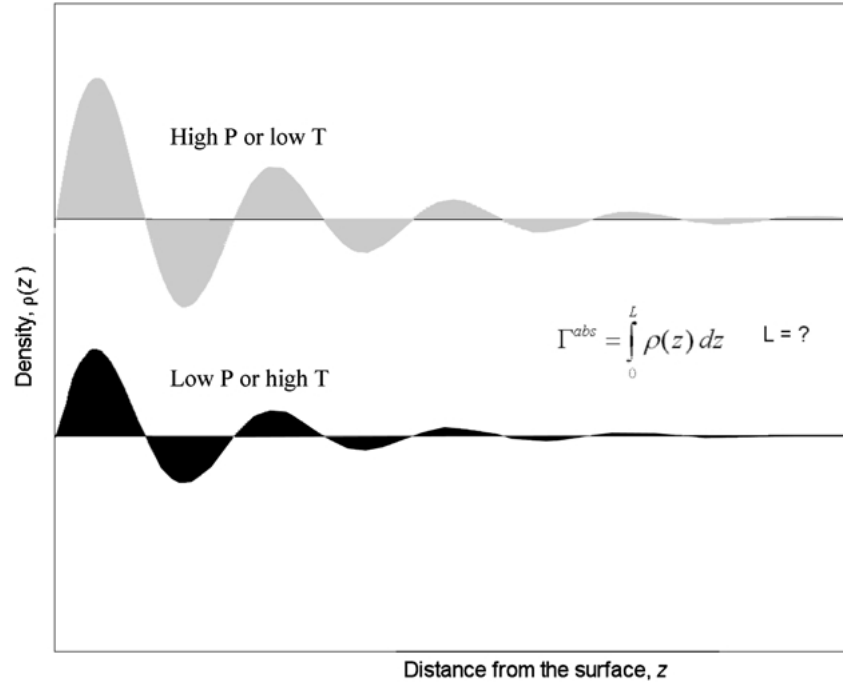


Figure 1. Density profiles next to a solid surface.

properties such as enthalpy. The adsorbed phase is not autonomous. It only exists in equilibrium with a fluid phase surrounding a solid. The adsorbed phase properties are expressed as differences from pure solid in the absence of any surrounding fluid. Some properties such as amount adsorbed are intuitively zero when fluid does not exist. Others, such as the chemical potential of the solid are not zero. Therefore, the changes in total thermodynamic properties are always in the form of differences as a pure solid is contacted with a fluid.

The density profile of a fluid near a solid surface is not uniform. It varies with the distance from the surface,  $z$  as illustrated in Fig. 1. A few observations need to be made:

1. The density is not necessarily higher than bulk fluid density at all locations. Figure 1 depicts layering where the density between layers is actually lower than fluid density.
2. At some distance,  $L$ , from the surface the density reaches the bulk fluid density.
3. The value of  $L$  increases as the bulk fluid density increases at constant temperature. It decreases with increasing temperature.

Considering these observations, it is impossible to estimate the “absolute” amount adsorbed, which is de-

fined in literature as the area under the density profile (Talu and Myers, 2001). On a unit area basis the absolute amount adsorbed is defined as,

$$\Gamma^{\text{abs}} = \int_0^L \rho(z) dz \quad (1)$$

In this equation the upper limit for integration  $L$  is not clearly defined. Furthermore,  $L$  is a function of temperature and pressure, which complicates the use of Eq. (1).

Realizing these complications, Gibbs (1928) was first to formalize a rigorous thermodynamic treatment of adsorption phenomena. His mathematical transformation depends on the definition of a “dividing surface” between the solid and the fluid phase. The word “surface” is used in a general sense and it does not imply any shape. The solid occupies one side of this mathematical surface and fluid occupies the other. In the Gibbs definition of dividing surface, the fluid phase properties are assumed to be constant and equal to their values far away from the surface. The actual changes occurring in the interfacial region are attributed to the adsorbed phase. Mathematically, the adsorbed phase is a surface therefore it does not have a volume. All other properties are referred to as “Gibbs surface excess” properties. (In the remainder of this manuscript,

the “surface excess” wording will be dropped for simplicity.) With Gibbs definition, the amount adsorbed is related to the shaded areas in Fig. 1 by:

$$\Gamma_a = \int_0^{\infty} (\rho(z) - \rho^g) dz \quad (2)$$

As can be seen, defining the new excess quantity changes the problematic upper integration limit to infinity. After the distance  $L$  in Eq. (1), the integrand in Eq. (2) is zero thus there is no net contribution towards the amount adsorbed.

Gibbs does not suggest any experimental method to locate the dividing surface. It is a purely mathematical definition. But practical use of thermodynamic relations requires that (1) either it is measured, or (2) it is calculated from other measurable quantities. Adsorbed phase properties are directly measurable only on liquid surfaces (Adamson, 1990). When solids are involved, the area is directly measurable for flat surfaces only. This independent measurement still does not determine the extent of the adsorbed phase since its thickness is an unknown variable (see Fig. 1). Gibbs’ definition of adsorption was historically intended to be used for these cases where the “surface area” is independently measurable. Experimental complications arise for practically very important class of adsorbents, microporous solids. Only the mass of the microporous adsorbent as a pure solid is directly measurable. The adsorbed phase properties are deduced from the changes occurring when a pure solid is contacted with the fluid. For microporous systems, Gibbs’ definition may be implemented as an integral over volume (Talu and Myers, 2001).

$$M_s N_a = \int_0^{\infty} (\rho(v) - \rho^g) dv \quad (3)$$

where  $N_a$  is the amount adsorbed per unit mass of the solid. Theoretically, the integration is performed over the volume accessible to fluid molecules. Determination of that volume for microporous solids is a major obstacle.

