

DIFFERENTIAL HEAT DETERMINATION THROUGH THE ESTIMATION OF PRESSURE DERIVATIVES

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ABSTRACT

A statistical method involving the estimation of pressure derivatives at constant temperature is suggested for the determination of the differential heat and its equivalence to the thermodynamic approach is shown. While the nonideal localized and mobile isotherms predict linear variation of the differential heat with surface coverage for a homogeneous surface the novel features like maxima are displayed when surface heterogeneity acts in opposition to attractive forces. The qualitative differences between the localized and mobile models are clearly seen in the differential heat variation with surface coverage and they are not masked by surface heterogeneity.

INTRODUCTION

DETERMINATION of the proper site energy distribution is a prerequisite for the quantitative prediction of the adsorption behaviour of a heterogeneous surface. In the past, several techniques involving the solution of the adsorption integral equation or deriving the statistical surface reaction rates, after postulating the site energy distribution, have been employed. The integral transform methods appropriate to these problems have been reviewed elsewhere¹.

One of the diagnostic tests for the presence of nonidealities like surface heterogeneity, induced heterogeneity and interactions between adsorbed molecules has been to study the variation of the differential heat as a function of surface coverage. The initial steep fall in the differential heat *vs* surface coverage is often due to the surface heterogeneity while an appreciable fall in the high coverage region points to the presence of significant interaction between adsorbed molecules².

It is often remarked that the nature of site energy distribution (surface heterogeneity) is mirrored in its differential heat behaviour. To what extent this behaviour is modified or masked in the presence of interaction between or mobility of adsorbed molecules is the central theme of the present work.

The usual thermodynamic method employed in computing the differential heat involves

measurement of adsorption isotherms at several temperatures. Then the Clausius-Clapeyron equation is employed².

$$(d \ln p / dT)_\theta = Q^{\text{diff}} / RT^2 \quad (1)$$

For a heterogeneous surface (*i.e.* if we adhere to the idea embodied in the random patch model (RPM)² of the surface wherein the surface is visualized as an assemblage of miniature uniform surfaces), the surface coverage will be different on each of these patches at the same temperature and pressure, the mean surface coverage (total uptake) will be constant and (1) is modified accordingly.

An alternative statistical formulation of the differential heat which yields the same result as the thermodynamic definition (1) but which involves only *the estimation of pressure derivatives at a constant temperature will be presented now.*

FORMULATION

The Clausius-Clapeyron equation (1) for a heterogeneous surface is

$$\begin{aligned} (d \ln p / dT)_\theta &= \frac{1}{p} (dp / dT)_\theta \\ &= \frac{-1}{p} (\partial \bar{\theta} / \partial T)_p / (\partial \bar{\theta} / \partial p)_T = Q^{\text{diff}} / RT^2 \end{aligned} \quad (2)$$

where the mean surface coverage $\bar{\theta}(T, p)$ is given by

$$\bar{\theta}(T, p) = \int_{Q_1}^{Q_2} \theta_{ii}(T, p) \delta(Q) dQ. \quad (3)$$

Within the framework of the random path model $\theta_{ii}(T, p)$ is denoted as the local isotherm which describes the surface coverage on the i th patch, $\delta(Q)$ is the site-energy distribution and Q_1, Q_2 are the limits of the heats of adsorption, representative values for these have been chosen in accordance with earlier work^{3, 4}.

To obtain the numerator and the denominator in (2) one has to differentiate under the integral in (3) assuming that the site energy distribution is unaffected by temperature and pressure. Then (2) can be rewritten as

$$\frac{\frac{1}{p} \int_{Q_1}^{Q_2} -(\partial\theta_{ii}/\partial T)_p \delta(Q) dQ}{\int_{Q_1}^{Q_2} (\partial\theta_{ii}/\partial p)_T \delta(Q) dQ} = Q^{\text{diff}}/RT^2 \quad (4)$$

where for brevity the explicit dependence of θ_{ii} on T, p, Q is not shown.

