Differentiation VI

Partial differentiation

18

Answers to additional problems

18.1 Total differential

$$dV = \left(\frac{\partial V}{\partial T}\right) dT + \left(\frac{\partial V}{\partial p}\right) dp + \left(\frac{\partial V}{\partial n}\right) dn$$

Equation from the question

$$dV = \alpha V \, dT - \kappa V \, dp + V_m \, dn$$

1	2	3	4	5	6	7
dV	$=$	$\left(\frac{\partial V}{\partial T}\right)$ / αV	dT	$+\left(\frac{\partial V}{\partial p}\right)$ / $-\kappa V$	dp	...

Comparing the **2** terms $\alpha V = \left(\frac{\partial V}{\partial T}\right)$ thermal expansivity $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)$

Comparing the **4** terms $-\kappa V = \left(\frac{\partial V}{\partial p}\right)$ isothermal compressibility, $\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)$

Comparing the **6** terms $V_m = \left(\frac{\partial V}{\partial n}\right)$ molar volume

- In this example subscripts have been omitted to enhance clarity.

18.2 Inserting terms into the template expression in eqn. (18.4) yields,

$$dE = \left(\frac{\partial E}{\partial V}\right)_{I,t} dV + \left(\frac{\partial E}{\partial I}\right)_{V,t} dI + \left(\frac{\partial E}{\partial t}\right)_{V,I} dt$$

18.3 From Worked Example 18.6, $\left(\frac{\partial G}{\partial p}\right)_T = V$ and $\left(\frac{\partial G}{\partial T}\right)_p = -S$

We differentiate the first expression by T $\left(\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial p}\right)_T\right)_p = \left(\frac{\partial V}{\partial T}\right)_p$

We differentiate the second expression by T $\left(\frac{\partial}{\partial p}\left(\frac{\partial G}{\partial T}\right)_p\right)_T = -\left(\frac{\partial S}{\partial p}\right)_T$

Euler reciprocity lets us equate these two equations $\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T$

18.4 Differentiating the equation with respect to T at constant volume, V,

$$\left(\frac{\partial H}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial p}{\partial T}\right)_V V$$

The $\partial U/\partial T$ term is the heat capacity at constant volume C_V. The equation becomes,

$$\left(\frac{\partial H}{\partial T}\right)_V = C_V + \left(\frac{\partial p}{\partial T}\right)_V V.$$

We can go further and say the derivative $(\partial p/\partial T)_V$ is the ratio of thermal expansivity α and isothermal compressibility κ (see Self test 18.4.1).

$$\text{Therefore, } \left(\frac{\partial H}{\partial T}\right)_V = C_V + \left(\frac{\alpha}{\kappa}\right)V$$

18.5 We start by multiplying the Clausius equality by 1 from the 'dodge' $1 = (\partial T/\partial T)$,

$$\mathrm{d}S = \frac{\mathrm{d}q}{T} \times \frac{\partial T}{\partial T}$$

We can safely substitute H for q if we do no expansion work. We then rearrange slightly,

$$\mathrm{d}S = \left(\frac{\partial H}{\partial T}\right) \times \frac{1}{T}\mathrm{d}T$$

where the term in brackets is simply C_p.
We therefore obtain the desired equation, $\mathrm{d}S = C_p/T\,\mathrm{d}T$.

18.6 **Strategy**

1. We rearrange the van der Waals equation to make T the subject.
2. We differentiate T with respect to V as, $(\partial T/\partial V)_n$.
3. We then differentiate this function with respect to p calling it $(\partial^2 T/\partial p\partial V)_n$.
4. We differentiate T with respect to p as $(\partial T/\partial p)_{n.}$
5. We then differentiate this function with respect to V calling it $(\partial^2 p/\partial V\partial p)$.
6. We compare the two results in parts 3 and 5.

Solution

1. $T = \dfrac{1}{nR}(p + an^2V^{-2})(V - nb)$
2. $\dfrac{\partial T}{\partial V} = \dfrac{1}{nR}\left(\left(p + \dfrac{an^2}{V^2}\right) \times 1 + (V - nb) \times -\dfrac{2an^2}{V^3}\right)$
3. $\dfrac{\partial^2 T}{\partial p\partial V} = \dfrac{1}{nR}$ Because the only term which includes p is $\dfrac{1}{nR} \times p$
4. $\dfrac{\partial T}{\partial p} = \dfrac{1}{nR}(V - nb)$
5. $\dfrac{\partial^2 T}{\partial V\partial p} = \dfrac{1}{nR}$
6. The answers in parts 3 and 5 are clearly the same.

