

13.4: The TdS Equations

The three TdS equations have been known to generations of students as the “tedious equations” – though they are not at all tedious to a true lover of thermodynamics, because, among other things, they *enable us to calculate the change of entropy* during various reversible processes in terms of either dV and dT , or dP and dT , or dV and dP , and even in terms of directly measurable quantities such as the coefficient of expansion and the bulk modulus.

i.) We can express entropy in terms of any two of PVT . Let us first express entropy as a function of V and T

$$dS = \left(\frac{\partial S}{\partial V} \right)_T dV + \left(\frac{\partial S}{\partial T} \right)_V dT. \quad (13.4.1)$$

Therefore

$$TdS = T \left(\frac{\partial S}{\partial V} \right)_T dV + T \left(\frac{\partial S}{\partial T} \right)_V dT. \quad (13.4.2)$$

From a Maxwell relation (equation 12.6.15), $\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V$. Also, in a constant volume process, $TdS = dU$ so that $T \left(\frac{\partial S}{\partial T} \right)_V = \left(\frac{\partial U}{\partial T} \right)_V = C_V$.

Therefore $TdS = T \left(\frac{\partial P}{\partial T} \right)_V dV + C_V dT$.

This is the first of the TdS equations.

ii.) This time, let us express entropy as a function of P and T

$$dS = \left(\frac{\partial S}{\partial P} \right)_T dP + \left(\frac{\partial S}{\partial T} \right)_P dT. \quad (13.4.3)$$

Therefore

$$TdS = T \left(\frac{\partial S}{\partial P} \right)_T dP + T \left(\frac{\partial S}{\partial T} \right)_P dT. \quad (13.4.4)$$

From a Maxwell relation (equation 12.6.16), $\left(\frac{\partial S}{\partial P} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_P$. Also, in a constant pressure process, $TdS = dH$ so that $T \left(\frac{\partial S}{\partial T} \right)_P = \left(\frac{\partial H}{\partial T} \right)_P = C_P$.

Therefore

$$TdS = -T \left(\frac{\partial V}{\partial T} \right)_P dP + C_P dT. \quad (13.4.5)$$

This is the second of the TdS equations.

iii.) If we express entropy as a function of P and V (recall that we can choose to express a function of state as a function of any two of P , V or T) we have

$$dS = \left(\frac{\partial S}{\partial P} \right)_V dP + \left(\frac{\partial S}{\partial V} \right)_P dV. \quad (13.4.6)$$

Therefore

$$TdS = T \left(\frac{\partial S}{\partial P} \right)_V dP + T \left(\frac{\partial S}{\partial V} \right)_P dV. \quad (13.4.7)$$

In a constant volume process, $TdS = C_V dT$, so that $T \left(\frac{\partial S}{\partial P} \right)_V = C_V \left(\frac{\partial T}{\partial P} \right)_V$.

And in a constant pressure process, $TdS = C_P dT$, so that

$$T\left(\frac{\partial S}{\partial V}\right)_P = C_P\left(\frac{\partial T}{\partial V}\right)_P. \quad (13.4.8)$$

Therefore

$$TdS = C_V\left(\frac{\partial T}{\partial P}\right)_V dP + C_P\left(\frac{\partial T}{\partial V}\right)_P dV. \quad (13.4.9)$$

This is the third of the TdS equations.

In summary, then, these are the three TdS equations:

$$TdS = T\left(\frac{\partial P}{\partial T}\right)_V dV + C_V dT \quad (13.4.10)$$

$$TdS = -T\left(\frac{\partial V}{\partial T}\right)_P dP + C_P dT \quad (13.4.11)$$

$$TdS = C_V\left(\frac{\partial T}{\partial P}\right)_V dP + C_P\left(\frac{\partial T}{\partial V}\right)_P dV \quad (13.4.12)$$

These equations can be used, for example, to calculate, by integration, the change of entropy between one state and another, provided that the equation of state is known in order that we can evaluate the partial derivatives.

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