

Energetics of gas sorption in glassy polymers

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(Received 20 November 1978; revised 26 February 1979)

The molar enthalpy for gas sorption in glassy polymers at a fixed concentration, often called the isosteric enthalpy of sorption, exhibits a clearly discernable minimum when plotted as a function of penetrant concentration. This unexpected behaviour has been observed in several glassy polymer systems including poly(ethylene terephthalate), polyacrylonitrile and polycarbonate. The behaviour can be modelled by analysing the temperature dependence of the various equilibrium parameters comprising the so-called dual mode sorption model for gas sorption in glassy polymers. The fundamental significance of the various enthalpies describing the temperature dependence of the Henry's law solubility constant, the Langmuir affinity constant and the Langmuir capacity constant are included in the discussion. Provision is made for non-ideal vapours and gases by introduction of the compressibility factor in the expression for the isosteric enthalpy. Application of relationships for calculating both the isosteric and the isothermal enthalpies of sorption is made to the case of CO₂ in poly(ethylene terephthalate) in the temperature range 35° to 115°C. These results and analyses complement the wealth of equilibrium and transport data which are consistent with the dual mode sorption model for penetrant sorption in glassy polymers.

INTRODUCTION

It is common to interpret sorption isotherms for gases in glassy polymers in terms of a model which is based on the hypothesis that gas is sorbed both by a Henry's law solution mechanism and an additional mechanism whose contribution is characterized by a Langmuir isotherm¹⁻⁷ as shown in equation (1):

$$C = k_D p + \frac{C_H' b p}{1 + b p} \quad (1)$$

The parameters k_D , C_H' and b can be determined by non-linear regression analysis of sorption data^{3,5}. The parameter k_D is the Henry's law constant which characterizes the uptake of gas by the mechanism of dissolution similar to that in liquids. A van't Hoff expression describes the temperature dependence of this equilibrium constant:

$$k_D = k_{D_0} \exp\left(\frac{-\Delta H_D}{RT}\right) \quad (2)$$

ΔH_D refers to the difference in enthalpy of a penetrant molecule in the Henry's law sorbed state compared with the gas phase, i.e.:

$$\Delta H_D \triangleq H_D - H_g \quad (3)$$

where H_D is the enthalpy of the penetrant sorbed in the

Henry's law environment and H_g is the enthalpy of the penetrant in the gas phase. The linear semilogarithmic plot of k_D versus $1/T$ in Figure 1 for CO₂ in poly(ethylene terephthalate) implies that ΔH_D is reasonably constant over the temperature range 35° to 115°C and roughly equal to $-1700 \text{ cal(gmol)}^{-1}$ ⁸. The data point at 35°C deviates from the straight line by more than the average experimental scatter, so ΔH_D may become more negative as temperature decreases. The range of temperatures considered here encompasses the glass transition temperature of this sample of PET (85°C). As one might expect, k_D does not change discontinuously due to this transition since the normal solution mode of sorption exists both above and below T_g .

The Langmuir capacity parameter, C_H' , represents the maximum number of moles that can be sorbed by the second mode in the polymer at the temperature of interest. The Langmuir capacity of glassy polymers appears to be due to non-equilibrium elements of free volume which arise during quenching to the glassy state from the rubbery state⁸. These non-equilibrium elements have been termed 'microvoids' or 'holes' for convenience¹. The Langmuir capacity in glassy polymers appears to be a significant function of temperature, whereas it is relatively insensitive to temperature for zeolites or charcoal. In fact, the Langmuir capacity of amorphous polymers disappears above T_g since in the rubbery state there is no longer the possibility of freezing-in 'non-average' chain separations for a long enough time to probe them with gas sorption^{8,9}.

The Langmuir mode affinity constant, b , measures the ratio of the sorption to desorption rate constants for gas in the Langmuir mode. Since b is an equilibrium constant, a van't Hoff expression describes its temperature variation:

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PHENOMENOLOGICAL INTERPRETATION OF SORPTION ENTHALPIES

If no attempt is made to partition the total sorption concentration into two distinct modes, an equally acceptable but perhaps physically less satisfying analysis can be performed. To maintain equilibrium between a penetrant in the pure gas phase (α) and in the sorbed phase (β), the change in the chemical potential, μ , of the penetrant in both phases must be equal, i.e.:

$$d\mu^\alpha = d\mu^\beta \tag{7}$$

Therefore, dividing by the absolute temperature, T , and expanding the resulting differentials for μ/T in the two phases gives equation (8):

$$\left(\frac{\partial\mu^\alpha/T}{\partial T}\right)_p dT + \left(\frac{\partial\mu^\alpha/T}{\partial p}\right)_T dp = \left(\frac{\partial\mu^\beta/T}{\partial T}\right)_{P,C} dT + \left(\frac{\partial\mu^\beta/T}{\partial p}\right)_{T,C} dp + \left(\frac{\partial\mu^\beta/T}{\partial C}\right)_{P,T} dC \tag{8}$$

