

## Surface Tension of Solids in the Absence of Adsorption

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A method has been recently proposed for determining the value of the surface tension of a solid in the absence of adsorption,  $\gamma^{S0}$ , using material properties determined from vapor adsorption experiments. If valid, the value obtained for  $\gamma^{S0}$  must be independent of the vapor used. We apply the proposed method to determine the value of  $\gamma^{S0}$  for four solids using at least two vapors for each solid and find results that support the proposed method for determining  $\gamma^{S0}$ .

The surface tension of a solid in the absence of adsorption,  $\gamma^{S0}$ , is of central importance in characterizing a solid; however, previously proposed methods for determining its value have led to controversy and a lack of experimental support.<sup>1–4</sup> Recently, a new method was proposed<sup>5</sup> that only requires a suitable adsorption isotherm for the solid–vapor interface to be added to Gibbsian thermodynamics to determine the expression for  $\gamma^{S0}$  in terms of the isotherm parameters and the surface tension of the adsorbing fluid. For an isotherm to be suitable, it must indicate a finite amount is adsorbed in the limit of the vapor-phase pressure,  $P^V$ , approaching the saturation vapor pressure,  $P_s$ ;<sup>6</sup> thus, neither the BET<sup>7</sup> nor FHH isotherm<sup>8–10</sup> may be used in the proposed method since both indicate that an infinite amount is adsorbed in this limit. The  $\zeta$  isotherm<sup>5</sup> is one that can be used, and it can be examined experimentally before it is applied to determine  $\gamma^{S0}$ . Using the  $\zeta$  isotherm with Gibbsian thermodynamics leads to an expression for the surface tension of the solid–vapor interface,  $\gamma^{SV}$ , that has the ratio of the vapor-phase pressure to the saturation vapor pressure,  $x^V$ , as its independent variable. Then, the expression for  $\gamma^{S0}$  is obtained by taking the limit of the expression for  $\gamma^{SV}$  as  $x^V$  goes to zero. Explicitly, the expression obtained for  $\gamma^{S0}$  is<sup>5</sup>

$$\gamma^{S0} = \gamma^{LV} + Mk_b T \ln\left(1 + \frac{c\alpha}{1 - \alpha}\right) \quad (1)$$

where  $\gamma^{LV}$  is the liquid–vapor surface tension of the adsorbing fluid,  $k_b$  is the Boltzmann constant, and the three temperature-dependent-isotherm parameters are denoted as  $\alpha$ ,  $c$ , and  $M$ .

This equation could be interpreted as indicating that  $\gamma^{S0}$  depends on the values of the adsorption parameters and  $\gamma^{LV}$ . However,  $\gamma^{S0}$  is a material property of a solid, and its value cannot depend on the vapor used to determine its value. Thus, two possibilities arise. When  $\gamma^{S0}$  is determined for a solid surface using adsorption measurements made with different vapors, its value will be found to depend on the vapor used. This would mean the method proposed for determining  $\gamma^{SV}$  by Ward and

Wu<sup>5</sup> is incorrect in some fundamental sense. The other possibility is that  $\gamma^{S0}$  is found to be the same for all vapors, supporting the proposed approach and indicating that for a particular solid surface at a given temperature, a relation exists between  $\gamma^{LV}$  and the adsorption-isotherm parameters. Using adsorption data from the literature, we examine these possibilities for four solids using at least two vapors in each case to determine the value of  $\gamma^{S0}$ . The value of  $\gamma^{S0}$  for each solid is found to be independent of the vapor used. Thus, we find results that support the second possibility.

The  $\zeta$  isotherm was obtained by approximating the adsorbed vapor as a collection of molecular clusters with at most one cluster adsorbed at one of the  $M$  adsorption sites. Each adsorbed cluster was approximated as a quantum-mechanical-harmonic oscillator with a binding energy that depended on the number of molecules in the cluster. The maximum number of molecules that could be in a cluster was denoted as  $\zeta$ . Using a canonical ensemble, the amount adsorbed at a solid–vapor interface,  $n^{SV}$ , was expressed as<sup>5</sup>

