Letters to the Editor

Isosteric heat of adsorption and isochoric heat of vaporization and sublimation

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Adsorption equilibrium is often described using the isosteric heat of adsorption, determined by the change in the pressure of the gas phase following an increase in the temperature with the adsorbed amount remaining the same. It is normally assumed that the adsorbate—vapor equilibrium changes following an increase in the temperature in a similar way as the liquid—vapor equilibrium, *i.e.*, "in a free process," irrespective of the presence of the adsorbent. Our calculations showed that the adsorbent determines wholly or partly the conditions for the constancy of the volume of the adsorbate during heating, and it is more correct to compare the isosteric heats of adsorption with isochoric heats of vaporization and sublimation. These heats can be calculated from the data on the enthalpy of vaporization and sublimation (ΔH) under orthobaric conditions (in the absence of external pressure except for the saturated vapor pressure).

The total differential of the function of the vapor pressure of a liquid or a crystal is determined through the partial derivatives

$$\frac{\mathrm{d}p''}{\mathrm{d}T} = \left[\frac{\partial p''}{\partial T}\right]_{V'} + \left[\frac{\partial p''}{\partial V'}\right]_T \frac{\mathrm{d}V'}{\mathrm{d}T}. \qquad (1)$$

From here on, a double prime (″) refers to the gas phase, and a prime (′) refers to the liquid or crystalline phase; p' is the additional pressure on the liquid phase, for example, due to an "inert" gas; V is the molar volume; and T is the temperature. Assuming that the vapor is an ideal gas ($p'' = RT/V''$) and replacing the derivative of the vapor pressure in Eq. (1) by the expression $\mathrm{d}p'' = (V'/V'')\mathrm{d}p'$, which follows from the fact that the chemical potentials of coexisting phases are equal, we can obtain after a series of transformations the following expression for the isochoric heat of vaporization or sublimation:

$$Q_V = RT^2(\partial \ln p''/\partial T)_V = \Delta H + TV'\alpha'/\beta'_T, \qquad (2)$$

where $\Delta H = RT^2 \mathrm{d}\ln p''/\mathrm{d}T$ is the heat of vaporization or sublimation under orthobaric conditions; $\beta'_T = -(\partial \ln V'/\partial p')_T$ is the isothermal compressibility of the condensed phase; and $\alpha' = \mathrm{d}\ln V'/\mathrm{d}T$ is the coefficient of thermal expansion of a liquid or a crystal under orthobaric conditions. The isochoric heat Q_V is greater than the corresponding heat of vaporization or sublimation under orthobaric conditions by the value of the work, which needs to be done for the compression of the condensed phase in order to compensate for the temperature variation of its volume in an isochoric process. For example, for liquid xenon at 170 K, ΔH = 12378 J mol^{-1}, and Q_V = 22723 J mol^{-1}; for crystalline xenon at 160 K, ΔH = 14983 J mol^{-1}, and Q_V = 24983 J mol^{-1} (see Ref. 1).

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According to the published data,[2] the isosteric heat of the adsorption of xenon on the NaX zeolite at 165 K varies from 21.1 to 24.8 kJ mol^{-1} as a function of the amount adsorbed. These values are close to the isochoric heats of vaporization and sublimation mentioned above. It can be suggested that the cavities of the NaX zeolite act as a reservoir for the adsorbed xenon ensuring that its volume remains constant when the temperature changes. Evidently, the conditions in this case are not strictly isochoric, since the volume of zeolite crystals changes slightly both in adsorption and following an increase in the temperature. These corrections can be found from experimental data on the deformation of zeolites.

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Cyclopropanation of buckminsterfullerene *via* olefin metathesis reaction

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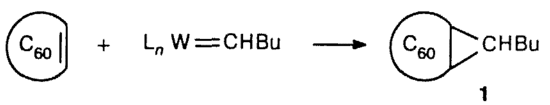
Buckminsterfullerene C_{60} is known to enter into cycloaddition reactions with carbenes during the interactions with diazocompounds, azides, chlorocarbenes,[1] and Fischer carbenes.[2] In this case methanofullerene and methanoannulene (fulleroid) derivatives are formed depending on the type of substituents in carbene.[3]

A catalytic reaction of olefin metathesis, which is the redistribution of alkylidene moieties resulting in new unsaturated molecules, occurs involving metalcarbene intermediates.[4]

$$L_nM{=}CHR^1 + R^2CH{=}CHR^3 \longrightarrow R^2CH{=}CHR^1 + L_nM{=}CHR^3$$

However, cyclopropanation of unsaturated compounds containing electron-withdrawing double bonds can take place under metathesis conditions.[5] For this reason, we should expect that tungsten carbene complexes formed in the metathesis reaction of 1-hexene in the presence of a homogeneous system WCl_6—1,1,3,3-tetramethyl-1,3-disilacyclobutane (SCB)[6], can add to electron-withdrawing bonds of fullerene to yield methanofullerene.



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The compound **1** obtained was characterized by spectral methods (IR, ^{1}H and ^{13}C NMR spectroscopy); its composition is consistent with the elemental analysis data.

The methanofullerene structure of adduct **1**, formed as a result of carbene addition to the (6,6) junction of fullerene is supported by the presence of signals of the bridgehead and foot carbons of the cyclopropane moiety (at δ 40.30 and 72.30) in its ^{13}C NMR spectrum, and the signal of the methine proton at δ 5.29 in its ^{1}H NMR spectrum. These data are consistent with the NMR spectral parameters of methanofullerenes.[3]

The result presented is the first example of the use of metathesis reaction for the synthesis of fullerene derivatives.

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