### Duality of Gibbs Definition

One common misconception about Gibbs’ definition is based on the statement “The solid properties are assumed to be invariant independent of pressure, temperature, or composition of the fluid phase. As such, the properties of the solid are fixed at the pure solid reference state.” The existence of fluid molecules in

the interfacial region relieves some of the free surface energy of the solid. Adsorption causes the chemical potential of the solid to change. The potential force exerted by the solid atoms in turn cause an increase in the density of the fluid phase. In reality, there are changes in both the solid and the fluid phase. With the Gibbs’ definition, the total net difference in properties from the pure solid reference state is mathematically attributed to the formation of the adsorbed phase. Therefore, the adsorbed phase properties include the changes occurring in the solid as well as the fluid. These two effects are indistinguishable since the adsorbed phase is not autonomous. It is not possible to have (thus to measure the properties of) the adsorbed phase without the solid or without the fluid.

### Measurements of Adsorption Equilibrium

The Gibbs’ definitions and related equations above are only conceptual visualizations. Measurement of adsorption requires the determination of Gibbs’ dividing surface. In essence, this fixes the integration volume in Eq. (3). Or by duality, it fixes the impenetrable solid volume. It is essential to understand the involved experimental techniques before discussing how to fix the dividing surface. Here, two common methods for pure isotherm measurements are discussed assuming ideal gas behavior for simplicity. Figure 2 shows schematics for both.

**Volumetric measurement:** A known mass of adsorbent ( $M_s$ ) is placed in a chamber. After activation and full evacuation, the gas is dosed into the chamber from a reservoir. The amount of gas introduced into the chamber ( $N_i$ ) can be easily determined by material balance based on P-V-T measurements of the reservoir. After equilibrium is reached which is indicated by a constant pressure in the system, the amount of

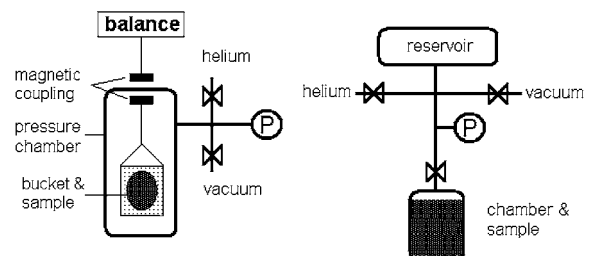


Figure 2. Schematic diagrams for volumetric and gravimetric isotherm measurements.

gas adsorbed per mass of solid,  $N_a$ , can be calculated as

$$N_a = \frac{N_t - \left(\frac{PV_c}{RT}\right)}{M_s} \quad (4)$$

where  $V_c$  is the “void” volume in the chamber. This is the volume, which the gas molecules *can access*. It is equal to easily measurable empty chamber volume ( $V_e$ ) minus the impenetrable volume occupied by the solid matrix, which can be expressed as  $v_s M_s$ .

$$V_c = V_e - v_s M_s \quad (5)$$

Thus,  $V_c$  is the volume of the fluid phase in the chamber up to the Gibbs dividing surface.

*Gravimetric measurement:* (In the following, masses are used for simplicity. The gravitational acceleration  $g$  cancels out from all equations.) The adsorbent is placed in a bucket connected to a balance in a pressure chamber. The mass ( $M_{bu}$ ) and volume ( $V_{bu}$ ) of the bucket and balance connections are measured before adsorbent is loaded. After activation, a measurement is performed under full vacuum to determine the exact mass of the solid ( $M_s$ ). The gas is introduced into the chamber. After equilibrium is reached as indicated by a constant mass, another measurement is obtained ( $M_t$ ). The amount adsorbed per mass of solid can be calculated as

$$N_a = \frac{M_t - M_{bu} - M_s + (M_w PV_b/RT)}{M_s M_w} \quad (6)$$

where  $M_w$  is the molecular weight of the gas and  $V_b$  is the buoyancy volume. This is the volume, which the gas molecules *cannot access*. It is equal to the bucket volume plus the volume of the impenetrable solid.

$$V_b = V_{bu} + v_s M_s \quad (7)$$

Equations (5) and (7) clearly show that the amount adsorbed and thus all other properties of the adsorbed phase are intricately related to the impenetrable solid volume ( $v_s$ ), or to the placement of the Gibbs dividing surface.

### Experimental Determination of Gibbs Dividing Surface

The necessity for experimental determination of Gibbs' dividing surface was addressed as early as 1930s (McBain and Britton, 1930; Coolidge, 1934; Emmett,

1942). It is discussed in some monographs (Ross and Olivier, 1964; Adamson, 1990; Steele, 1974; Young and Crowell, 1972). More recently several articles appeared on the practical and theoretical implications of the Gibbs dividing surface sparked by attempts to use adsorption as gas storage media and by the enhanced capabilities of computer simulations (Malbrunot, 1997; Neimark and Ravikovitch, 1997; Sircar, 2001a, 2001b; Staudt et al., 1997; Suzuki et al., 1987; Talu and Myers, 2001).