For a change at constant C , we have

$$dT \left[\left(\frac{\partial\mu^\alpha/T}{\partial T}\right)_p - \left(\frac{\partial\mu^\beta/T}{\partial T}\right)_{P,C} \right] = dp \left[\left(\frac{\partial\mu^\beta/T}{\partial P}\right)_{T,C} - \left(\frac{\partial\mu^\alpha/T}{\partial P}\right)_T \right] \tag{9}$$

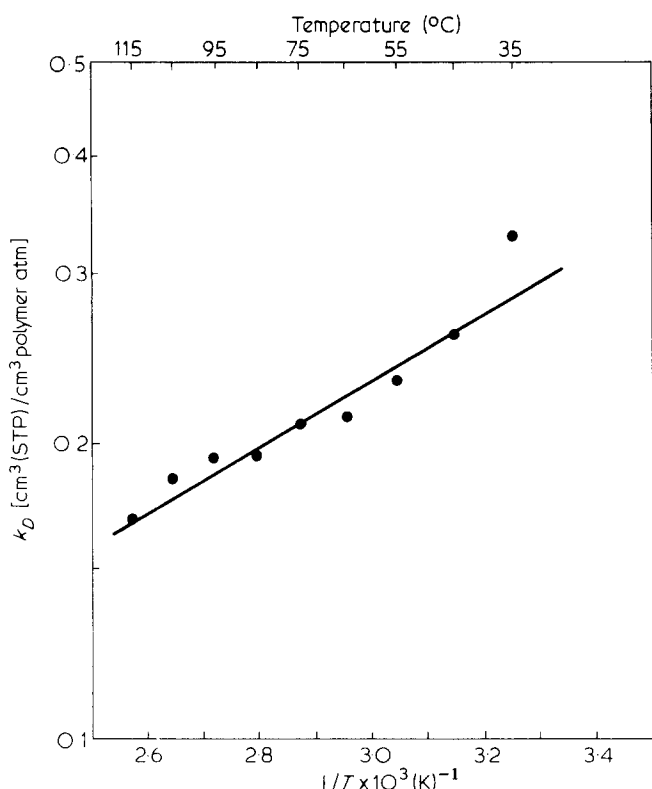


Figure 1 van't Hoff plot of Henry's law coefficient, k_D , for CO_2 in poly(ethylene terephthalate)

$$b = b_0 \exp \left[\frac{-\Delta H_b}{RT} \right] \tag{4}$$

ΔH_b refers to the difference in enthalpy of penetrant in the Langmuir sorbed state compared with the gas phase, i.e.:

$$\Delta H_b = H_H - H_g \tag{5}$$

where H_H is the enthalpy of the penetrant in the Langmuir sorbed state and H_g is the enthalpy of the penetrant in the gas phase¹⁰. The linear semilogarithmic plot of b versus $1/T$ in Figure 2 for CO_2 in PET indicates a constant value for ΔH_b equal to $-3000 \text{ cal (gmol)}^{-1}$ over the temperature range of interest. Subtraction of equation (5) from equation (3) yields:

$$H_D - H_H = 1300 \text{ cal (gmol)}^{-1} \tag{6}$$

Equation (6) indicates that the enthalpy of a CO_2 molecule sorbed in the Henry's law mode is higher than the enthalpy of a CO_2 molecule sorbed in the Langmuir mode. Michaels *et al.*¹ have considered this situation and suggested that the process of sorption entails 'condensing' the gas, opening a 'void' in the polymer, and inserting the sorbate into the void. For the Langmuir case, since the microvoids supposedly already exist, no extra energy is required to separate chains enough to insert a sorbate molecule. In the case of the Henry's law species, chains must be separated to accommodate the CO_2 molecule, thereby causing the enthalpy of sorption for this mode to be less negative. The small magnitude of the difference in sorbed enthalpies may arise because CO_2 is a slender molecule and can be accommodated relatively easily with little distortion of the basic polymer matrix.

