3 Entropy Equations

- These results can be used to measure anything, e.g

We will give an example of how the changes in entropy as a function of T, P or T, V can be expressed in terms of C_p, C_V, κ_T, and β_p

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

$$\boxed{dS = \frac{C_p}{T} dT - \beta_p V \, dp}$$

Second TdS eqn. first involves T, V

Usually measure per volume $s = S/V$ $c_p = C_p/V$

Then keeping V fixed

$$ds = \frac{c_p}{T} dT - \beta_p \, dp$$

this is called the second TdS equation. The first involves T, V

- Many more can be derived. In particular consider $S(T, V)$

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

$$= \frac{C_V}{T} dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

Now use the maxwell relation from $F(T,V)$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$$

$$= \frac{C_V}{T} dT + \left(\frac{\partial p}{\partial T}\right)_V dV$$

$$\boxed{dS = \frac{C_V}{T} dT + \frac{\beta_p}{\kappa_T} dV}$$

The Heat Capacity Equations

1. $C_p - C_V$

Actually out of C_p, C_V, κ_T, and β_p only three are independent

From the first and second $T\,dS$ eqn:

$$C_V\,dT + \frac{T\beta_p}{\kappa_T}\,dV = C_p\,dT - T\beta_p\,dp$$

Keeping the pressure fixed $dp = 0$ and dividing by dT we have

$$C_V + \frac{T\beta_p}{\kappa_T}\left(\frac{\partial V}{\partial T}\right)_p = C_p$$

Then $\left(\frac{\partial V}{\partial T}\right)_p = V\beta_p$ or the result

$$\boxed{C_V + \frac{T\beta_p^2}{\kappa_T}V = C_p}$$

the importance is that C_V can be hard to measure directly. It can be inferred from C_p. C_V is hard since it takes a lot of force to prevent ice from expanding when freezing

Usually we measure the specific heat per volume

$$c_V + \frac{T\beta_p^2}{\kappa_T} = c_p$$

We have not assumed an ideal gas here. For an ideal gas you will find $T\beta_p^2/\kappa_T = \frac{N k_B}{V}$ and so you will recover the ideal gas result,

$$C_V + Nk_B = C_p$$

(2) Consider an adiabatic process

$$dS = 0 = \frac{C_p}{T}\,dT - \beta_p V\,dp \quad \leftarrow \text{2nd } TdS$$

$$dS = 0 = \frac{C_V}{T}\,dT + \frac{\beta_p}{K_T}\,dV \quad \leftarrow \text{1st } TdS$$

Rearranging we have

this is dp/dV at fixed S

$$\frac{C_p}{C_V} = -\frac{V}{K_T}\frac{dp}{dV} \quad \text{or} \quad \left(\frac{\partial p}{\partial V}\right)_S = \frac{1}{\left(\frac{\partial V}{\partial p}\right)_S}$$

Now

$$K_S \equiv -V\left(\frac{\partial V}{\partial p}\right)_S \quad \text{is the adiabatic compressibility}$$

So we find a simple way to convert the isothermal compressibility K_T to the adiabatic one

$$\boxed{\frac{C_p}{C_V} = \frac{K_S}{K_T}}$$

The Heat capacity equations are very useful

1 Measuring C_V is very difficult directly in liquids since it take a great deal of pressure (megatons) to prevent liquids from expanding.

C_P can be measured directly, by inserting a small resistor into the sample.

2 The speed of sound involves the the adiabatic compressibility

sound speed $\rightarrow C_s^2 = \sqrt{\dfrac{1}{\rho K_s}}$ $\qquad \rho \equiv$ density

Also in use is the Bulk modulus: $V\left(\dfrac{\partial p}{\partial V}\right)_S \equiv B_s \equiv \dfrac{1}{K_s}$