18.7

$$\left(\frac{\partial U}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial U}{\partial V}\right)_T \mathrm{d}V = T\left(\left(\frac{\partial S}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial S}{\partial V}\right)_T \mathrm{d}V\right) - p\mathrm{d}V$$

Total differential of dU Total differential of dS

We then simplify by saying $\mathrm{d}V = 0$. Therefore,

$$\left(\frac{\partial U}{\partial T}\right)_V \mathrm{d}T = T\left(\frac{\partial S}{\partial T}\right)_V \mathrm{d}T$$

Dividing both sides by dT yields, $\left(\dfrac{\partial U}{\partial T}\right)_V = C_V = T\left(\dfrac{\partial S}{\partial T}\right)_V$

18.8 1. $\dfrac{\partial I}{\partial c} = \dfrac{0.62\,nFA\,D^{2/3}\omega^{1/2}}{\sqrt[6]{\upsilon}}$

$$\frac{\partial^2 I}{\partial\omega\partial c} = \frac{1}{2} \times \frac{0.62\,nFA\,D^{2/3}\omega^{-1/2}}{\sqrt[6]{\upsilon}} = \frac{0.62\,nFA\,D^{2/3}}{2\sqrt{\omega}\,\sqrt[6]{\upsilon}}$$

so $\dfrac{\partial^2 I}{\partial\omega\partial c} = \dfrac{0.31\,nFA\,D^{2/3}}{\sqrt{\omega}\,\sqrt[6]{\upsilon}}$

2. $$\frac{\partial I}{\partial \omega} = \frac{1}{2} \times \frac{0.62\,nFAc\,D^{2/3}\omega^{-1/2}}{\sqrt[6]{\upsilon}} = \frac{0.62\,nFAc\,D^{2/3}}{2\sqrt{\omega}\,\sqrt[6]{\upsilon}}$$

so $$\frac{\partial^2 I}{\partial c \partial \omega} = \frac{0.31\,nFA\,D^{2/3}}{\sqrt{\omega}\,\sqrt[6]{\upsilon}}$$

We see how, $\dfrac{\partial^2 I}{\partial c \partial \omega} = \dfrac{\partial^2 I}{\partial \omega \partial c}$

18.9 We note how the exponential's argument $i\phi$ is complex as defined in Chapter 25.

Next, we calculate the individual derivatives found in the expression for Λ^2,

$$\frac{\partial \psi}{\partial \theta} = N\cos\theta\, e^{i\phi} \quad \frac{\partial^2 \psi}{\partial \theta^2} = -N\sin\theta\, e^{i\phi}$$

$$\frac{\partial \psi}{\partial \phi} = iN\sin\theta\, e^{i\phi} \quad \frac{\partial^2 \psi}{\partial \phi^2} = i^2 N\sin\theta\, e^{i\phi} = -N\sin\theta\, e^{i\phi}$$

We then substitute for these values,

$$\Lambda^2\psi = \frac{\partial^2 \psi}{\partial \theta^2} + \frac{\cos\theta}{\sin\theta}\frac{\partial \psi}{\partial \theta} + \frac{1}{\sin^2\theta}\frac{\partial^2 \psi}{\partial \phi^2}$$

$$\Lambda^2\psi = -N\sin\theta\, e^{i\phi} + \frac{\cos\theta}{\sin\theta} \times N\cos\theta\, e^{i\phi} + \frac{1}{\sin^2\theta} \times -N\sin\theta\, e^{i\phi}$$

$$\Lambda^2\psi = \frac{Ne^{i\phi}}{\sin\theta}(-\sin^2\theta + \cos^2\theta - 1)$$

Simplifying this expression and using the trigonometric identity, $\sin^2\theta + \cos^2\theta = 1$ (see Chapter 11),

$$\Lambda^2\psi = \frac{Ne^{i\phi}}{\sin\theta}(-\sin^2\theta + \cos^2\theta - (\sin^2\theta + \cos^2\theta))$$

which simplifies to give us,

$$\Lambda^2\psi = \frac{-2N\sin^2\theta\, e^{i\phi}}{\sin\theta} = -2N\sin\theta\, e^{i\phi}$$

We can write this last expression as, $\Lambda^2\psi = -2\psi = -l \times (l+1)\,\psi$.