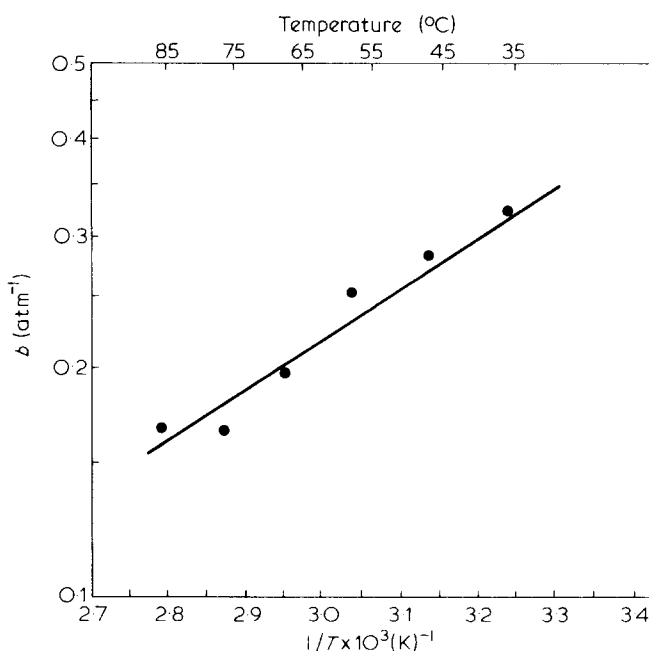


Figure 2 van't Hoff plot of Langmuir affinity coefficient, b , for CO_2 in poly(ethylene terephthalate)

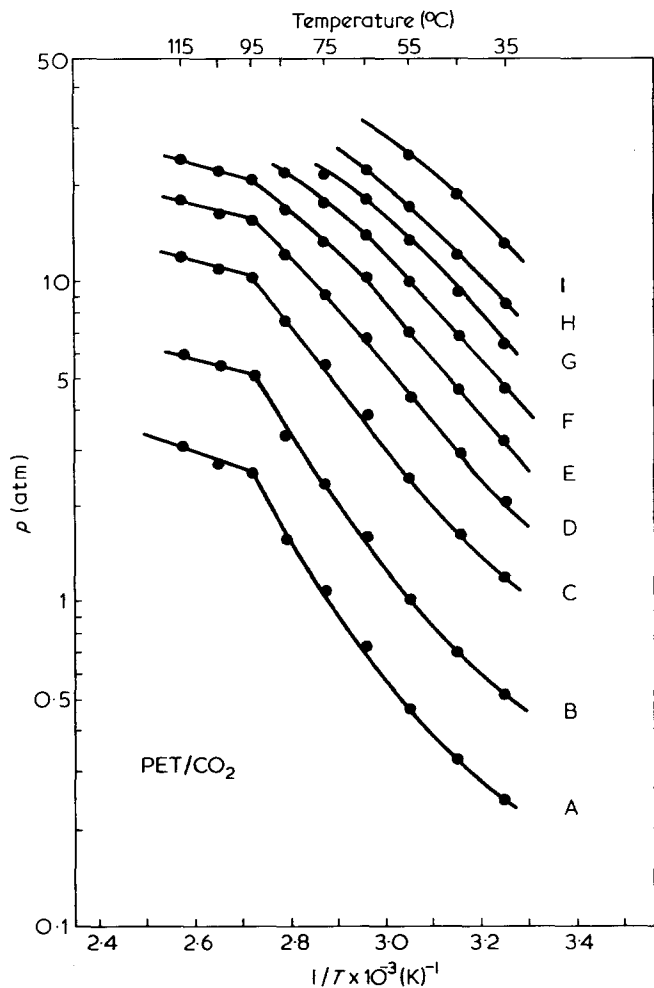


Figure 3 Semilogarithmic plots of p versus $1/T$ to permit determination of the isosteric enthalpy of sorption for CO_2 in poly(ethylene terephthalate). The sharp change in slope at 95°C is near to the 85°C glass transition of this semicrystalline sample. A, C = 0.5; B, 1; C, 2; D, 3; E, 4; F, 5; G, 6; H, 7; I, 9

