



Characterization of nanopores by standard enthalpy and entropy of adsorption of probe molecules

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Abstract

Numerous theories have been developed for the determination of pore size distribution in adsorbent materials. The calculated pore size distribution is sensitive to the model selected for adsorption in slits, spheres, or cylinders and cannot be independently verified by experimental methods. Physical constants which are independent of theory can be determined from equilibrium thermodynamic experiments. Given an adsorbent material and a probe molecule, these constants are: (1) pore volume; (2) standard molar enthalpy of adsorption at the limit of zero pressure; (3) standard molar entropy of adsorption at finite pressure. The standard enthalpy and entropy changes are from the initial state of a perfect gas to the final state of a hypothetical adsorbed gas that obeys Henry's law. These standard thermodynamic properties characterize the interaction of a single probe molecule with the surface of the nanopores.

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1. Introduction

The characterization of a porous material starts with the determination of the pore volume and the pore size distribution. Pores less than 2 nm in size are called micropores for the adsorption of diatomics or simple polyatomic molecules with molecular diameters in the range 0.3–0.5 nm (here the word nanopore will be used interchangeably with micropore). In addition to the pore volume, there is a need for physical constants which describe the adsorptive characteristics of nanopores interacting with specific probe molecules. Complexities such as hysteresis are avoided by restricting the discussion to nanoporous materials. The focus will be on low-pressure adsorption in the Henry's law region where the difference between absolute and excess adsorption (Myers [1]) may be ignored.

The molar entropy of adsorption for the Langmuir theory is given by [1]:

$$\frac{\Delta s}{R} = \frac{\Delta h}{RT} + \ln \left(\frac{KP^\circ}{m} \right) \quad (1)$$

where m is the saturation capacity in mol kg^{-1} , K the Henry constant in $\text{mol kg}^{-1} \text{Pa}^{-1}$, and P° is the standard pressure (1 atm). For the independent sites of the Langmuir theory, Δh is the molar enthalpy of adsorption and Δs is the molar entropy of adsorption. Values for Δs are of order $-10R$, which is the entropy of condensation for an independent site. However, the Langmuir theory is only an approximation for real systems and we seek constants Δh and Δs which are independent of any particular theory.

The driving force for adsorption is the difference in chemical potentials in the adsorbed and gas phases, which is in turn determined by the difference between the opposing effects of energetic and entropic terms. Thermodynamic studies of adsorption have traditionally concentrated on the energetic driving force but the equally important entropic term has been neglected, for reasons which will become apparent.

Gas–solid energies for simple polyatomic molecules are of order 10 kT, but approximate values for their entropy of adsorption are unknown. How does the pore size and shape affect the energy of a specific probe molecule? What factors determine the degree of hindered translation and rotation of a molecule inside a nanopore? Can values of energy and entropy be correlated or estimated? These questions are considered in this paper.

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2. Energy

The standard enthalpy of adsorption is defined here as the limiting value of the enthalpy of adsorption at zero pressure:

$$\Delta h^\circ = \lim_{P \rightarrow 0} \Delta h \quad (2)$$

where Δh is molar enthalpy of adsorption:

$$\Delta h = \frac{1}{n} \int_0^n \Delta \bar{h} \, dn \quad (3)$$

where n is the specific adsorption in mol kg^{-1} and $\Delta \bar{h}$ is the differential enthalpy of adsorption (called isosteric heat) which is measured by calorimetry or by differentiating two or more adsorption isotherms (Myers and Monson [2]):

$$\Delta \bar{h} = R \left[\frac{\partial \ln P}{\partial (1/T)} \right]_n \quad (4)$$

From Eq. (3), the limiting values of the differential and molar enthalpies are identical:

$$\Delta h^\circ = \Delta \bar{h}^\circ \quad (5)$$

Fig. 1 shows experimental values of the differential enthalpy of adsorption of ethylene on NaX (FAU) at 298.15 K (Siperstein and Myers [3]). The standard enthalpy, $\Delta h^\circ = -41.8 \pm 0.5 \text{ kJ mol}^{-1}$, is for the interaction of a single molecule of ethylene with the adsorbent. In terms of the gas–solid potential energy U_{1S} :

$$\Delta h^\circ = \frac{\int U_{1S} e^{-U_{1S}/kT} \, dV}{\int e^{-U_{1S}/kT} \, dV} - kT \quad (6)$$

where the integration is performed over the entire volume of the solid adsorbent. Eq. (6) shows that the standard energy of adsorption ($\Delta h^\circ + kT$) is the Boltzmann-averaged energy of a single molecule inside the pores of the solid material. For a given probe molecule, Δh° may be regarded as a physical constant because its value does not depend on any assumptions about intermolecular forces or the structure of the material.