The most commonly used experimental technique to measure the Gibbs dividing surface is based on the assumption that helium is not adsorbed under certain conditions. A helium experiment is performed in the same apparatus. Depending on the technique the left hand side of Eq. (4) or (6), is set equal to zero to back calculate  $v_s$ . In effect, the assumption implies that the density of helium in the adsorbed phase is equal to the bulk gas density.

Usually the pressure levels are kept low to approach the non-adsorbing helium assumption as closely as possible. The temperature in these experiments are kept at ambient or above ambient for the same reason. Unfortunately, the protocol for these measurements are only detailed in old research papers. Later papers only mention that helium was used at low pressure and around ambient temperature. Recently, this important detail is not even mentioned in some papers.

A consensus does not exist in the scientific community on how to perform this very important measurement, regardless of the fact that all reported data depend on this single measurement. For very heavily adsorbing compounds, the error associated with this measurement may become insignificant. For light gas adsorption and for mixture adsorption, the impact can be very significant as has been shown by Sircar (1985). It is possible to convert and compare data only if the determination of dividing surface is fully disclosed. Complicated conversions can be avoided if a standard set of conditions is consistently used internationally. Such standard conditions for this fundamentally important aspect of adsorption needs to be addressed by scientific organizations such as IUPAC and/or International Adsorption Society.

### Does Helium Adsorb?

The non-adsorbing helium assumption obviously depends on the temperature and pressure level. We collected data over a wide temperature and pressure range

for helium/silicalite system. The solid was 1/16" pellets of silicalite (UOP, HISIV 3000, Lot #917797020012). UHP helium was used in the experiments. The data was collected in a Rubotherm<sup>TM</sup> magnetic suspension balance. With this unique apparatus, the gas phase density is directly measured. In addition, the sample bucket can be uncoupled to tare the balance during experiments which provides a very stable reading free of any zero-drift.

The bucket mass and volume were measured independently with helium before sample was loaded. The balance reading at any time can be written as

$$M_t = M_{bu} + M_s + M_a - (V_{bu} + v_s M_s) \rho^g \quad (8)$$

where  $M_a$  is the total mass adsorbed. If helium does not adsorb ( $M_a = 0$ ), the raw mass change versus density data at different temperatures and pressures should collapse to a single line according to the following equation.

$$\frac{M_t - M_{bu} - M_s}{M_s} = -\left(\frac{V_{bu}}{M_s} + v_s\right) \rho^g \quad (9)$$

Figure 3 shows our extensive data for Eq. (9). Obvious from the deviations from a single straight line, helium is

adsorbed under certain conditions even in a fairly inert solid such as silicalite. There is also ample evidence of helium adsorption on other solids by other researchers (Kaneko et al., 1994; Maggs et al., 1960; Springer et al., 1969; Suzuki et al., 1987).

"Is there any condition that the helium does not adsorb?" is the next question to be answered. If such a condition exists, it would be as pressure approaches zero. The amount adsorbed as pressure approaches zero can be expressed with the Henry's law as

$$N_a = HP \quad (10)$$

The ideal gas law is closely followed at the same limit. Combining Eqs. (8) and (10) with ideal gas law gives,

$$M_t = M_{bu} + M_s + [M_s HRT - (V_{bu} + v_s M_s)] \rho^g \quad (11)$$

If the slope of raw data as  $M_t$  vs.  $\rho^g$  at the origin is denoted as  $\alpha$ , the derivative of Eq. (11) can be rearranged to read,

$$HRT - v_s = \frac{\alpha + V_{bu}}{M_s} = \beta \quad (12)$$

All quantities on the right hand side of Eq. (12) (therefore  $\beta$ ) are directly measurable. Figure 4 shows how