Substituting for the various partial derivatives and rearranging (11):

$$\left[\frac{dp}{dT} \right]_C = \frac{-H^\alpha + H^\beta}{(V^\beta - V^\alpha)T} \quad (10)$$

where $S^\alpha, S^\beta, H^\alpha, H^\beta, V^\alpha$ and V^β refer to the partial molar entropies, enthalpies and volumes of the sorbate in phases α and β , respectively. Assuming $V^\beta \ll V^\alpha$ implies $V^\beta - V^\alpha \approx -zRT/p$, so equation (10) becomes:

$$\left[\frac{dp}{dT} \right]_C = - \left(\frac{H^\beta - H^\alpha}{zRT^2} \right) p \quad (11)$$

so,

$$\left[\frac{d \ln p}{d(1/T)} \right]_C = \left(\frac{H^\beta - H^\alpha}{zR} \right) \equiv \frac{\Delta H_I}{zR} \quad (12)$$

where ΔH_I is the isosteric heat of sorption which is a measure of the average difference in enthalpy between a molecule in the sorbed state and in the gaseous state. Semilogarithmic plots of p versus $1/T$ at constant sorption concentration are presented in Figure 3 for the CO_2/PET sorption data reported earlier⁸.

The resultant values of ΔH_I determined from the slopes of these curves at 55°C , using the appropriate values of z , are plotted as the dots in Figure 4 as a function of concentration. Kollen¹², Barrie⁹ and Huvard¹³ have reported similar shaped curves for various penetrants in glassy PET, polycarbonate and poly(acrylonitrile), respectively.

DUAL MODE INTERPRETATION OF ISOSTERIC SORPTION ENTHALPIES

The minimum in Figure 4 can be explained in terms of the dual mode sorption model if one accounts for the temperature dependence of C'_H using an apparent van't Hoff expression:

$$C'_H = C'_{H_0} \exp \left[\frac{-\Delta H^*}{RT} \right] \quad (13)$$

where ΔH^* is simply an apparent enthalpy characterizing the temperature dependence of C'_H and may not have a simple physical meaning. Combination of equations (13), (2) and (4) with equation (1) for the total concentration, yields:

$$C = k_{D_0} \exp \left(\frac{-\Delta H_D}{RT} \right) p + \frac{C'_{H_0} b_0 \exp \left(\frac{-(\Delta H^* + \Delta H_b)}{RT} \right) p}{1 + b_0 \exp \left(\frac{-\Delta H_b}{RT} \right) p} \quad (14)$$

One can define $\Delta H_{HT} = \Delta H^* + \Delta H_b$ which can, in principle, be either positive, negative or zero depending on the values of ΔH^* and ΔH_b . Solving for the secant slope, $C/p = \bar{k}$, in terms of equation (14):

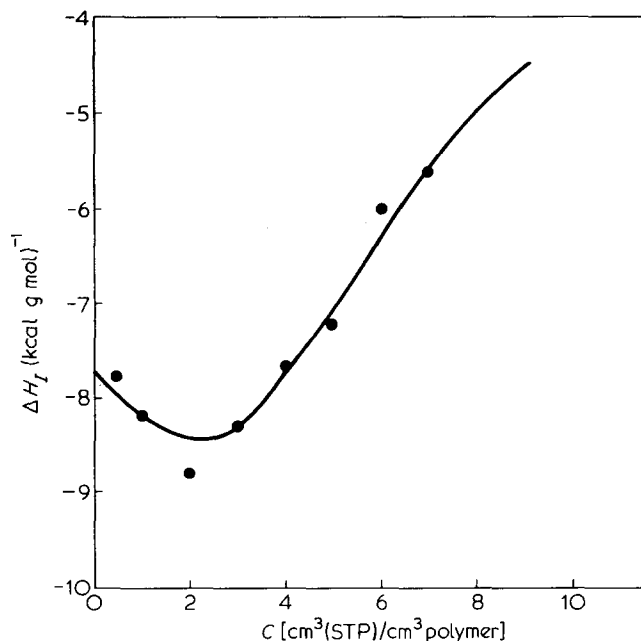


Figure 4 Isosteric enthalpies of sorption for CO_2 in poly(ethylene terephthalate) as a function of concentration. The points were evaluated from the slopes of lines in Figure 3 at 55°C according to equation (12). The line is the predicted value of ΔH_I using equation (17) at 55°C