The statistical definition of the differential heat can be given as follows: Assume that due to non-idealities on each of the patches (like interaction between the adsorbed molecules) the differential heat varies as a function of the local surface coverage. Thus the integral heat of adsorption on the i th patch is:

$$Q_{ii}^{\text{int}} = \int_0^{\theta_{ii}} Q_{ii}^{\text{diff}} d\theta_{ii} \quad (5)$$

and we define an overall integral heat* as

$$Q^{\text{int}} = \int_{Q_1}^{Q_2} \left[\int_0^{\theta_{ii}} Q_{ii}^{\text{diff}} d\theta_{ii} \right] \delta(Q) dQ \quad (6)$$

weighted over the site energy distribution and the corresponding mean surface coverage as [c.f. (3)]

$$\bar{\theta} = \int_{Q_1}^{Q_2} \left[\int_0^{\theta_{ii}} d\theta_{ii} \right] \delta(Q) dQ. \quad (7)$$

* Note that the distribution of sites is defined in terms of pure binding energies for the adsorbed molecules on each patch: in other words the differential heat extrapolated to zero local surface coverage where interactions are not important.

But the statistical differential heat Q^{diff} is

$$Q^{\text{diff}} = dQ^{\text{int}}/d\bar{\theta} \quad (8)$$

Then using (6)–(8) a differential heat can be evaluated along the path of constant temperature.

Since separate adsorption equilibrium prevails on each of the patches between gas and adsorbed phases, the chemical potential of the adsorbed phase on the i th patch will be equal to the chemical potential of the gas phase itself. Hence the chemical potential of the entire adsorbed phase can be denoted by the μ_s . Thus,

$$\mu_g(p, T) = \mu_s(p, T) \quad (9)$$

Equation (9) implies that at constant coverage p and T are not independent. Hence the temperature can be solved in terms of pressure and vice versa. In fact the presence of such a relationship is readily apparent from (7) for a constant $\bar{\theta}$.

If the equilibrium pressure p is varied by dp there will be corresponding changes in Q^{int} and $\bar{\theta}$, hence

$$dQ^{\text{int}}/dp = \int_{Q_1}^{Q_2} Q_{ii}^{\text{diff}} (\partial\theta_{ii}/\partial p)_T \delta(Q) dQ \quad (10)$$

$$d\bar{\theta}/dp = \int_{Q_1}^{Q_2} (\partial\theta_{ii}/\partial p)_T \delta(Q) dQ. \quad (11)$$

In deriving (10) and (11) the inner integrals in braces are differentiated in (6) and (7) with respect to p . Finally the differential heat Q^{diff} can be expressed as

$$Q^{\text{diff}} = \frac{\int_{Q_1}^{Q_2} Q_{ii}^{\text{diff}} (\partial\theta_{ii}/\partial p)_T \delta(Q) dQ}{\int_{Q_1}^{Q_2} (\partial\theta_{ii}/\partial p)_T \delta(Q) dQ} \quad (12)$$

The integral in the denominator is nothing but the pressure derivative of the mean surface coverage which can be measured from experimental isotherms.

It remains to be shown that the relationships given by (12) and (4) are identical. It is easily shown that since adsorption equilibrium prevails between each of the surface patches and the gas phase, if the Clausius–Clapeyron equation is ap-

plied to the individual patch, we have

$$-\frac{1}{p}(\partial\theta_{li}/\partial T)_p = Q_{li}^{diff}(\partial\theta_{li}/\partial p)_T/RT^2. \quad (13)$$

Using (13) in (12) we find that (12) and (4) are indeed identical. Therefore (12) offers us a way to calculate the thermodynamic differential heat through the measurements of pressure derivative at constant temperature.

However, using (12) presupposes a knowledge of $\theta_{li}(T, p)$, $\delta(Q)$ and hence the quality of thermodynamic description inherent in (2) is lost. However by measuring the pressure derivatives and a study of the adsorption integral equation $\theta_{li}(T, p)$, $\delta(Q)$ can be fixed^{5, 6} and (12) furnishes a way to compute the differential heat for comparison with experiment, and to check the validity of assuming $\theta_{li}(T, p)$, $\delta(Q)$ *a-priori*.

Mention may be made of the numerical methods employed in the computation of the differential heat. Since the local isotherm has an implicit dependence on pressure, a numerical method involving Mueller's iteration (supplied as a library package RTMI) was used to solve for θ_{li} as a function of pressure and the heat of adsorption. The integrals involved in (12) were computed using 8 point Gauss-Legendre quadrature with variable division of the integration interval, to reach a desired accuracy (IE-7 in the present case) for Q^{diff} . The corresponding values agreed with those computed using a Romberg⁸ (QATR, library package) procedure within the desired accuracy.