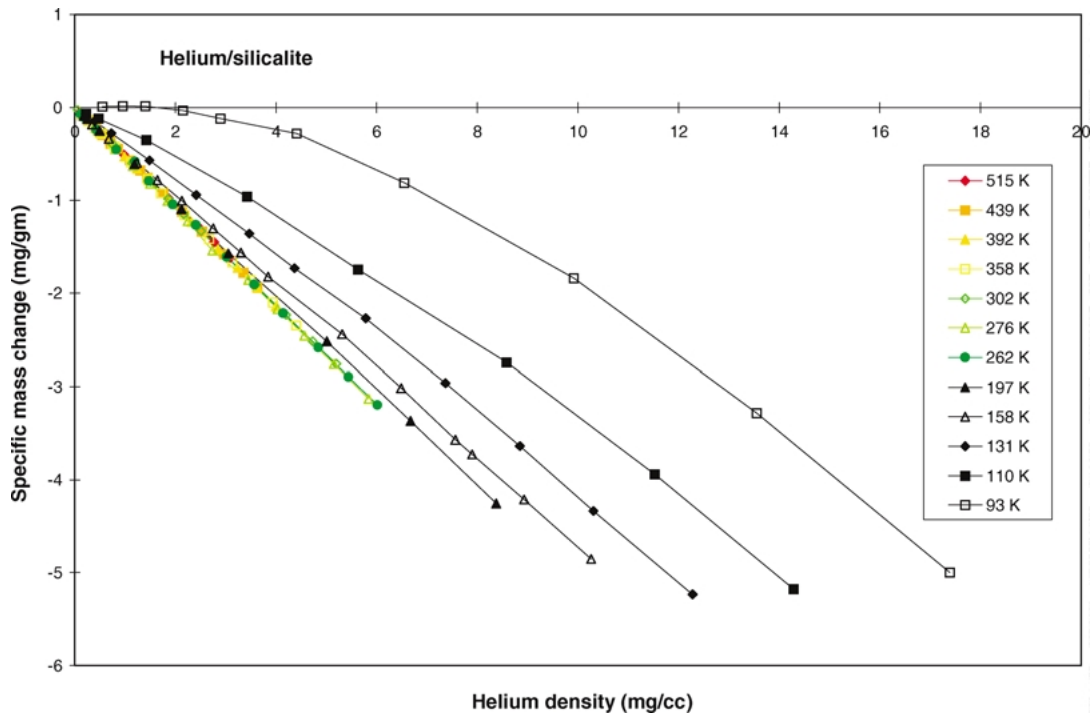


Figure 3. Observed specific mass change of silicalite with helium density.

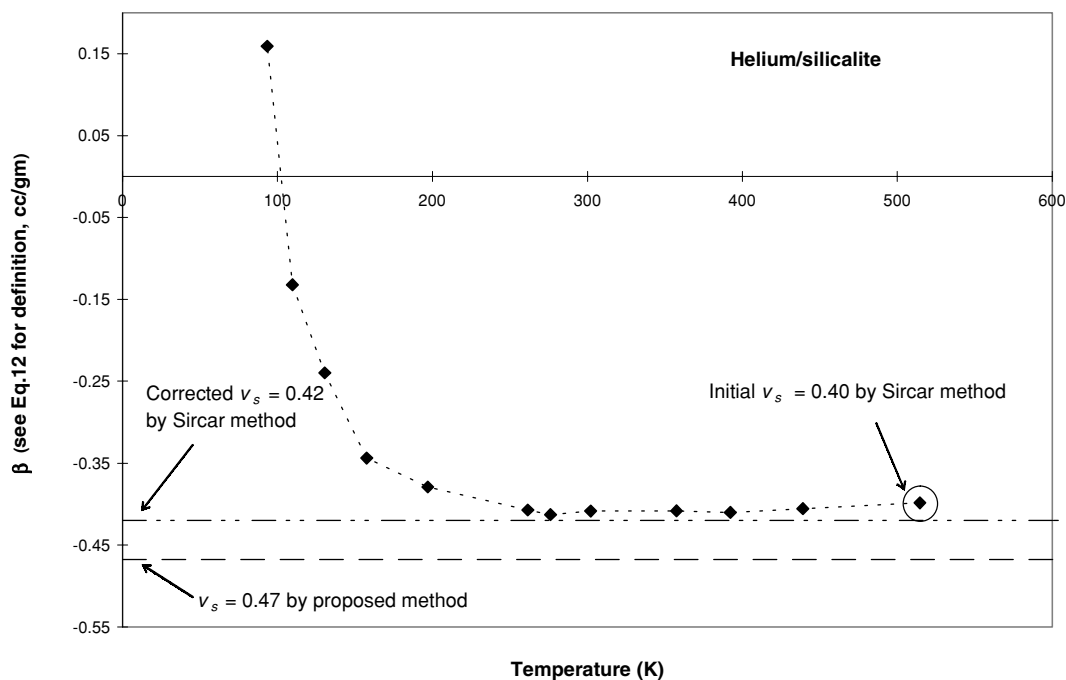


Figure 4. The  $\beta$ -plot for Gibbs dividing surface.

$\beta$  varies with temperature for our data. We call this a  $\beta$ -plot.

In the  $\beta$ -plot, first notice that the data seems to go through a minimum and it does not seem to have a discernible asymptotic value. The minimum is not an experimental artifact as will be elaborated later. Second, the temperature variation is too large to be attributed to the thermal expansion coefficient of the solid through  $v_s$ . Expansion effect of the adsorbent is orders of magnitude smaller (the thermal expansion coefficient of the stainless steel bucket is included in  $V_{bu}$  during the calculations). The large temperature variation can only be explained by the existence of adsorption and the large dependence of Henry constant on temperature. The temperature dependency of Henry constant can be expressed approximately as

$$H = H_0 \exp \frac{H_1}{RT} \quad (13)$$

where  $H_1$  is the isosteric heat of adsorption, and  $H_0$  is related to the entropy of adsorption.

### Experimental Determination of Helium Adsorption

Determination of helium adsorption depends on where the dividing surface is located either by fixing the im-

penetrable solid volume for gravimetric measurements, or by fixing pore volume for volumetric measurements. In addition to the commonly used helium experiments to measure the solid volume, a number of methods have been used to measure pore volume by using liquid nitrogen, argon, krypton, xenon, n-hexane, methanol, triisopropyl benzene, carbon tetra chloride to name a few. It must be noted that each of these methods yields a different result for the same solid because of the difference in the molecular size of the probe molecule, and hence the difference in the volumes they can penetrate. Another approach following Fernbacher and Wenzel (1972) is the use of skeletal densities along with the mass of the solid to obtain the impenetrable solid volume especially for crystalline solids. All these attempts are based on some arbitrary assumption and yield to different values for the same solid.

