

## 6.2: Other Relations

### The TdS Equations

The entropy  $S$  is a function of the state of the system. We can take it to be a function of any two of the three variables ( $p, T, V$ ). Taking  $S$  to be a function of  $p$  and  $T$ , we write

$$TdS = T \left( \frac{\partial S}{\partial T} \right)_p dT + T \left( \frac{\partial S}{\partial p} \right)_T dp \quad (6.2.1)$$

For the first term on the right hand side, we can use

$$T \left( \frac{\partial S}{\partial T} \right)_p dT = \left( \frac{\partial Q}{\partial T} \right)_p dT = C_p dT \quad (6.2.2)$$

where  $C_p$  is the specific heat at constant pressure. Further, using the last of the Maxwell relations, we can now write Equation 6.2.2 as

$$TdS = C_p dT - T \left( \frac{\partial V}{\partial T} \right)_p dp \quad (6.2.3)$$

The **coefficient of volumetric expansion** (due to heating) is defined by

$$\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p \quad (6.2.4)$$

Equation 6.2.3 can thus be rewritten as

$$TdS = C_p dT - \alpha TV dp \quad (6.2.5)$$

If we take  $S$  to be a function of  $V$  and  $T$ ,

$$TdS = T \left( \frac{\partial S}{\partial T} \right)_V dT + T \left( \frac{\partial S}{\partial V} \right)_T dV \quad (6.2.6)$$

Again the first term on the right hand side can be expressed in terms of  $C_v$ , the specific heat at constant volume, using

$$T \left( \frac{\partial S}{\partial T} \right)_V = C_v \quad (6.2.7)$$

Further using the Maxwell relations, we get

$$TdS = C_v dT + T \left( \frac{\partial p}{\partial T} \right)_V dV \quad (6.2.8)$$

Equations 6.2.3 (or 6.2.5 and 6.2.8) are known as the  $TdS$  equations.

### Equations for Specific Heats

Equating the two expressions for  $TdS$ , we get

$$(C_p - C_v)dT = T \left[ \left( \frac{\partial p}{\partial T} \right)_V dV + \left( \frac{\partial V}{\partial T} \right)_p dp \right] \quad (6.2.9)$$

By the equation of state, we can write  $p$  as a function of  $V$  and  $T$ , so that

$$dp = \left( \frac{\partial p}{\partial T} \right)_V dT + \left( \frac{\partial p}{\partial V} \right)_T dV \quad (6.2.10)$$

Using this in Equation 6.2.9, we find

$$(C_p - C_v)dT = T \left[ \left( \frac{\partial p}{\partial T} \right)_V + \left( \frac{\partial V}{\partial T} \right)_p \left( \frac{\partial p}{\partial V} \right)_T \right] dV + T \left( \frac{\partial V}{\partial T} \right)_p \left( \frac{\partial p}{\partial T} \right)_V dT \quad (6.2.11)$$

However, using Equation 6.1.9, taking  $X = V$ ,  $Y = p$  and  $Z = T$ , we have

$$\left(\frac{\partial p}{\partial T}\right)_V + \left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial p}{\partial V}\right)_T = 0 \quad (6.2.12)$$

Thus the coefficient of  $dV$  in Equation 6.2.11 vanishes and we can simplify it as

$$C_p - C_v = T \left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial p}{\partial T}\right)_V = -T \left[\left(\frac{\partial V}{\partial T}\right)_p\right]^2 \left(\frac{\partial p}{\partial V}\right)_T \quad (6.2.13)$$

where we have used Equation 6.2.12 again. We have already defined the **coefficient of volumetric expansion**  $\alpha$ . The **isothermal compressibility**  $\kappa_T$  is defined by

$$\frac{1}{\kappa_T} = -V \left(\frac{\partial p}{\partial V}\right)_T \quad (6.2.14)$$

In terms of these we can express  $C_p - C_v$  as

$$C_p - C_v = V \frac{\alpha^2 T}{\kappa_T} \quad (6.2.15)$$

This equation is very useful in calculating  $C_v$  from measurements of  $C_p$  and  $\alpha$  and  $\kappa_T$ . Further, for all substances,  $\kappa_T > 0$ . Thus, we see from this equation that  $C_p \geq C_v$ . (The result  $\kappa_T > 0$  can be proved in statistical mechanics.)

In the  $TdS$  equations, if  $dT$ ,  $dV$  and  $dp$  are related adiabatically,  $dS = 0$  and we get

$$C_p = T \left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial p}{\partial T}\right)_S, \quad C_v = -T \left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_S \quad (6.2.16)$$

This gives

$$\frac{C_p}{C_v} = - \left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial p}{\partial T}\right)_S \left[ \left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_S \right]^{-1} \quad (6.2.17)$$

We have the following relations among the terms involved in this expression,

$$\begin{aligned} \left(\frac{\partial p}{\partial T}\right)_S &= \left(\frac{\partial V}{\partial T}\right)_S \left(\frac{\partial p}{\partial V}\right)_S = \left(\frac{\partial V}{\partial T}\right)_S \frac{1}{V \kappa_S} \\ \left(\frac{\partial V}{\partial T}\right)_p &= \left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial T}{\partial p}\right)_V \left(\frac{\partial V}{\partial T}\right)_p = - \left(\frac{\partial p}{\partial T}\right)_V \frac{1}{\left(\frac{\partial p}{\partial V}\right)_T} = \left(\frac{\partial p}{\partial T}\right)_V V \kappa_T \end{aligned} \quad (6.2.18)$$

Using these we find

$$\frac{C_p}{C_v} = \frac{\kappa_T}{\kappa_S} \quad (6.2.19)$$

Going back to the Maxwell relations and using the expressions for  $TdS$ , we find

$$\begin{aligned} dU &= C_v dT + \left[ T \left(\frac{\partial p}{\partial T}\right)_V - p \right] dV \\ dH &= C_p dT + \left[ V - T \left(\frac{\partial V}{\partial T}\right)_p \right] dp \end{aligned} \quad (6.2.20)$$

these immediately yield the relations

$$\begin{aligned} C_v &= \left(\frac{\partial U}{\partial T}\right)_V, \quad C_p = \left(\frac{\partial H}{\partial T}\right)_p \\ \left(\frac{\partial U}{\partial V}\right)_T &= T \left(\frac{\partial p}{\partial T}\right)_V - p, \quad \left(\frac{\partial H}{\partial p}\right)_T = V - T \left(\frac{\partial V}{\partial T}\right)_p \end{aligned} \quad (6.2.21)$$

## Gibbs-Helmholtz Relation

Since the Helmholtz free energy is defined as  $F = U - TS$ ,

$$dF = dU - TdS - SdT = -SdT - pdV \quad (6.2.22)$$

This gives immediately

$$S = -\left(\frac{\partial F}{\partial T}\right)_V, \quad p = -\left(\frac{\partial F}{\partial V}\right)_T \quad (6.2.23)$$

Using this equation for entropy, we find

$$U = F + TS = F - T\left(\frac{\partial F}{\partial T}\right)_V \quad (6.2.24)$$

This is known as the Gibbs-Helmholtz relation. If  $F$  is known as a function of  $T$  and  $V$ , we can use these to obtain  $S$ ,  $p$  and  $U$ . Thus, all thermodynamic variables can be obtained from  $F$  as a function of  $T$  and  $V$ .

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