However, the Gauss-Legendre method is considerably faster than the Romberg procedure.

First we consider localized adsorption with interactions, for modelling which the well-known Fowler-Guggenheim isotherm denoted henceforth as (FG)⁹ is employed. One could, in principle, use more refined models like the quasi-chemical approximation model¹⁰. But since the main objective is to illustrate the pressure derivative method of computing the thermodynamic differential heat, only the first order model like FG (with both attractive and repulsive) is chosen in the present work.

For treating the mobile adsorption, an isotherm analogous to the Hill-de Boer model (denoted as HD)¹¹ is employed. The interaction parameter A which appears in the model (see table 1) has however a higher value than due to interactions of the van der Waals' type alone. In other words, the single parameter A (see table 1) accounts for both through bond and through space interactions lumped together^{4, 12, 13}. Detailed classification of the nature of the interaction forces can be found elsewhere^{12, 13}.

For dealing with surface heterogeneity three popular site energy distributions are used, *viz* the negative exponential distribution^{3, 4}, positive exponential¹⁴ and the constant distribution^{4, 14}. The differential heat can be computed as a statistical average using (12).

A reference to table 1 clearly shows that the difference between the mobile and localized

Table 1 Site Energy Distributions, Isotherms and Pressure Derivatives

Positive Exponential $\delta(Q) = C_p \exp(Q/Q_M)$	Negative Exponential $\delta(Q) = C_N \exp(-Q/Q_M)$	Constant $\delta(Q) = 1/(Q_2 - Q_1)$
Fowler-Guggenheim	Local Isotherm $p = \left(\frac{\theta_{li}}{1-\theta_{li}}\right) b_0^l \exp(-Q/RT) \exp\left(\frac{A\theta_{li}}{RT}\right)$	Pressure derivative $\frac{d\theta_{li}}{dp} = \left[\frac{A\theta_{li}(1-\theta_{li}) + RT}{RT\theta_{li}(1-\theta_{li})}\right]^{-1} p^{-1}$
Hill de Boer	$p = \left(\frac{\theta_{li}}{1-\theta_{li}}\right) b_0^m \exp(-Q/RT) \times \exp\left(\frac{A\theta_{li}}{RT}\right) \exp\left[\frac{\theta_{li}}{(1-\theta_{li})}\right]$	$\frac{d\theta_{li}}{dp} = p^{-1} \left[\frac{A\theta_{li}(1-\theta_{li}) + RT}{RT\theta_{li}(1-\theta_{li})} + \frac{1}{(1-\theta_{li})^2}\right]^{-1}$

$Q_1 = 17$ kcal/mol, $Q_2 = 31$ kcal/mol, $Q_M = 2$ kcal/mol, b_0^l (localized model) = 1E8 torr b_0^m (mobile model) = 1E5, $C_p = 1/\{Q_M[\exp(Q_2/Q_M) - \exp(Q_1/Q_M)]\}$, $C_N = 1/\{Q_M[\exp(-Q_1/Q_M) - \exp(-Q_2/Q_M)]\}$

moles is readily seen in the $1/(1-\theta_{11})^2$ term within the square brackets for the mobile model

$$(\partial\theta_{11}/\partial p)_T^l = [1/\theta_{11}(1-\theta_{11}) + A/RT]^{-1} p^{-1}, \quad (14)$$

$$(\partial\theta_{11}/\partial p)_T^m = [1/\theta_{11}(1-\theta_{11}) + A/RT + 1/(1-\theta_{11})^2]^{-1} p^{-1}. \quad (15)$$

In the low coverage (pressure) region where both FG and HD isotherms reduce to Henry's law, the pressure derivatives will be inversely proportional to the entropy change factor b_0 . Since the latter isotherm has a lower value of b_0^4 , we would expect the pressure derivative ratio to be roughly equal to the ratio of b_0^l/b_0^m .

On the other hand in the high coverage region the influence of the $(1-\theta_{11})^{-2}$ term can be quite significant and therefore the mobile isotherm would predict a lower value for the pressure derivative.