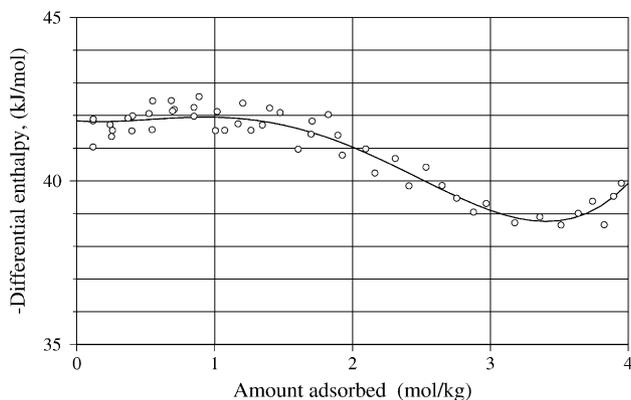


Fig. 1. Differential enthalpy of adsorption of C_2H_4 in NaX (FAU) at 298.15 K. (O) Experimental points from Siperstein and Myers [3]. Solid line is polynomial fit of experimental data. Standard enthalpy of adsorption is limit at zero pressure: $\Delta h^\circ = -41.8 \pm 0.5 \text{ kJ mol}^{-1}$.

3. Entropy

The entropy will be derived from:

$$T\Delta S = \Delta H - \Delta G \quad (7)$$

where ΔS is the entropy of a system ($\text{J kg}^{-1} \text{K}^{-1}$) consisting of a solid adsorbent plus the molecules adsorbed inside its pores, relative to clean adsorbent and adsorbate molecules in the perfect-gas reference state, all properties being measured at the same temperature T . The Gibbs free energy of the solid phase consists of two terms, one for the adsorbed gas (μn) and another for the grand potential of the solid adsorbent (Myers and Monson [2]):

$$\Delta G = \mu n + \Delta \Omega \quad (8)$$

Physically, the grand potential term $\Delta \Omega$ is the free energy of the solid adsorbent (J kg^{-1}) relative to its clean state with no gas adsorbed in its pores. μ is the chemical potential of the adsorbed gas and n is the amount of gas adsorbed in the pores (mol kg^{-1}). Combination of these equations followed by reduction to dimensionless form gives for the entropy:

$$\frac{\Delta s}{R} = \frac{\Delta h}{RT} - \frac{\mu}{RT} - \frac{\Delta \Omega}{nRT} \quad (9)$$

where Δs and Δh are molar entropy ($\Delta S/n$) and molar enthalpy ($\Delta H/n$), respectively. The three terms on the right-hand-side of Eq. (9) are evaluated as follows. The first term, the molar enthalpy of the adsorbed gas, is obtained from the integral of its differential enthalpy according to Eq. (3). The second term, the chemical potential of the adsorbed gas, is given by its fugacity (f) in the equilibrium bulk gas (Prausnitz et al. [4]):

$$\mu = RT \ln \left(\frac{f}{P^\circ} \right) \quad (10)$$

where P° is the standard pressure (1 atm) of the perfect-gas reference state. Finally, the third term for the grand potential is calculated from the adsorption isotherm (Myers and Monson [2]):

$$-\left(\frac{\Delta \Omega}{nRT} \right) = \frac{1}{n} \int_0^n \frac{d \ln P}{d \ln n} \, dn \quad (11)$$