The purpose in performing helium measurements is to locate the dividing surface. In turn, the location of the dividing surface is necessary to analyze helium measurements. The problem is already ill defined; inclusion of other assumptions cannot help bring clarity.

### The Sircar Method

The best approach to locate the dividing surface to date has been proposed by Sircar (2001b) building on the

ideas first proposed by Suzuki et al. (1987). Both efforts attempt to make a first-pass correction for helium adsorption, thus to approach the true Gibbs' dividing surface more closely. To perform this correction, helium is assumed non-adsorbing at the highest experimental temperature whatever that might be. With the gravimetric technique Eq. (12) is used with  $H = 0$  giving directly  $v_s$  thus fixing the Gibbs dividing surface.

$$v_s = -\beta^\infty \quad (14)$$

where  $\beta^\infty$  is the value of  $\beta$  at the highest temperature. Then, two other temperatures are chosen to effectively calculate  $H_0$  and  $H_1$  from

$$H_0 \exp \frac{H_1}{RT} = \frac{\beta - \beta^\infty}{RT} \quad (15)$$

The two studies differ by which two temperatures are chosen to perform this step. Suzuki et al. (1987) suggest using the highest two temperatures, while Sircar suggests using the lowest two.

Once  $H_0$  and  $H_1$  are determined, the Henry constant thus helium adsorption is back calculated at any

temperature by Eq. (13). Helium adsorption can even be back calculated at the highest temperature where it was set equal to zero in the first place. Use of this back-calculated Henry constant provides a better estimate of the  $v_s$  from Eq. (12) applied at the highest temperature without assuming  $H = 0$ . This in effect is a better estimate of the Gibbs dividing surface.

Sircar's approach using the lowest two temperatures for determining  $H_0$  and  $H_1$  is more accurate since the Henry constant values are largest at the lowest temperature, thus reducing experimental uncertainty. The inherent assumption in both approaches is that  $H_0$  and  $H_1$  do not vary with temperature.  $H_0$  is temperature independent being the limit of Henry constant as temperature approach infinity. Taking  $H_1$  constant implies that the specific heat of the adsorbed phase is same as gas the phase, which is a first order approximation.

Figure 5 shows the implementation of Sircar method to our helium data. The parameter values are listed in Table 2. Some values in Fig. 5 are negative preventing the use of common semi-logarithmic plots for Henry constant. This is a result of the minimum in the  $\beta$ -plot (Fig. 4), which will be discussed later. By Sircar method, the correction for Henry constant is

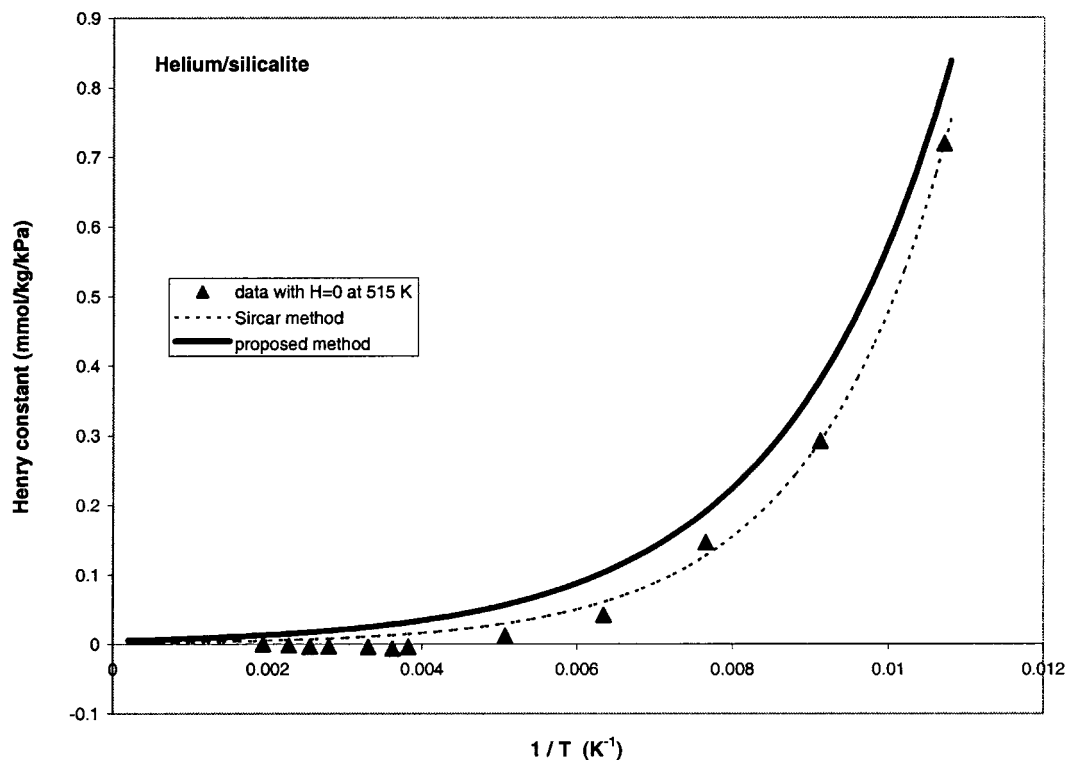


Figure 5. Henry constants for helium in silicalite.