RESULTS AND DISCUSSION

In figure 1 the differential heat is plotted as a function of $\log(p)$ for the case of localized adsorption. The qualitative difference between

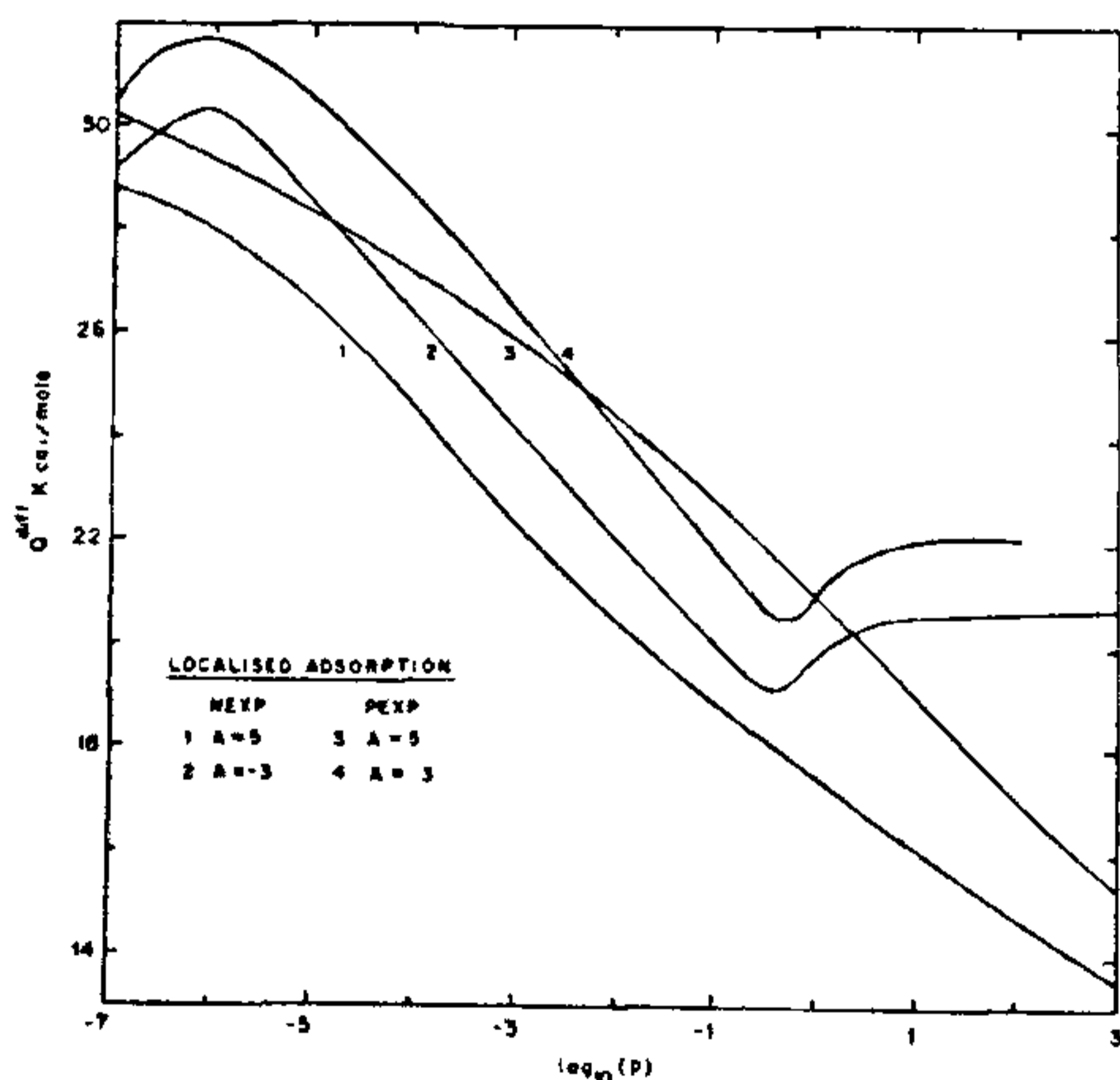


Figure 1. Plots of differential heat vs pressure for two distributions. Curves 1, 2 and 3, 4 denote repulsive and attractive interactions respectively for the positive and negative exponential distributions.

the operation of attractive and repulsive forces is clearly seen in the absence of maxima in the low and high coverage region, for the repulsive model. Besides, since surface heterogeneity and interaction forces are acting in collusion, the differential heat values are lower for the repulsive case.

