



Fig. 16 BET up (adsorption) and down (desorption) moisture isotherm.

ΔG is negative in going from the down curve to the up curve, because

$$\Delta G = V \int_{P_u}^{P_d} V dP = V[P_u - P_d] < 0 \quad (8.22)$$

Several common tablet excipients give rise to Langmuir isotherms. An excipient study by Sangvekar (1974), when all the data are lumped together, gives an equation of the type

$$\frac{1}{y} = \frac{A}{P} + B \quad (8.23)$$

Usually, in pharmaceutical and engineering literature, the moisture equilibrium curves are shown in a sense opposite to that shown in Fig. 15, i.e.,

$$P = \phi(y) \quad (8.24)$$

The high RH tail of the curve is usually above 85% RH and therefore does not apply to most realistic pharmaceutical conditions, but it is applicable to one often-conducted test (40°C, 75%RH). Zografi and Kotny (1986) have described these types of moisture isotherms by either a BET equation or a GAB equation.

For routine isotherms, the high relative humidity tail is difficult to obtain with reasonable precision, and one approach (Carstensen, 1980) is to approximate them by Langmuir isotherms (i.e., not use the high-end portion).

9. AMORPHATES

Solids which are not crystalline are denoted amorphous. If one melts a (stable) solid and recools it, then it should crystallize when the melting point is arrived at.

This requires nucleation, and nucleation propensity is a function of the viscosity of the liquid in which it occurs. Materials that are viscous about their melting point are therefore prone to form supercooled solutions.