SNS College of Technology

(An Autonomous Institution)

19ASB202/ Aero Engineering Thermodynamics

Unit -4/ GAS MIXTURES

Maxwell's Relations

The fundamental thermodynamic relation $\mathrm{d}E = T\mathrm{d}S - P\mathrm{d}V$ implies that the natural variable in which to express E are S and V :. $E = E(S,V)$

That means that on purely mathematical grounds, we can write

$$\mathrm{d}E = \left(\frac{\partial E}{\partial S}\right)_V \mathrm{d}S + \left(\frac{\partial E}{\partial V}\right)_S \mathrm{d}V$$

But comparison with the fundamental thermodynamic relation, which contains the physics, we can make the following identifications:

$$T = \left(\frac{\partial E}{\partial S}\right)_V \qquad \text{and} \qquad P = -\left(\frac{\partial E}{\partial V}\right)_S$$

These (especially the second) are interesting in their own right. But we can go further, by differentiating both sides of the first equation by V and of the second by S:

$$\left(\frac{\partial T}{\partial V}\right)_S = \left(\frac{\partial}{\partial V}\left(\frac{\partial E}{\partial S}\right)_V\right)_S \qquad \text{and} \qquad \left(\frac{\partial P}{\partial S}\right)_V = -\left(\frac{\partial}{\partial S}\left(\frac{\partial E}{\partial V}\right)_S\right)_V$$

Using the fact that the order of differentiation in the second derivation doesn't matter, we see that the right hand sides are equal, and thus so are the left hand sides, giving

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

By starting with F, H and G, we can get three more relations.

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$$dE = TdS - PdV \Rightarrow T = \left.\frac{\partial E}{\partial S}\right|_V \quad \& \quad P = -\left.\frac{\partial E}{\partial V}\right|_S \Rightarrow \left.\frac{\partial P}{\partial S}\right|_V = -\left.\frac{\partial T}{\partial V}\right|_S$$

$$dF = -SdT - PdV \Rightarrow S = -\left.\frac{\partial F}{\partial T}\right|_V \quad \& \quad P = -\left.\frac{\partial F}{\partial V}\right|_T \Rightarrow \left.\frac{\partial P}{\partial T}\right|_V = \left.\frac{\partial S}{\partial V}\right|_T$$

$$dH = TdS + VdP \Rightarrow T = \left.\frac{\partial H}{\partial S}\right|_P \quad \& \quad V = \left.\frac{\partial H}{\partial P}\right|_S \Rightarrow \left.\frac{\partial V}{\partial S}\right|_P = \left.\frac{\partial T}{\partial P}\right|_S$$

$$dG = -SdT + VdP \Rightarrow S = -\left.\frac{\partial G}{\partial T}\right|_P \quad \& \quad V = \left.\frac{\partial G}{\partial P}\right|_T \Rightarrow \left.\frac{\partial V}{\partial T}\right|_P = -\left.\frac{\partial S}{\partial P}\right|_T$$

The two equations involving derivatives of S are particularly useful, as they provide a handle on S which isn't easily experimentally accessible.

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