The maxima observed in the presence of attractive forces can be clearly understood. At low pressure the high energy sites are populated where the local surface coverage can be very high. Hence with an increase in the pressure, the cooperative attractive interaction among the adsorbed molecules causes the differential heat to increase with surface coverage. On further increasing the pressure, lower energy sites are filled where the local surface coverage may be low and the contribution of the interaction forces to the differential heat is negligible. Since the differential heat reflects the adsorption energy of the patch which is newly occupied, surface heterogeneity is manifested by a progressive fall in the differential heat.

In the high pressure region almost all the patches have appreciable surface coverage. The rise of the differential heat with a further increase in pressure, can therefore be understood, as a result of the attractive interactions. Since there are no further low energy sites to be newly filled the fall in the differential heat due to the surface heterogeneity alone is negligible in the high coverage region. This can clearly be demonstrated if we put the interaction energy parameter equal to zero. However the cooperative interaction among adsorbed molecules can now give rise to a perceptible increase in the differential heat.

In accounting for the interaction forces we have chosen $A = 5$ for repulsive forces and $A = -3$ for attractive forces. An added complication that one can observe for larger values of the attractive interaction parameter is that there can be phase transitions in the adsorbed layer and hence there will be two values for the surface coverage (if two phases coexist) at a given pressure or there can be discontinuity in the heat of adsorption. However, for the values of the attractive interaction parameter chosen, this is not

possible at high temperatures where $RT \cong 1$ kcal/mol.

The positive exponential distribution predicts the largest value of the differential heat both for attractive and repulsive FG models. The negative exponential distribution predicts the lowest heat, with constant distribution displaying intermediate values. The differential heat values of these distributions follow the order of the mean heat of adsorption. Also the pressure derivatives obey the following order: positive exponential > constant > negative exponential. This is obvious as the pressure derivative increases monotonically with the energy of adsorption and for the positive exponential distribution the highest energy sites are weighted most.

In figure 2 we plot differential heat as a function of $\log \theta$ for both attractive, repulsive models. The qualitative differences between these distributions are once again obvious for comparable ranges of pressure. There is a narrow region of pressure wherein the surface coverage rises rather fast for the positive exponential distribution. When attractive forces are operative, for the positive exponential distribution also