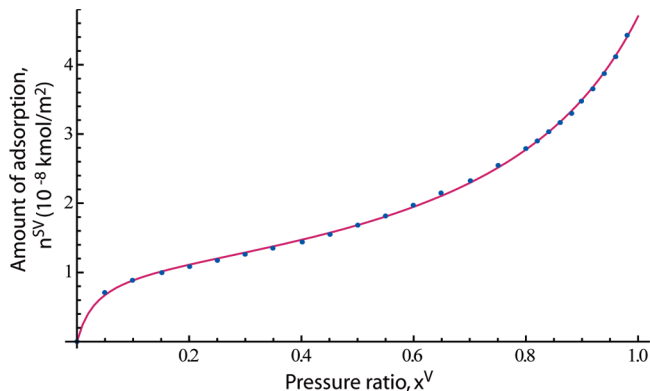
$$n^{SV} = \frac{Mc\alpha x^V [1 - (1 + \zeta)(\alpha x^V)^\zeta + \zeta(\alpha x^V)^{1+\zeta}]}{(1 - \alpha x^V)[1 + (c - 1)\alpha x^V - c(\alpha x^V)^{1+\zeta}]} \quad (2)$$

A comparison between the measured amount adsorbed and that calculated is assessed using the parameter  $\Delta(\zeta)$  which, for a given value of  $\zeta$ , is a measure of the mean-square difference between the measured amount adsorbed and that calculated

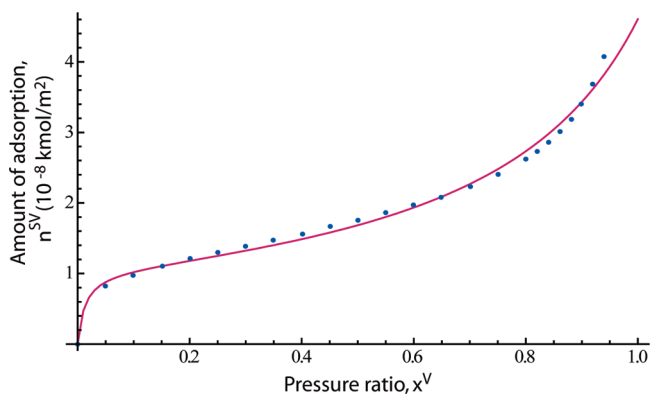
$$\Delta(\zeta) \equiv \frac{\sqrt{\sum_{j=1}^{N_m} [n_{\text{mes}}^{SV}(x_j^V) - n_{\text{cal}}^{SV}(\zeta, x_j^V)]^2}}{\sum_{j=1}^{N_m} n_{\text{mes}}^{SV}(x_j^V)} \quad (3)$$

where  $n_{\text{mes}}^{SV}(x_j^V)$  is the amount measured at  $x_j^V$  and  $n_{\text{cal}}^{SV}(\zeta, x_j^V)$  is the amount calculated. The number of measurements is denoted as  $N_m$ . For a given set of adsorption measurements, the

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**Figure 1.** The measured amount of argon adsorbed on  $\alpha$ -alumina at 77 K is shown as solid dots.<sup>11</sup> The solid line was calculated using eq 2 and the values of the adsorption parameters listed in Table 1.



**Figure 2.** The measured amount of nitrogen adsorbed on  $\alpha$ -alumina at 77 K is shown as solid dots.<sup>11</sup> The solid line was calculated using eq 2 and the values of the adsorption parameters listed in Table 1.

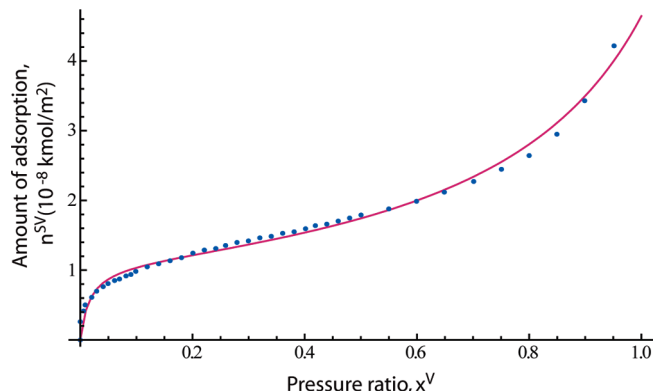
parameter  $\zeta$  is treated as a threshold parameter. If it is taken to be smaller than the threshold value and the isotherm parameters determined from the nonlinear regression package available in Mathematica, the value of the error,  $\Delta(\zeta)$ , is larger than that when  $\zeta$  is the threshold value. If  $\zeta$  is taken to be larger than the threshold value, the error in the calculations does not decrease further.<sup>5</sup>