Table 1. Helium adsorption in silicalite.

$P$	$W_t$	$N_a$	$P$	$W_t$	$N_a$	$P$	$W_t$	$N_a$
Temperature = 93 K			Temperature = 158 K			Temperature = 276 K		
105.8	0.010	0.0839	113.8	-0.183	0.0063	263.1	-0.248	0.0058
185.2	0.017	0.1468	221.4	-0.339	0.0164	460.8	-0.447	0.0067
273.0	0.015	0.2136	404.7	-0.593	0.0360	663.8	-0.631	0.0125
418.0	-0.030	0.3130	540.0	-0.782	0.0503	862.5	-0.820	0.0162
564.7	-0.118	0.4029	700.1	-1.004	0.0670	1064.3	-1.006	0.0210
864.0	-0.280	0.5891	906.1	-1.301	0.0857	1296.6	-1.223	0.0258
1290.4	-0.810	0.7765	1091.0	-1.560	0.1041	1580.0	-1.539	0.0187
1970.8	-1.836	1.0239	1091.6	-1.562	0.1039	1998.2	-1.857	0.0450
2718.1	-3.283	1.2061	1271.2	-1.820	0.1196	2341.0	-2.169	0.0532
3520.2	-4.999	1.3509	1765.1	-2.438	0.1850	2656.4	-2.454	0.0610
Temperature = 110 K			2162.7	-3.015	0.2166	2999.2	-2.759	0.0704
51.7	-0.068	0.0168	2529.5	-3.570	0.2388	3410.5	-3.129	0.0804
107.4	-0.120	0.0405	2642.6	-3.726	0.2493	Temperature = 302 K		
324.6	-0.352	0.1245	2999.2	-4.211	0.2834	34.4	-0.025	0.0018
786.0	-0.957	0.2726	3458.5	-4.854	0.3214	72.2	-0.059	0.0022
1300.9	-1.742	0.4065	Temperature = 197 K			134.9	-0.109	0.0044
1998.2	-2.745	0.5973	72.4	-0.089	0.0041	296.2	-0.248	0.0077
2704.4	-3.943	0.7380	99.9	-0.124	0.0056	465.2	-0.387	0.0124
3376.2	-5.177	0.8423	201.6	-0.251	0.0108	716.4	-0.599	0.0183
Temperature = 131 K			486.3	-0.609	0.0250	943.7	-0.795	0.0225
58.4	-0.070	0.0146	872.3	-1.096	0.0430	1171.1	-0.985	0.0279
105.5	-0.146	0.0215	1260.7	-1.571	0.0639	1368.2	-1.150	0.0324
198.1	-0.276	0.0401	2080.5	-2.516	0.1202	1586.8	-1.329	0.0383
403.9	-0.569	0.0797	2786.6	-3.369	0.1564	1922.8	-1.611	0.0456
658.3	-0.942	0.1253	3513.3	-4.255	0.1889	2279.3	-1.909	0.0534
949.9	-1.358	0.1793	Temperature = 262 K			2670.1	-2.232	0.0624
1198.7	-1.731	0.2204	106.2	-0.113	0.0006	3012.9	-2.517	0.0696
1593.7	-2.269	0.2976	231.3	-0.235	0.0041	3314.5	-2.757	0.0783
2039.3	-2.962	0.3615	446.8	-0.448	0.0091	Temperature = 358 K		
2457.5	-3.637	0.4133	647.6	-0.583	0.0297	107.9	-0.075	0.0026
2875.8	-4.335	0.4576	805.3	-0.793	0.0198	201.3	-0.147	0.0033
3444.8	-5.235	0.5278	1065.0	-1.044	0.0269	392.8	-0.282	0.0076
			1319.6	-1.265	0.0400	590.2	-0.418	0.0126
			1655.4	-1.606	0.0446	834.8	-0.592	0.0175
			1957.1	-1.907	0.0497	1080.7	-0.768	0.0221
			2279.3	-2.212	0.0590	1281.6	-0.922	0.0231
			2670.1	-2.581	0.0700	1628.0	-1.155	0.0329
			3006.0	-2.895	0.0800	1998.2	-1.414	0.0408
			3328.2	-3.197	0.0892	2347.8	-1.667	0.0459
						2615.2	-1.855	0.0509
						2964.9	-2.099	0.0578
						3314.5	-2.345	0.0641

(Continued on next page.)

Table 1. (Continued)