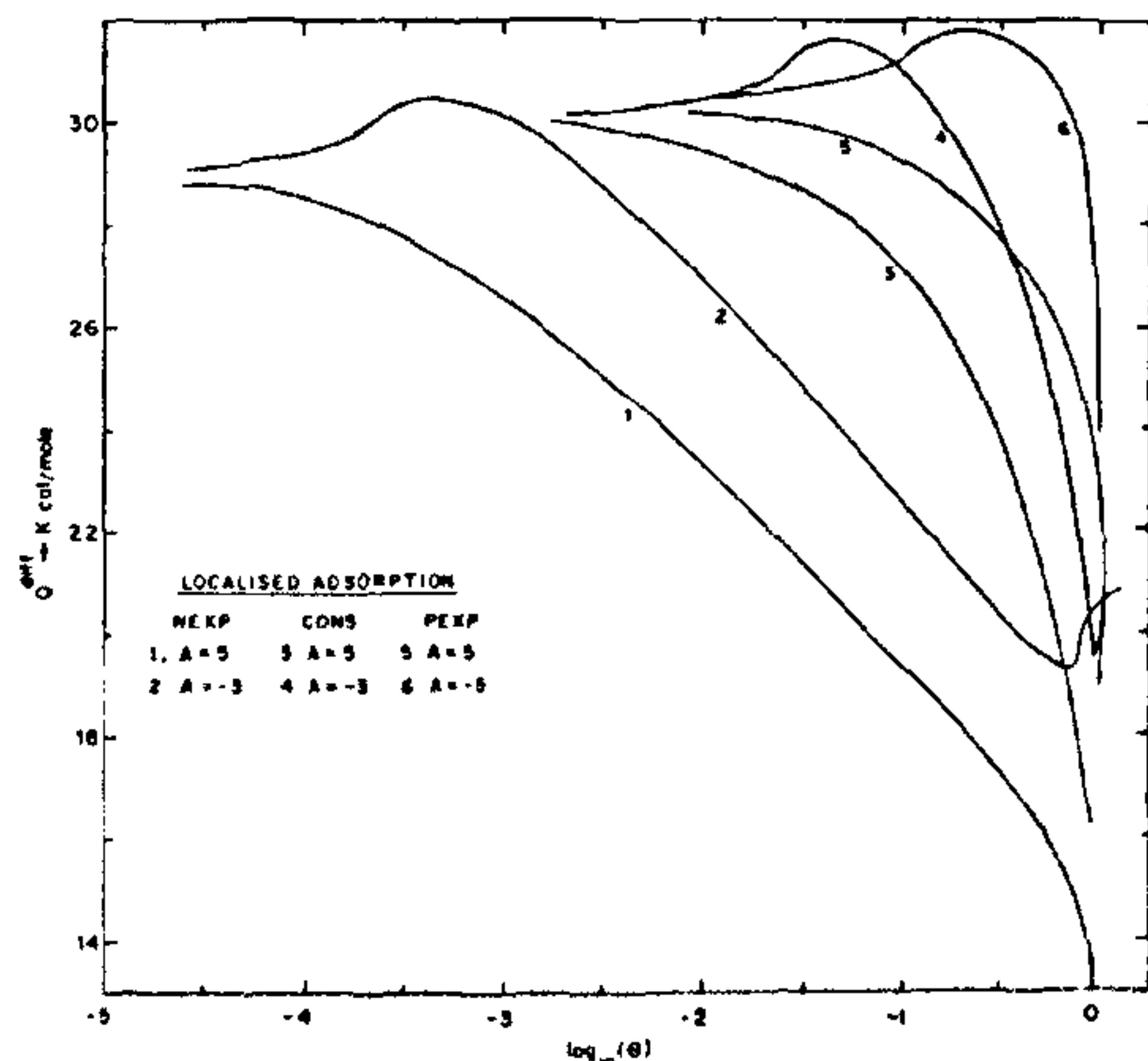


Figure 2. Plots of differential heat vs $\log(\theta)$ for three distributions: Negative exponential (1, 2) constant (3, 4) and positive exponential distribution (5, 6). A = 5, A = -3 denote repulsive and attractive interactions respectively.

the differential heat rises in the high coverage region, but for clarity this is not shown in the figure.

The mean surface coverage corresponding to the maxima, varies for these three distributions and they obey the following order: negative exponential < constant < positive exponential. Besides the separation between the differential heat curves are more apparent on a Q^{diff} vs $\log(\theta)$ plot than on a Q^{diff} vs $\log(p)$ plot. All the distributions predict a very steep fall in differential heat in the high coverage region, when repulsive forces are operative and the slope of the repulsive model is much higher than that of the attractive model.

We now analyze the mobile models. In the previous section it has been mentioned that the pressure derivative for the mobile model is considerably larger than that of the localized model for low pressures. Besides the fall of the differential heat is much smaller compared to the localized model as seen from figure 3.

Since mobile model predicts a higher surface coverage in comparison to the localized model, we investigate the differential heat behaviour starting with a lower pressure (1E-9 torr in the present study). Besides the small maxima observed with localized models, is not present for