The measured amount of Ar adsorbing at 77 K on  $\alpha$ -alumina that was reported by Matejova et al.<sup>11</sup> is shown as solid dots in Figure 1. The amount of  $N_2$  adsorbing on  $\alpha$ -alumina at 77 K has been reported by two laboratories.<sup>11,12</sup> These measurements are shown in Figures 2 and 3. The solid lines in these three figures were calculated using eq 2, the value of  $\zeta$ , and the mean values of the isotherm parameters that are listed in Table 1. The mean-square difference between the calculations and the measurements,  $\Delta(\zeta)$ , for Ar and  $N_2$  adsorbing on  $\alpha$ -alumina was 0.2 and 0.8%, respectively. Note that for the measurements from two independent laboratories, there is no measurable difference between the inferred values of the isotherm parameters. We treat these parameters and  $\zeta$  listed in Table 1 as material properties.

When the solid surface is exposed to a vapor phase, the expression for  $\gamma^{SV}(x^V)$  obtained by Ward and Wu<sup>5</sup> is

$$\gamma^{SV}(x^V) = \gamma^{LV} + Mk_b T \ln \left( \frac{(1 - \alpha x^V)[1 + (c - 1)\alpha x_w^V]}{(1 - \alpha x_w^V)[1 + (c - 1)\alpha x^V]} \right) \quad (4)$$

Note that the value of  $\gamma^{SV}(x^V)$  depends on the value of  $x_w^V$ , the



**Figure 3.** The measured amount of nitrogen adsorbed on  $\alpha$ -alumina at 77 K is shown as solid dots.<sup>12</sup> The solid line was calculated using eq 2 and the values of the adsorption parameters listed in Table 1.

relative vapor-phase pressure at wetting. The contact angle formed when a liquid and its vapor are held in a cylinder has been shown to depend on the pressure at the three-phase line.<sup>6,14,15</sup> To estimate the value of  $x_w^V$ , we consider liquid  $N_2$  or liquid Ar at 77 K held in a cylinder that has a radius of 0.3 mm, which is exposed to normal gravity,  $g$ , and forms a contact angle of zero. If the molecular weight of the fluid is denoted  $W$  and the specific volume of the liquid at saturation as  $v_f$ , then the Bond number ( $\equiv Wgr_{cy}^2/(v_f\gamma^{LV})$ ) is 0.085 or less. Thus, the liquid–vapor interface may be approximated as spherical.<sup>16</sup> The conditions for equilibrium at the liquid–vapor interface in the cylinder require the equality of the chemical potentials in the liquid and vapor phases and the validity of the Laplace equation.<sup>6</sup> If the liquid is approximated as incompressible and the vapor as an ideal gas, then<sup>15</sup>

$$x_w^V = \exp \left[ \frac{v_f}{v_g} \left( x_w^V - \frac{2\gamma^{LV}}{P_s r_{cy}} - 1 \right) \right] \quad (5)$$

This equation may be solved iteratively to determine  $x_w^V$ . For Ar and  $N_2$ , one finds that  $x_w^V$  deviates from unity by less than  $10^{-5}$ . If cylinders larger than 0.3 mm were considered, the deviation from unity would be even smaller.<sup>5</sup> Thus, we approximate  $x_w^V$  as unity. Then, eq 4 simplifies to

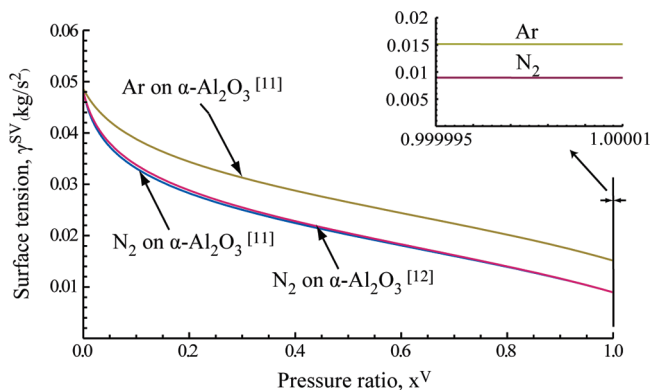
$$\gamma^{SV}(x^V) = \gamma^{LV} - Mk_b T \ln \left( \frac{(\alpha - 1)[1 + (c - 1)\alpha x^V]}{(\alpha x^V - 1)[1 + (c - 1)\alpha]} \right) \quad (6)$$