$P$	$W_t$	$N_a$	$P$	$W_t$	$N_a$	$P$	$W_t$	$N_a$
Temperature = 392 K			Temperature = 439 K			Temperature = 515 K		
199.3	-0.127	0.0043	129.8	-0.081	0.0008	103.2	-0.050	0.0017
402.3	-0.271	0.0051	242.2	-0.140	0.0042	160.4	-0.075	0.0033
597.1	-0.393	0.0098	377.6	-0.219	0.0064	312.4	-0.151	0.0055
803.0	-0.527	0.0133	498.1	-0.294	0.0070	524.2	-0.258	0.0078
1007.9	-0.658	0.0175	646.9	-0.368	0.0126	712.3	-0.344	0.0122
1201.9	-0.784	0.0210	648.6	-0.391	0.0071	861.9	-0.425	0.0125
1552.6	-1.006	0.0283	780.1	-0.441	0.0157	1046.5	-0.508	0.0173
1902.2	-1.232	0.0343	1001.3	-0.569	0.0195	1312.6	-0.631	0.0229
2341.0	-1.525	0.0395	1187.2	-0.676	0.0225	1593.7	-0.775	0.0255
2663.2	-1.726	0.0465	1323.3	-0.757	0.0241	2005.1	-0.978	0.0311
2992.3	-1.943	0.0507	1323.7	-0.757	0.0242	2320.4	-1.121	0.0382
2992.3	-1.941	0.0511	1614.3	-0.922	0.0295	2635.8	-1.279	0.0417
3300.8	-2.142	0.0555	1953.6	-1.121	0.0340	2985.4	-1.449	0.0466
			2320.4	-1.335	0.0392	3335.1	-1.618	0.0519
			2327.3	-1.335	0.0403			
			2731.8	-1.580	0.0432			
			3088.3	-1.778	0.0505			
			3348.8	-1.934	0.0527			

$P$  is pressure in kPa.

$W_t$  is raw data as mass change per solid mass in mg/gm.

$N_a$  is surface excess amount adsorbed in mol/kg.

most significant at the highest temperature since it was assumed to be zero in the first place. During first pass, the value of impenetrable solid volume is 0.40 cc/gm ( $\beta^\infty$  value at 515 K). The second pass value of  $v_s$  with the corrected Henry constant is 0.42 cc/gm, about 5% higher. The isosteric heat for helium in silicalite is 4.7 kJ/mol. The back-calculated Henry constant at 515 K is  $5.01 \times 10^{-3}$  mmol/kg/kPa. It was assumed to be zero initially, this constitutes a self-inconsistency in the method.

### The Proposed Method

We propose a self-consistent alternative method, which does not assume that helium adsorption is zero at any temperature. Substitution of Eq. (13) into Eq. (12) yields

$$\beta = RTH_0 \exp \frac{H_1}{RT} - v_s \quad (16)$$

The data for  $\beta$  can be directly regressed to determine  $H_0$ ,  $H_1$  and  $v_s$  as temperature independent constants. There are no additional assumptions. With this formu-

lation helium adsorbs at all conditions. The Henry constant value approaches  $H_0$  as temperature approaches infinity. In fact, this approach does necessitate a minimum in the  $\beta$  plot shown in Fig. 4.

The location of the minimum in the  $\beta$ -plot can be obtained from the derivative of Eq. (16) which gives

$$RT_{\min} = H_1 \quad (17)$$

At the minimum, the thermal energy is equal to the heat of adsorption. The minimum has to occur since the value of  $\beta$  starts high at low temperatures and has to approach infinity as temperature approaches infinity (see Eq. (16)). Our data is the first in literature showing this thermodynamically required minimum. The temperature levels used in other studies may not have been high enough to observe the minimum.

Parameter values listed in Table 2 were obtained by non-linear regression of the data shown in Fig. 4 according to Eq. (16). The value obtained for  $v_s$  is 0.47 cc/gm, 18% higher than the value concluded with the Sircar method. The helium isosteric heat is 3.9 kJ/mol, 17% lower. The major difference occurs in the Henry constant at 515 K. It was initially

Table 2. Parameter values in the methods.

	$v_s$ (cc/gm)	$H_0$ [mmol/(kg · kPa)]	$H_1$ (kJ/mol)	$H$ at 515 K [mmol/(kg · kPa)]
Sircar's method, 1st estimate	0.4	$1.67 \times 10^{-3}$	4.7	0
Sircar's method, 2nd estimate	0.42	$1.67 \times 10^{-3}$	4.7	$5.01 \times 10^{-3}$
Proposed method	0.47	$5.19 \times 10^{-3}$	3.9	$12.9 \times 10^{-3}$