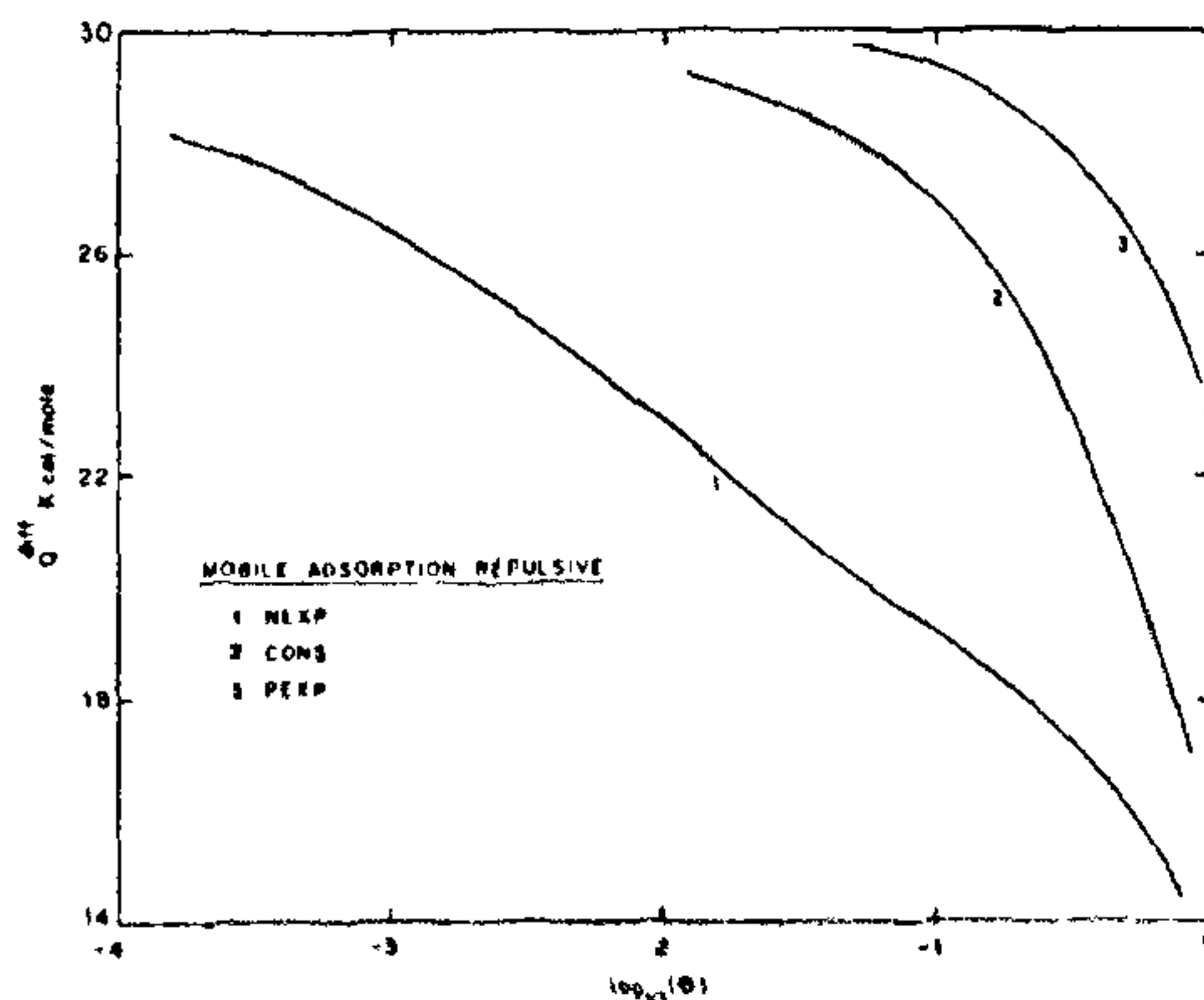


Figure 3. Plots of differential heat vs $\log(\theta)$ for mobile adsorption with repulsive interactions. Curves 1, 2, 3 denote negative exponential, constant and positive exponential respectively.

the range of pressures studied. A simple explanation would be that since the pressure derivatives are much larger in comparison with the localized models, the rate of filling of newer (low energy sites) sites is much larger than that of the localized models. Hence the consequent fall of the differential heat, more than off sets the increase due to the cooperative attractive interactions.

It may be noted that if the effects of surface heterogeneity would have been absent *i.e.* the site energy distribution is a Dirac delta-function centred around Q (which is the heat of an ideal uniform surface) then both the mobile and localized models would predict the same linear fall or rise with the surface coverage. The slope will be given by the interaction parameter A . A , by convention, is positive for repulsive forces and negative for attractive forces. However, since the surface coverage for the mobile model is higher in comparison to the localized models, the differential heat at any pressure will be smaller for the mobile model.

When the site-energy distribution weights the local surface coverage, a different situation can arise in which the slope can change, even in sign, both for the mobile and localized models. This is especially true when the attractive forces are acting in opposition to the effects due to surface heterogeneity.

For clarity, the attractive and repulsive models are plotted separately in figures 3 and 4. When repulsive forces are operative, the greatest fall in the differential heat is in the high coverage region. Compared to the localized models, the fall in the differential heat is much less for the mobile models, for comparative values of pressure. Besides the maxima are almost non-existent at low pressure.