The value of  $\gamma^{SV}$  may now be calculated as a function of  $x^V$  using eq 6 and the values of the isotherm parameters listed in Table 1. If the limit is taken of eq 6 as  $x^V$  goes to zero, one obtains eq 1. We emphasize that the values of the adsorption parameters were determined strictly from the adsorption measurements. Thus, the calculated value of  $\gamma^{S0}$  for each vapor may be viewed as a prediction. For Ar and  $N_2$  adsorbing on  $\alpha$ -alumina, the results are shown in Figure 4. This figure includes results obtained from two independent studies of  $N_2$  adsorption on  $\alpha$ -alumina. In each case, the different vapors indicate the same value of  $\gamma^{S0}$ . In Table 1, note that the adsorption of Ar and  $N_2$  on titania, magnesia, and borosilicate glass indicate the same value of  $\gamma^{S0}$ .

The range of pressures where the contact angle can exist is indicated in Figure 4 by the almost-vertical line near  $x^V$  equal unity. The values of  $\gamma^{SV}$  as a function of  $x^V$  in this range of

**TABLE 1:  $\zeta$ -Isotherm Parameters and Solid Surface Tension**

material	vapor	$T$ (K)	$\gamma^{LV}$ (kg/s <sup>2</sup> )	$M$ (10 <sup>-9</sup> kmol/m <sup>2</sup> )	$c$	$\alpha$	$\zeta$	$\Delta(\zeta)$ , %	$\gamma^{S0}$ (kg/s <sup>2</sup> )
$\alpha$ -alumina <sup>11</sup>	Ar	77	0.01514	10.769 $\pm$ 0.1572	37.60 $\pm$ 5.41	0.7726 $\pm$ 0.0045	100	0.2	0.0486 $\pm$ 0.0017
$\alpha$ -alumina <sup>11</sup>	N <sub>2</sub>	77	0.00895	10.4974 $\pm$ 0.1205	102.33 $\pm$ 52.07	0.7727 $\pm$ 0.0041	140	0.8	0.0483 $\pm$ 0.0032
$\alpha$ -alumina <sup>12</sup>	N <sub>2</sub>	77	0.00895	10.9844 $\pm$ 0.3776	80.48 $\pm$ 22.74	0.7643 $\pm$ 0.0156	100	0.8	0.0481 $\pm$ 0.0042
titania <sup>11</sup>	Ar	77	0.01514	10.8066 $\pm$ 0.1734	64.51 $\pm$ 14.03	0.7632 $\pm$ 0.0052	130	0.2	0.0521 $\pm$ 0.0025
titania <sup>11</sup>	N <sub>2</sub>	77	0.00895	9.3383 $\pm$ 0.6851	253.90 $\pm$ 201.45	0.8315 $\pm$ 0.0215	120	1.1	0.0516 $\pm$ 0.0031
magnesia <sup>11</sup>	Ar	77	0.01514	13.2577 $\pm$ 0.1200	59.23 $\pm$ 4.68	0.6622 $\pm$ 0.0063	140	0.1	0.0556 $\pm$ 0.0012
magnesia <sup>11</sup>	N <sub>2</sub>	77	0.00895	9.5109 $\pm$ 0.2406	270.00 $\pm$ 202.45	0.8808 $\pm$ 0.0271	100	1.2	0.0552 $\pm$ 0.0041
borosilicate glass <sup>11</sup>	Ar	77	0.01514	11.4864 $\pm$ 0.1564	52.10 $\pm$ 4.90	0.6476 $\pm$ 0.0085	80	0.1	0.0475 $\pm$ 0.0014
borosilicate glass <sup>11</sup>	N <sub>2</sub>	77	0.00895	9.9651 $\pm$ 0.4056	32.06 $\pm$ 20.08	0.9163 $\pm$ 0.0211	130	1.6	0.0463 $\pm$ 0.0041



**Figure 4.** The calculated values of  $\gamma^{SV}$  are shown for  $\alpha$ -alumina exposed to Ar and to N<sub>2</sub> at 77 K. The results shown for N<sub>2</sub> are based on adsorption measurements made in two independent laboratories.<sup>11,12</sup> Note that all three studies indicate the same value of  $\gamma^{S0}$  for  $\alpha$ -alumina at 77 K.

pressures are indicated to be essentially constant; thus, the contact angle for this range of pressures is predicted to depend only on the value of  $\gamma^{SL}$ , and this surface tension is controlled by the adsorption at the solid–liquid interface.<sup>5,15,17</sup>

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