Fig. 2 shows the entropy of adsorption of SF_6 on silicalite at 25 °C calculated from Eqs. (9)–(11) using experimental data reported previously (Dunne et al. [5]). The molar entropy of adsorption $\Delta s/R$ approaches a saturation value of about -12 and has a limit of $+\infty$ at zero pressure. The standard enthalpy of adsorption is defined at the limit of zero pressure by Eq. (2), but this state fails for entropy because of its singularity at the origin. Fifty years ago, de Boer [6] proposed the adoption of a particular spreading pressure ($\Pi = 0.338 \text{ dyne cm}^{-1}$) for the standard state, but this approach applies only to flat surfaces of known surface area. A different kind of standard state is needed for nanopores. Returning to Eq. (9), the objective is to define a standard state at low but finite loading for the determination of a standard

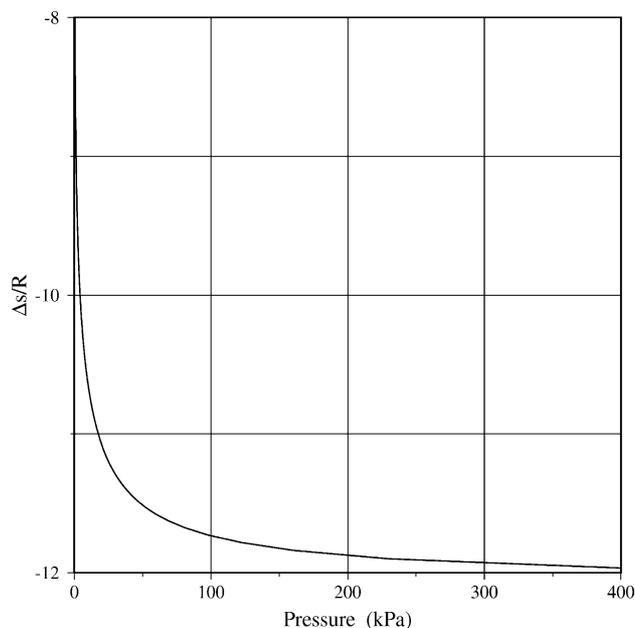


Fig. 2. Molar entropy of adsorption of SF_6 in ZSM-5 (silicalite) at 298.15 K calculated from Eq. (9) using experimental data for the adsorption isotherm and differential enthalpy from Dunne et al. [5]. The limit at saturation is approximately $\Delta s/R = -12$. The zero pressure limit is $\Delta s \rightarrow \infty$.

entropy of adsorption. At low loading where the adsorbate obeys Henry's law:

$$n = KP \quad (12)$$

It can be shown that the solid adsorbent obeys Raoult's law (Myers and Monson [2]), which leads to:

$$\Delta\Omega = -nRT \quad (13)$$

So that the last term in Eq. (9) approaches a limit of unity at zero pressure. The limit $\Delta\Omega = -nRT$ is also obtained by substituting Eq. (12) into (11). The grand potential refers to the solid adsorbent. Focusing on the two terms for the adsorbate on right-hand-side of Eq. (9), and using Eq. (10):

$$\frac{\Delta s^\circ}{R} = \frac{\Delta h^\circ}{RT} - \ln\left(\frac{P}{P^\circ}\right) \quad (14)$$

where the fugacity of the bulk gas in Eq. (10) is replaced by its (low) pressure in the Henry's law region. Following the spirit of the proposal by de Boer mentioned above, the standard state is defined by setting the pore density equal to the bulk density of the gas:

$$\frac{n}{V_p} = \frac{P^\circ}{RT} \quad (15)$$

Substitution of Eqs. (12) and (15) in Eq. (14) gives an expression for the standard entropy of adsorption:

$$\frac{\Delta s^\circ}{R} = \frac{\Delta h^\circ}{RT} + \ln\left(\frac{RTK}{V_p}\right) \quad (16)$$

which may be compared with Eq. (1) for the entropy of an independent site according to the Langmuir theory.

Eq. (15) for the equality of densities in the adsorbed and gas phases resembles the perfect gas law, but the perfect gas law is not obeyed by a gas adsorbed in a nanopore. The left-hand-side of Eq. (15) is the absolute molar density of molecules in the nanopores and the right-hand-side of Eq. (15) is the molar density of molecules in the perfect-gas reference state.