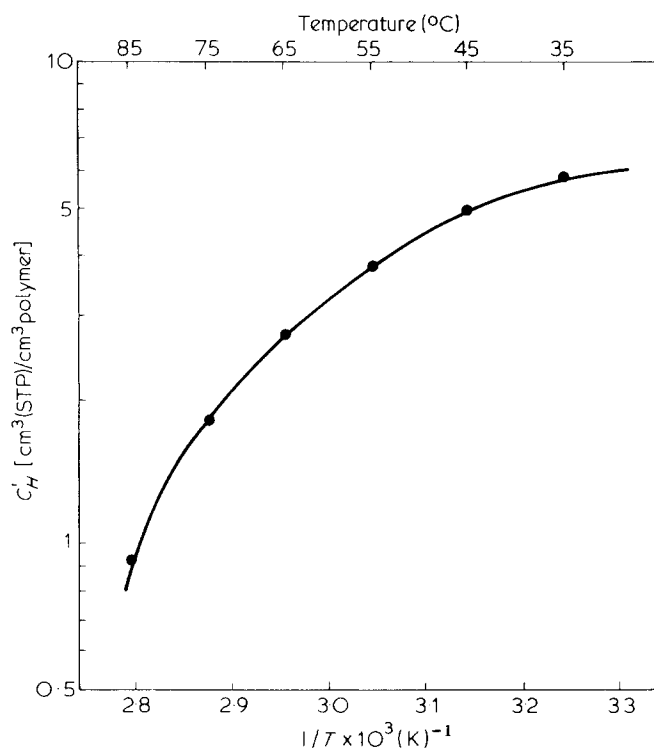


Figure 5 van't Hoff type plot of the Langmuir capacity of poly(ethylene terephthalate) for CO₂. The apparent enthalpy ΔH^* , which can be evaluated from the slope of this plot may not have a simple physical meaning

$$\bar{k} = C/p = k_{D0} \exp\left(\frac{-\Delta H_D}{RT}\right) + \frac{C'_H b_0 \exp\left(\frac{-\Delta H_{HT}}{RT}\right)}{1 + b_0 \exp\left(\frac{-\Delta H_b}{RT}\right)_p} \quad (15a)$$

$$\bar{k} = k_D + \frac{C'_H b}{1 + bp} \quad (15b)$$

Applying the definition of the isosteric heat of sorption (equation 12):

$$\frac{\Delta H_I}{R} = z \left(\frac{\partial \ln p}{\partial (1/T)} \right)_C = z \left(\frac{\partial \ln(C/\bar{k})}{\partial (1/T)} \right)_C = -z \left(\frac{\partial \ln \bar{k}}{\partial (1/T)} \right)_C \quad (16)$$

one finds after considerable algebraic rearrangement:

$$\Delta H_I = z \frac{k_D \Delta H_D + \frac{C'_H b \Delta H_{HT}}{1 + bp} - \frac{C'_H b^2 \Delta H_b p}{(1 + bp)^2}}{k_D + \frac{C'_H b}{1 + bp} - \frac{C'_H b^2 p}{(1 + bp)^2}} \quad (17)$$

The isosteric enthalpy reflects redistribution of sorbate between Henry's law and Langmuir populations as temperature and pressure are varied at constant total concentration. If the enthalpies appearing in the above equations are functions of temperature, additional terms enter into the expression for the isosteric enthalpy of sorption. For the present discussion, however, this effect will be neglected. The line in Figure 4 was calculated at 55°C using equation (17) and the appropriate values of z , k_D , C'_H , b and the independently determined values $\Delta H_D = -1700 \text{ cal (gmol)}^{-1}$, $\Delta H_b =$

$-3000 \text{ cal (gmol)}^{-1}$, $\Delta H^* = -6391 \text{ cal (gmol)}^{-1}$ evaluated from consideration of the temperature dependence of k_D , b , and C'_H , respectively. The values of ΔH_D and ΔH_b could be determined from consideration of all the data (35°C to 115°C for k_D and 35°C to 85°C for b) since the sorption enthalpies were reasonably constant. For C'_H , as shown in Figure 5, the apparent sorption enthalpy, ΔH^* is temperature dependent, so the slope of the curve at 55°C was used to evaluate ΔH^* . The calculated line reproduces the data points well and accounts for the minimum at a concentration of approximately 2 cm³ (STP)/(cm³ polymer). The origin of this minimum can be understood better by consideration of some limiting cases of equation (17).

In the limit as k_D goes to zero and ΔH^* goes to zero, one finds the classical Langmuir case with C'_H approximately constant, so $\Delta H_I = \Delta H_b$. If k_D goes to zero but $\Delta H^* < \Delta H_b$, ΔH_I becomes infinitely negative as C approaches C'_H due to a mathematical artefact. For cases such as gases in glassy polymers where $k_D \neq 0$, the mathematical artefact is suppressed by the Henry's law term and appears only as a minimum in the range of concentrations near to the value of C'_H at the temperature of interest.