Therefore, the wavefunction is indeed a spherical harmonic with $l = 1$ (it is actually $Y_{l,m_l} = Y_{1,1}$).

18.10 As in Additional Problem 18.9, we first note that the argument of the exponential $i\phi$ is complex as defined in Chapter 25.

We calculate the individual derivatives found in the expression for Λ^2,

$$\frac{\partial \psi}{\partial \theta} = (\cos^2\theta - \sin^2\theta)\, Ne^{i\phi}$$

$$\frac{\partial^2 \psi}{\partial \theta^2} = (-2\sin\theta\cos\theta - 2\cos\theta\sin\theta)\, Ne^{i\phi} = -4\sin\theta\cos\theta\, Ne^{i\phi}$$

$$\frac{\partial \psi}{\partial \phi} = i\,N\sin\theta\cos\theta\, e^{i\phi}$$

$$\frac{\partial^2 \psi}{\partial \phi^2} = i^2 N\sin\theta\cos\theta\, e^{i\phi} = -N\sin\theta\cos\theta\, e^{i\phi}$$

then, we substitute for these values,

$$\Lambda^2\psi = \frac{\partial^2\psi}{\partial\theta^2} + \frac{\cos\theta}{\sin\theta}\frac{\partial\psi}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}$$

$$\Lambda^2\psi = -4\sin\theta\cos\theta N e^{i\phi} + \frac{\cos\theta}{\sin\theta}\times\left(\cos^2\theta - \sin^2\theta\right)N e^{i\phi} + \frac{1}{\sin^2\theta}\times -N\sin\theta\cos\theta e^{i\phi}$$

Simplifying this expression gives,

$$\Lambda^2\psi = \frac{N\cos\theta e^{i\phi}}{\sin\theta}(-4\sin^2\theta + \cos^2\theta - \sin^2\theta - 1)$$

Using the trigonometric identity, $\sin^2\theta + \cos^2\theta = 1$ (see Chapter 11),

$$\Lambda^2\psi = \frac{N\cos\theta e^{i\phi}}{\sin\theta}(-5\sin^2\theta + \cos^2\theta - (\sin^2\theta + \cos^2\theta))$$

which simplifies to,

$$\Lambda^2\psi = \frac{-6N\sin^2\theta\cos\theta e^{i\phi}}{\sin\theta} = -6N\sin\theta\cos\theta e^{i\phi}$$

This can be written as, $\Lambda^2\psi = -6\psi = -2\times(2+1)\psi$.

The wavefunction is therefore a spherical harmonic with $l = 2$. (It is actually $Y_{l,m_l} = Y_{2,1}$.)

An alternative approach would have us use some of the trigonometric relationships found in Chapter 11. We notice that, $\psi = \frac{N}{2}\sin 2\theta e^{i\phi}$,

$$\frac{\partial\psi}{\partial\theta} = N\cos 2\theta e^{i\phi} = 2\frac{\cos 2\theta}{\sin 2\theta}\psi$$

$$\frac{\partial^2\psi}{\partial\theta^2} = -2N\sin 2\theta e^{i\phi} = -4\psi$$

$$\frac{\partial^2\psi}{\partial\phi^2} = i^2\frac{N}{2}\sin 2\theta\, e^{i\phi} = -\psi$$

then, we substitute for these values,

$$\Lambda^2\psi = -4\psi + 2\frac{\cos\theta}{\sin\theta}\frac{\cos 2\theta}{\sin 2\theta}\psi + \frac{1}{\sin^2\theta}\times -\psi$$

Substituting for $\sin 2\theta$ and $\cos 2\theta$ gives,

$$\Lambda^2\psi = \psi\left(-4 + \frac{2\cos\theta(2\cos^2\theta - 1)}{2\sin^2\theta\cos\theta} - \frac{1}{\sin^2\theta}\right)$$

which we can simplify further as,

$$\Lambda^2\psi = \frac{\psi}{\sin^2\theta}(-4\sin^2\theta + 2\cos^2\theta - 2)$$

Using the trigonometric identity, $\sin^2\theta + \cos^2\theta = 1$,

$$\Lambda^2\psi = \frac{\psi}{\sin^2\theta}(-4\sin^2\theta + 2\cos^2\theta - 2(\sin^2\theta + \cos^2))$$

which simplifies to $\quad \Lambda^2\psi = \frac{\psi}{\sin^2\theta}\times -6\sin^2\theta$

and hence, $\quad \Lambda^2\psi = -6\psi$