The reference states for the standard entropy of adsorption are a hypothetical perfect gas at 1 atm for the gas phase and a hypothetical gas in the nanopores which obeys Henry's law exactly. This selection of a Henry's law state for the adsorbed gas means that cooperative forces between adsorbed molecules are negligible, just as intermolecular forces are negligible for a perfect gas. The standard adsorption enthalpy characterizes the Boltzmann-averaged interaction of a single probe molecule within the nanopores. The standard adsorption entropy characterizes the degree of confinement and hindered rotation of the probe molecule.

For sufficiently large macropores in which the fraction of molecules adsorbed on the pore walls is negligible, it can be shown that Eq. (16) gives $\Delta s^\circ = 0$. Since its value is zero for a macropore with negligible adsorption, the standard entropy of adsorption is the loss of translational and rotational freedom experienced by a molecule passing from the perfect gas state to a confined state in a nanoporous material.

4. Pore volume

If the atomic structure of the solid is known, the helium pore volume (Myers and Monson [2]) is:

$$V_p = \frac{1}{m} \int e^{-U_{\text{He-s}}/kT} dV \quad (17)$$

where $U_{\text{He-s}}$ is the helium–solid interaction potential. The domain of the integration is over the entire mass, m , of the sample. The pore volume of ZSM-5 (silicalite) from Eq. (17) is $175 \text{ cm}^3 \text{ kg}^{-1}$ (Talu and Myers [7]). This definition of pore volume is consistent with experimental measurements of adsorption, which required the helium dead space for volumetric measurements and the buoyancy of the solid in helium for gravimetric measurements.

The pore volume is estimated by Breck [8] from pore filling of liquids ($n\text{-C}_6\text{H}_{14}$, H_2O) or from the saturation capacity of adsorption isotherms near the normal boiling point of a condensable gas using:

$$V_p = \frac{n_{\text{sat}}}{\rho_p} \quad (18)$$

By assuming that the molar density in the pores, ρ_p , is equal to the molar density of the bulk liquid.

Values of entropy calculated from Eq. (16) are fairly insensitive to errors in the value of V_p : a doubling of V_p corresponds to an change of 0.693 in the value of $\Delta s^\circ/R$.

5. Adsorption second virial coefficient

The expression for the standard entropy of adsorption, Eq. (16), may be written in the form:

$$K = \frac{V_p}{RT} \exp\left(\frac{\Delta s^\circ}{R}\right) \exp\left(\frac{-\Delta h^\circ}{RT}\right) \quad (19)$$

The adsorbent second virial coefficient defined by the limit:

$$B_{1S} = \lim_{P \rightarrow 0} \frac{nRT}{P} \quad (20)$$

is the integral of the gas–solid interaction potential (Steele [9]):

$$B_{1S} = \frac{1}{m} \int e^{-U_{1s}/kT} dV \quad (21)$$

Comparing Eqs. (12) and (20), Henry's constant is simply related to the adsorption second virial coefficient:

$$B_{1S} = RTK \quad (22)$$

Substituting Eq. (22) into Eq. (19):

$$B_{1S} = V_p \exp\left(\frac{\Delta s^\circ}{R}\right) \exp\left(\frac{-\Delta h^\circ}{RT}\right) \quad (23)$$

Eq. (23) indicates that a van't Hoff plot of $\ln(B_{1S})$ versus $(1/T)$ should be linear if the standard enthalpy, standard entropy, and pore volume are constants. Temperature appears explicitly in the pre-exponential factor for the Henry constant in Eq. (19). However, all three constants (standard enthalpy, standard entropy, and pore volume) are weak functions of temperature and the linearity of van't Hoff plots for K and B_{1S} is due to the overwhelming dominance of the temperature variable in the exponential factor for standard enthalpy.