ISOTHERMAL INTEGRAL HEAT OF SORPTION

The calorimetrically measured molar enthalpy of sorption ΔH_c , for an integral sorption experiment from zero to some final concentration, C , is given by equation (18) for sorption by the two mechanisms characterized by the Henry's law term, C_D , and the Langmuir term, C_H , respectively:

$$\Delta H_c = \frac{\int \Delta H_D dC_D + \int \Delta H_b dC_H}{\int dC} \quad (18)$$

Assuming ΔH_D and ΔH_b are reasonably constant, we have;

$$\Delta H_c = \frac{\Delta H_D C_D + \Delta H_b C_H}{C_D + C_H} \quad (19)$$

In the limit of zero concentration, ΔH_c becomes

$$\Delta H_{c0} = \frac{\Delta H_D + K \Delta H_b}{1 + K} \quad (20)$$

where $K = C'_H b / k_D$. On the other hand, equation (17) indicates that in the limit of zero concentration the isosteric enthalpy becomes:

$$\Delta H_{I0} = \frac{\Delta H_D + (\Delta H_b + \Delta H^*) K}{1 + K} \quad (21)$$

For the case of CO₂ in PET at 55°C this corresponds to:

$$\Delta H_{c0} = -2700 \text{ cal (gmol)}^{-1}$$

$$\Delta H_{I0} = -7760 \text{ cal (gmol)}^{-1}$$

The difference between these two limiting enthalpies of sorption

$$\Delta H_{I0} - H_{c0} = \frac{\Delta H^* K}{1 + K}$$

would be equal to zero only if C'_H were independent of temperature, i.e. $\Delta H^* = 0$. The extrapolation of calorimetrically measured enthalpies of sorption at 55°C to zero concentration should approach $-7760 \text{ cal (gmol)}^{-1}$ if the temperature dependence of C'_H is due to decreased polymer/penetrant interaction. On the other hand, if the temperature dependence of C'_H is due to reduction in Langmuir capacity caused simply by progressive elimination of frozen microvoids as the glass transition is approached, the extrapolation of calorimetrically measured enthalpies of sorption at 55°C to zero concentration should approach $-2700 \text{ cal (gmol)}^{-1}$. Both of the above statements assume that ΔH_b is essentially independent of fractional site saturation consistent with the classical Langmuir isotherm treatment which assumes homogeneity of sorption sites. Although energetic heterogeneity of sorption sites is known to exist in some microporous solids, only simple Langmuirian sorption has been reported in glassy polymers. A single microvoid affinity constant, essentially independent of fractional site saturation, satisfactorily describes the interaction between CO₂ and a number of glassy polymers^{3,8,13}. Since the two predictions of limiting sorption enthalpies are significantly different, direct calorimetry measurements during the sorption process should provide an additional test of the fundamental validity of partitioning of the total sorption concentration into two populations.

CONCLUSIONS

An analytical expression has been derived for prediction of the molar enthalpy of sorption at constant concentration (isosteric enthalpy of sorption) in dual mode sorption systems. The expression was shown to provide an excellent description of the data derived by formal thermodynamic analysis of CO₂ sorption isotherms in PET. Fitting data to a model, however, does not unambiguously prove the physical significance of the model parameters. An experimental test based on calorimetry was described which would indicate whether the apparent enthalpy, ΔH^* , derived from an assumed van't Hoff form of the temperature dependence of the Langmuir sorption capacity, makes a *real* contribution to the measurable heat of sorption of CO₂ in PET. If the calorimetrically measured molar enthalpy of sorption for CO₂ in PET at low concentrations is closer to

$-2700 \text{ cal (gmol)}^{-1}$ than to $-7800 \text{ cal (gmol)}^{-1}$, this would suggest that ΔH^* is not a true heat of sorption and that the use of a van't Hoff expression for C'_H , while convenient, has no fundamental basis.

A recent interpretation of C'_H in terms of unrelaxed volume in the glass seems to provide a satisfying phenomenological explanation for the temperature dependence of C'_H ⁸. Additional fundamental support for this interpretation would be provided if calorimetry work demonstrates that ΔH^* is not a true heat of sorption.

ACKNOWLEDGEMENTS

The authors acknowledge the support of this work by the National Science Foundation through grants at North Carolina State University and the University of Texas.

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