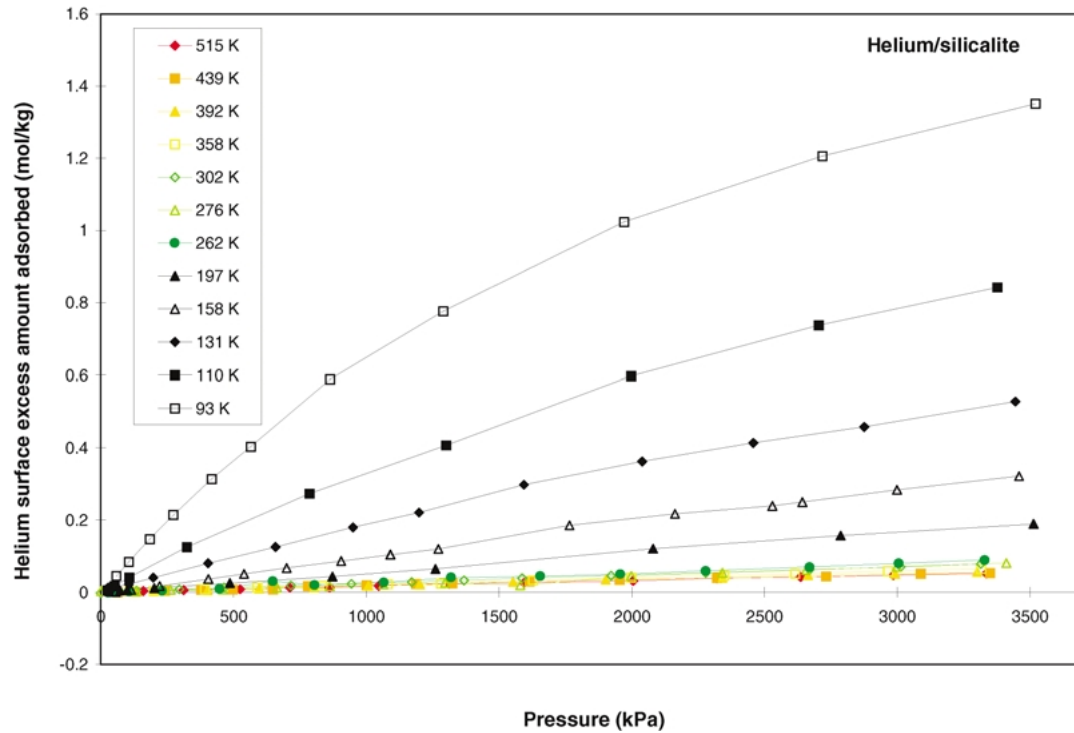


Figure 6. Helium isotherms in silicalite.

assumed to be zero and then back calculated to be  $5.01 \times 10^{-3}$  mmol/kg/kPa with the Sircar method. It is  $1.29 \times 10^{-2}$  mmol/kg/kPa, or 157% higher with the proposed method.

### Helium Isotherms

With the Gibbs dividing surface fixed without assuming non-adsorbing helium, the helium adsorption isotherms can be calculated. Figure 6 shows the results for our data. Helium adsorption is very significant at lower temperatures. It is small but finite even at the highest temperature. Table 1 lists the isotherm data. The table also includes raw data as measured mass change per solid mass without any buoyancy correction. Reporting raw data is unusual. It is included here

to enable re-calculations by other researchers while the scientific community searches for a standard method to analyze adsorption data on microporous solids.

### Conclusions

Gibbs definition provides the only rigorous thermodynamic framework for adsorption equilibrium. This mathematical transformation poses an experimental challenge when applied to microporous solids; the dividing surface must also be determined by “adsorption” experiments. Lacking any other sound alternative, helium is usually used to locate the dividing surface. Commonly, helium is assumed not to adsorb around ambient temperature and low pressure in contrast with ample evidence that it does adsorb. Here, we formulated a

self-consistent technique to analyze helium data to fix the location of the dividing surface without any ambiguity, and to calculate the Gibbs surface excess helium adsorption. Contrary to previous attempts to do the same, our method does not assume non-adsorbing helium at any temperature. Helium adsorption is shown to be significant even at temperatures as high as 515 K.

This work was inspired by the need for a consistent method to determine the Gibbs dividing surface. It would be naïve to presume that every experimentalist will devote such an extensive effort just to determine the dividing surface. It may not be necessary either. The helium experiments serve only as a reference state in thermodynamic sense. It is essential that the reference state be completely defined when reporting thermodynamic data, which often has not been the case for adsorption data in literature. From an applications standpoint, it is also very important to realize that all adsorption data is based on a reference state. As long as calculations are performed using the same reference states, the results will be the same. Conversion between different reference states requires additional information and effort. This extra effort may be circumvented if international organizations such as International Adsorption Society help build a consensus for a standard set of conditions to perform helium experiments for the determination of Gibbs dividing surface.

## Nomenclature

$H$	Henry's constant (mmol/(kg · kPa))
$H_0$	Fit parameter in Eqs. (12), (14) and (15) (mmol/(kg · kPa))
$H_1$	Isosteric heat of adsorption (kJ/mol)
$M_{bu}$	Mass of the bucket (gm)
$M_s$	Mass of the adsorbent (gm)
$M_t$	Reading of the balance (gm)
$M_w$	Molecular weight of adsorbate (gm/mol)
$N_a$	Surface excess amount adsorbed per unit mass of the adsorbent (mol/gm)
$N_t$	Total amount of gas charged into the chamber (mol)
$P$	Pressure (kPa)
$R$	Universal gas constant (J/(mol · K))
$T$	Temperature (K)
$V$	Volume accessible to the gas molecules (cm <sup>3</sup> )
$V_b$	Buoyancy volume (cm <sup>3</sup> )
$V_{bu}$	Volume of the bucket (0.6875 cm <sup>3</sup> )
$V_c$	Void volume in the chamber (cm <sup>3</sup> )

$V_e$	Volume of empty chamber (cm <sup>3</sup> )
$v_s$	Impenetrable solid volume per unit mass of adsorbent (cm <sup>3</sup> /gm)
$W_t$	Mass change of the sample per unit solid mass (mg/gm)
$Z$	Distance from the adsorbent surface (cm)

## Greek Letters

$\alpha$	Slope of $M_t$ vs. $\rho^g$ curve at the origin (cm <sup>3</sup> )
$\beta$	Parameter in Eq. (11) (cm <sup>3</sup> /gm)
$\Gamma^{abs}$	Excess amount adsorbed per unit area of adsorbent (mol/cm <sup>2</sup> )
$\rho(z)$	Density of the fluid in the vicinity of the solid (mol/cm <sup>3</sup> )
$\rho^g$	Bulk gas phase density (mol/cm <sup>3</sup> )

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