The positive exponential distribution predicts the highest differential heat and the lowest fall. The trend is exactly opposite for the negative exponential. However, the central feature to note is that while the nature of the local isotherm is reflected to a large extent in the differential heat behaviour, it is obvious that the local isotherm does not mask the qualitative differences between the distributions.

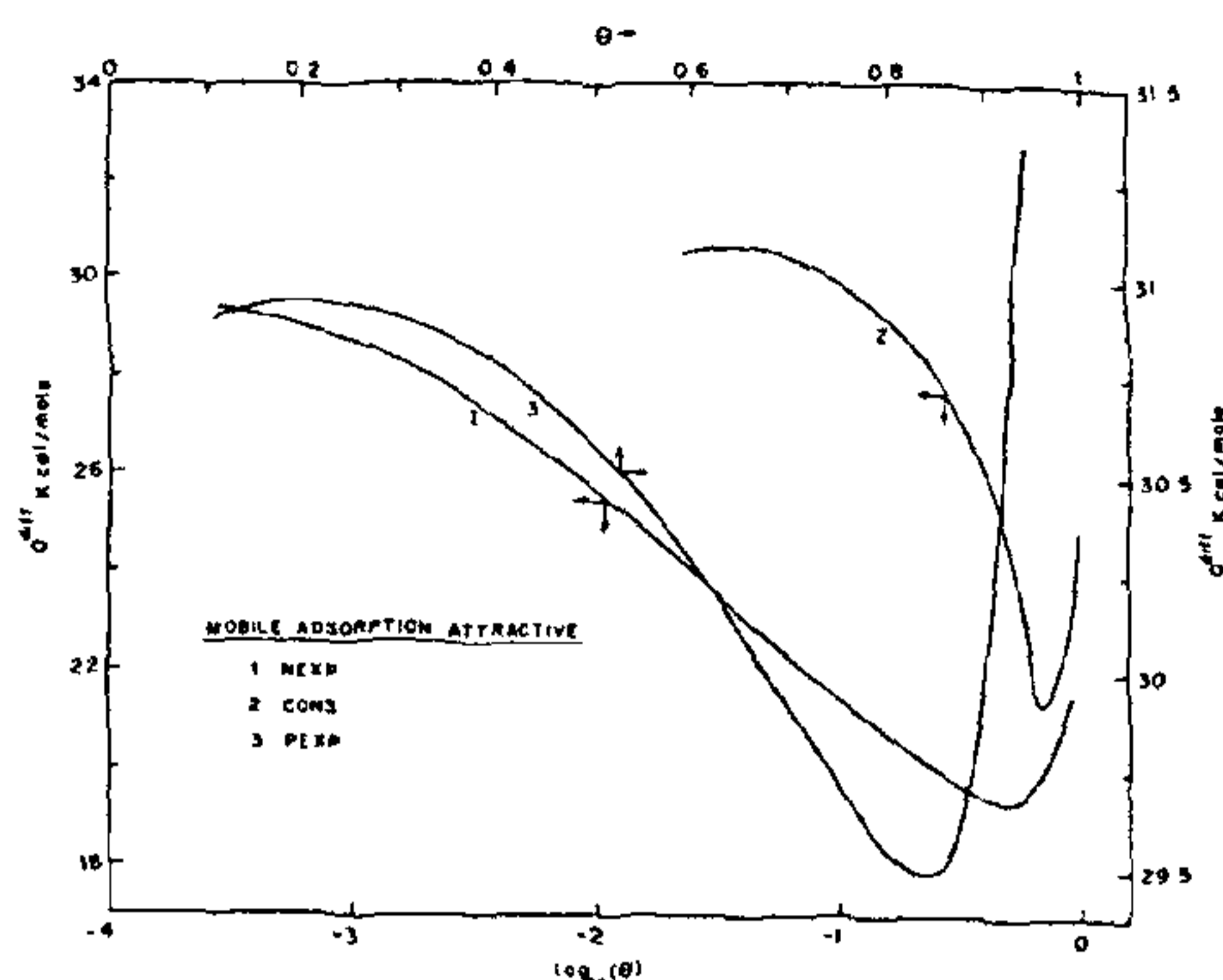


Figure 4. Plots of differential heat vs $\log \theta$ for mobile adsorption with attractive interactions. 1, 2, 3 represent the three distributions as in figure 3.

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