6. ZSM-5 zeolite (silicalite)

Standard enthalpies and entropies are given in Table 1 for several probe molecules. The dimensionless standard enthalpy of adsorption $|\Delta h^\circ/RT|$ lies in the range 6–17. Since silicalite is a nonpolar material, dispersion forces dominate and an approximate corresponding states relationship gives

Table 1
Standard enthalpies (Δh°) and entropies (Δs°) of adsorption on ZSM-5 (silicalite) calculated from Eq. (16)

Gas	T (K)	$-\Delta h^\circ$ (kJ mol ⁻¹)	$-\Delta h^\circ/(RT_c)$	$-\Delta s^\circ/R$
Ar	305.75	15.8	12.6	3.0
CH ₄	297.15	21.1	13.3	3.6
C ₂ H ₆	296.15	31.1	12.2	4.6
C ₃ H ₈	309.45	41.4	13.5	5.3
SF ₆	298.15	35.9	13.6	5.6

Experimental data for Henry's constant and standard enthalpy taken from Dunne et al. [5]. Pore volume $V_p = 175 \text{ cm}^3 \text{ kg}^{-1}$.

Table 2

Comparison of entropy loss accompanying adsorption on ZSM-5 (silicalite) at 298.15 K with translational and rotational entropy in the gas phase. Values of entropy are for one translational degree and one rotational degree of freedom in the perfect-gas state (McQuarrie [10])

Gas	$-\Delta s^\circ/R$	s_{trans}°/R	s_{rot}°/R
Ar	3.0	6.20	0.0
CH ₄	3.6	5.75	1.64
C ₂ H ₆	4.6	6.06	3.00
C ₃ H ₈	5.3	6.25	4.19
SF ₆	5.6	6.85	4.50

a dimensionless standard enthalpy $\Delta h^\circ/RT_c$ of about -13 for simple polyatomic molecules, where T_c is the critical temperature of the gas.

The standard entropies of adsorption $|\Delta s^\circ|$ increase with the size of the probe molecule. Thus, for a given pore size (silicalite), a larger molecule is more confined and loses more of its translational entropy than a smaller molecule. It is interesting to compare the entropy loss upon adsorption with translational and rotational entropies in the perfect gas state in Table 2. Argon loses about one-half of one translational degree of freedom, while the larger SF₆ molecule loses nearly one translational degree of freedom. Theoretical calculations of standard entropy are needed to verify these experimental results.

Table 3

Standard enthalpies and entropies of adsorption in ZSM-22 (TON) calculated from Eq. (16)

Gas	T (K)	$-\Delta h^\circ$ (kJ mol ⁻¹)	$-\Delta h^\circ/(RT_c)$	$-\Delta s^\circ/R$
CH ₄	309.0	27.2	17.2	5.0
C ₂ H ₆	310.0	39.0	15.4	6.6
<i>n</i> -C ₅ H ₁₂	523.0	63.3	16.2	11.0
<i>n</i> -C ₆ H ₁₄	523.0	77.1	18.3	13.2
<i>n</i> -C ₇ H ₁₆	523.0	89.4	19.9	15.2
<i>n</i> -C ₈ H ₁₈	523.0	100.6	21.3	16.8

Experimental data for Henry's constant and standard enthalpy for C1–C2 taken from Savitz et al. [11]; data for C5–C8 from Ocakoglu et al. [12]. Pore volume $V_p = 69 \text{ cm}^3 \text{ kg}^{-1}$.

Table 4

Standard enthalpies and entropies of adsorption in NaX (FAU) calculated from Eq. (16)

Gas	T (K)	$-\Delta h^\circ$ (kJ mol ⁻¹)	$-\Delta h^\circ/(RT_c)$	$-\Delta s^\circ/R$
O ₂	306.31	15.0	11.7	3.8
Ar	304.12	12.7	10.1	2.7
CH ₄	304.41	19.2	12.2	3.6
C ₂ H ₆	293.15	26.9	10.6	4.0
C ₃ H ₈	293.15	34.4	11.2	4.3
SF ₆	295.45	28.4	10.7	3.6
Polar molecules				
N ₂	305.62	19.9	19.0	4.4
C ₂ H ₄	293.15	41.8	17.8	6.6
CO ₂	293.15	48.6	19.2	7.7

Experimental data for Henry's constant and standard enthalpy from Dunne et al. [13]. Pore volume $V_p = 320 \text{ cm}^3 \text{ kg}^{-1}$.

