Exact and Inexact Differentials

Chem 345

One issue in thermodynamics concerns whether the total differential (eq 1) of a multivariable function ($F = F(x, y)$ represents any two-variable function) is exact or inexact.

$$dF = \left(\frac{\partial F}{\partial x}\right)_y dx + \left(\frac{\partial F}{\partial y}\right)_x dy \tag{1}$$

If dF is an **exact differential**, $\int_i^f dF$ will be the same for all paths between the initial (x_i, y_i) and final (x_f, y_f) points, and the integral will be simply $\int_i^f dF = F_f - F_i$. Thermodynamic state functions, like U and H, should have exact differentials.

If dF is an **inexact differential**, $\int_i^f dF$ will depend on which path is used between the initial (x_i, y_i) and final (x_f, y_f) points. Functions with inexact differentials cannot be treated as thermodynamic state functions.

Determining Whether a Differential is Exact

The relationship shown in eq 2 must hold if a differential like the one in eq 1 is exact. In essence, eq 2 states that the sensitivity in the y direction of the slope in the x direction equals the sensitivity in the x direction of the slope in the y direction.

$$\frac{\partial}{\partial y}\left(\frac{\partial F}{\partial x}\right) = \frac{\partial}{\partial x}\left(\frac{\partial F}{\partial y}\right) \tag{2}$$

The differential in eq 3 is an example of an **exact** differential, as is demonstrated in eq 4.

$$dg = (x^2 + y^2)dx + (2xy)dy \tag{3}$$

$$\frac{\partial g}{\partial x} = x^2 + y^2, \quad \frac{\partial}{\partial y}\left(\frac{\partial g}{\partial x}\right) = 2y \qquad \frac{\partial g}{\partial y} = 2xy, \quad \frac{\partial}{\partial x}\left(\frac{\partial g}{\partial y}\right) = 2y \tag{4}$$

The differential in eq 5 is an example of an **inexact** differential, as is demonstrated in eq 6.

$$dh = (x^2 + y^2)dx - (2xy)dy \tag{5}$$

$$\frac{\partial h}{\partial x} = x^2 + y^2, \quad \frac{\partial}{\partial y}\left(\frac{\partial h}{\partial x}\right) = 2y \qquad \frac{\partial h}{\partial y} = -2xy, \quad \frac{\partial}{\partial x}\left(\frac{\partial h}{\partial y}\right) = -2y \tag{6}$$

Check: Integrate dg and dh Over Two Paths

We can compare actual integrations over different paths for the differentials in eqs 3 and 5. Two stepwise paths, A and B, are defined below. Note that for both paths, the inital (x, y) is $(0, 0)$ and the final point is $(3, 1)$.

Path A	step 1	$x = 0 \to 3$	$y = 0 \quad (dy = 0)$
	step 2	$x = 3 \quad (dx = 0)$	$y = 0 \to 1$
Path B	step 1	$x = 0 \to 4$	$y = 0 \quad (dy = 0)$
	step 2	$x = 4 \quad (dx = 0)$	$y = 0 \to 1$
	step 3	$x = 4 \to 3$	$y = 1 \quad (dy = 0)$

$\int$ dg Path A: Sum over two steps, $\mathbf{g = 9 + 3 = 12}$

1. $x = 0 \to 3, y = 0$ $\int dg = \int_0^3 (x^2 + 0)dx + 0 = \frac{1}{3}x^3]_0^3 = 9 - 0 = \mathbf{9}$
2. $x = 3, y = 0 \to 1$ $\int dg = \int_0^1 0 + 6ydy = 3y^2]_0^1 = 3 - 0 = \mathbf{3}$

$\int$ dg Path B: Sum over three steps, $\mathbf{g = \frac{64}{3} + 4 - \frac{40}{3} = 12}$

1. $x = 0 \to 4, y = 0$ $\int dg = \int_0^4 (x^2 + 0)dx + 0 = \frac{1}{3}x^3]_0^4 = \frac{64}{3} - 0 = \mathbf{\frac{64}{3}}$
2. $x = 4, y = 0 \to 1$ $\int dg = \int_0^1 0 + 8ydy = 4y^2]_0^1 = 4 - 0 = \mathbf{4}$
3. $x = 4 \to 3, y = 1$ $\int dg = \int_4^3 (x^2 + 1)dx = \frac{1}{3}x^3 + x]_4^3 = 12 - (4 + \frac{64}{3}) = -\mathbf{\frac{40}{3}}$

$\int dg$ is path independent

$\int$ dh Path A: Sum over two steps, $\mathbf{h = 9 - 3 = 3}$

1. $x = 0 \to 3, y = 0$ $\int dh = \int_0^3 (x^2 + 0)dx + 0 = \frac{1}{3}x^3]_0^3 = 9 - 0 = \mathbf{9}$
2. $x = 3, y = 0 \to 1$ $\int dh = \int_0^1 0 - 6ydy = 3y^2]_0^1 = -3 - 0 = -\mathbf{3}$

$\int$ dh Path B: Sum over three steps, $\mathbf{h = \frac{64}{3} - 4 - \frac{40}{3} = 4}$

1. $x = 0 \to 4, y = 0$ $\int dh = \int_0^4 (x^2 + 0)dx + 0 = \frac{1}{3}x^3]_0^4 = \frac{64}{3} - 0 = \mathbf{\frac{64}{3}}$
2. $x = 4, y = 0 \to 1$ $\int dh = \int_0^1 0 - 8ydy = -4y^2]_0^1 = -4 - 0 = -\mathbf{4}$
3. $x = 4 \to 3, y = 1$ $\int dh = \int_4^3 (x^2 + 1)dx = \frac{1}{3}x^3 + x]_4^3 = 12 - (4 + \frac{64}{3}) = -\mathbf{\frac{40}{3}}$

$\int dh$ depends on the integration path

Examine dV_m for a Perfect Gas

The perfect gas law provides an equation $V_m = \frac{RT}{p}$. The total differential in terms of the variables T and p is therefore,

$$dV_m = \left(\frac{\partial V_m}{\partial p}\right) dp + \left(\frac{\partial V_m}{\partial T}\right) dT = \left(\frac{-RT}{p^2}\right) dT + \left(\frac{R}{p}\right) dT \tag{7}$$

Now apply the test to learn whether the differential is exact or inexact.

$$\frac{\partial}{\partial T}\left(\frac{\partial V_m}{\partial p}\right) = \frac{\partial}{\partial T}\left(\frac{-RT}{p^2}\right) = \frac{-R}{p^2} \tag{8}$$

$$\frac{\partial}{\partial p}\left(\frac{\partial V_m}{\partial T}\right) = \frac{\partial}{\partial p}\left(\frac{R}{p}\right) = \frac{-R}{p^2} \tag{9}$$

Since eq 8 and eq 9 give the same result, dV_m is an exact differential, and $\int_i^f dV_m = V_f - V_i$.