Table 5
Standard enthalpy (Δh°) and entropy (Δs°) of nanoporous materials using methane probe molecule at 298.15 K

Zeolite material	Structure type	Pore topology	Pore diameter (Å)	V_p (cm ³ /kg)	$-\Delta h^\circ/RT_c$	$-\Delta s^\circ/R$
UTD-1	DON	1-D	8.1 × 8.2	106	9.0	1.2
ZSM-12	MTW	1-D	5.6 × 6.0	97	13.2	3.4
ZSM-22	TON	1-D	4.6 × 5.7	69	17.2	5.0
ZSM-35 (ferrierite)	FER	2-D	3.5 × 4.8, 4.2 × 5.4	105	17.5	4.6
ZSM-5 (silicalite)	MFI	3-D	5.1 × 5.5, 5.3 × 5.6	175	13.3	3.6
NaX (faujasite)	FAU	3-D	7.4 × 7.4	320	12.1	3.6

Calculated from Eq. (16) using experimental data for Henry's constants and standard enthalpies from Savitz et al. [11]. Structure types from Baerlocher et al. [14].

7. ZSM-22 zeolite (TON)

The standard enthalpy and entropies reported in Table 3 for *n*-alkanes are especially interesting because the translational and rotational degrees of freedom of these molecules are severely restricted by the narrow cylindrical pores about 0.5 nm in diameter in ZSM-22. Even though the temperature difference between the C1–C2 and C5–C8 measurements is over 200 °C, the enthalpies are fairly consistent. The entropy loss for *n*-octane corresponds to about two translational degrees of freedom, which is consistent with a restriction to one-dimensional translational motion in the narrow pore.

8. NaX zeolite (FAU)

NaX zeolite has strong electric field gradients which interact with molecules like N₂, CO₂, and C₂H₄ having large quadrupole moments. Table 4 shows that the standard enthalpy of these polar molecules is approximately 60% dispersion and 40% electrostatic energy. The energies of the nonpolar molecules can be correlated by corresponding states: $\Delta h^\circ/RT_c$ is about –11 for simple polyatomics. The standard entropies of the nonpolar molecules $|\Delta s^\circ/R|$ are 3.6 ± 1 , indicating that the supercavity and its connecting channels in NaX are large compared to the diameter of these molecules. The absolute values of the standard entropies of the polar molecules are significantly larger than those for the nonpolar molecules because of bonding of the quadrupole moments with the sodium cations in NaX.

9. Methane probe molecule for different nanomaterials

Several zeolitic materials are characterized by a methane probe molecule in Table 5. The first three zeolites have non-intersecting elliptical pores with diameters increasing in the order TON < MTW < DON. As expected, the absolute value of the standard enthalpy increases strongly with decreasing pore size because the pore diameter is not much larger than the molecular diameter of the methane molecule. The increased steric constraint of TON compared to DON is also apparent in the values for the standard entropy.

The two zeolites with intersecting elliptical pores, FER and MFI, show similar effects: the zeolite with smaller pores (FER) has larger (absolute) values of standard enthalpy and standard entropy.

The large spherical cavities in FAU zeolite and the intersecting pores in MFI have nearly the same values of standard enthalpy and entropy for a methane probe molecule in spite of the difference in their pore structure.

10. Summary and conclusions

Physical constants are defined for the interaction of a single probe molecule with nanoporous materials. The standard enthalpy is the molar enthalpy of adsorption at the limit of zero pressure. The standard entropy is calculated from the Henry constant at a single temperature, the standard enthalpy, and the pore volume.

The value of the Henry constant decreases exponentially with temperature but the variation of the standard enthalpy and entropy with temperature is comparatively weak.

For a given nanoporous material, the dimensionless standard enthalpy $\Delta h^\circ/RT_c$ is approximately constant for simple, nonpolar probe molecules. For a specific probe molecule in different nanoporous materials, the absolute value of the standard enthalpy increases with decreasing pore diameter.

For a given nanoporous material, the absolute value of the standard entropy increases with the molecular diameter of the probe molecule due to hindered translational and rotational motion for the larger molecule. For a specific probe molecule in different nanoporous materials, the absolute value of the standard entropy varies inversely with the pore size for the same reason.

The standard enthalpy and standard entropy are obtained by integrating the gas–solid potential energy for a single probe molecule interacting with the walls of the nanoporous material. Theoretical calculations to support the experimental values reported here are in progress.

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