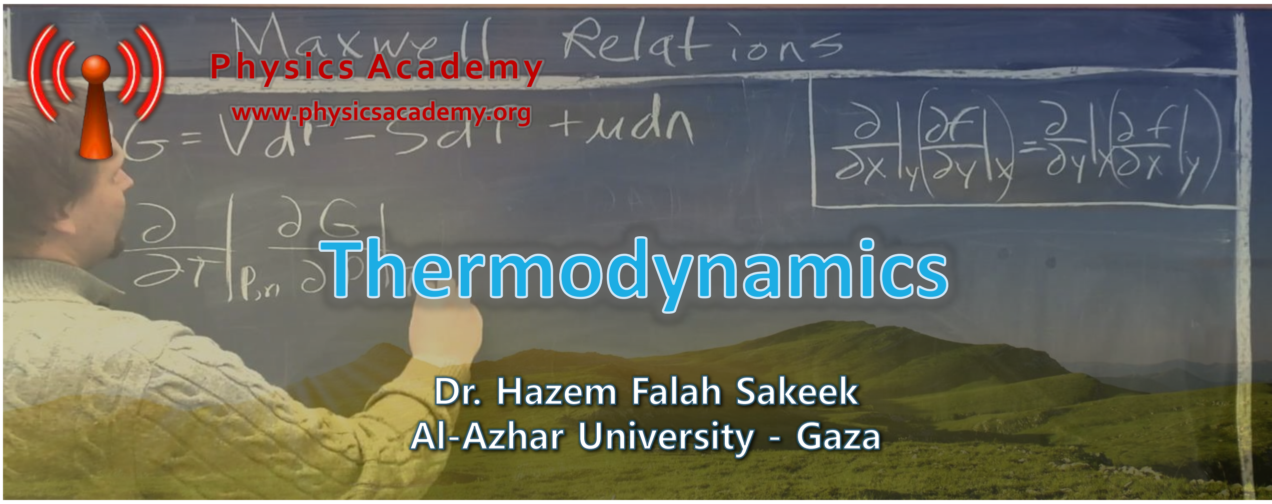

Thermodynamics

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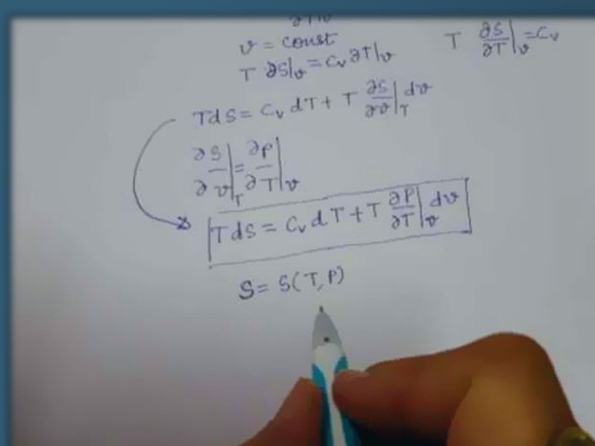
Unit 5: Pure Substance

Lecture 30: Heat-capacity equations

Unit 5: Pure Substance

- Enthalpy
- The Helmholtz functions
- Gibbs functions
- Maxwell's Equations
- The Tds equations
- Energy equations
- Heat-capacity equations



Heat-capacity Equations

$$T dS = C_v\, dT + T\left(\frac{\partial P}{\partial T}\right)_V dV$$ The first Tds equation

$$T dS = C_P\, dT - T\left(\frac{\partial V}{\partial T}\right)_P dP$$ The second Tds equation

Equating the first and second $T\ dS$ equations,

$$C_P\, dT - T\left(\frac{\partial V}{\partial T}\right)_P dP = C_v\, dT + T\left(\frac{\partial P}{\partial T}\right)_V dV$$

solving for dT

$$dT = \frac{T\left(\frac{\partial P}{\partial T}\right)_V}{C_P - C_v} dV + \frac{T\left(\frac{\partial V}{\partial T}\right)_P}{C_P - C_v} dP$$

$$dT = \frac{T\left(\frac{\partial P}{\partial T}\right)_V}{C_P - C_v} dV + \frac{T\left(\frac{\partial V}{\partial T}\right)_P}{C_P - C_v} dP$$

But

$$dT = \left(\frac{\partial T}{\partial V}\right)_P dV + \left(\frac{\partial T}{\partial P}\right)_V dP$$

Therefore,

$$\left(\frac{\partial T}{\partial V}\right)_P = \frac{T\left(\frac{\partial P}{\partial T}\right)_V}{C_P - C_v}$$

$$\left(\frac{\partial T}{\partial P}\right)_V = \frac{T\left(\frac{\partial V}{\partial T}\right)_P}{C_P - C_v}$$

Both the above equations yield the result that

$$C_P - C_v = T\left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial P}{\partial T}\right)_V$$

It was shown

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

$$C_P - C_v = -T\left(\frac{\partial V}{\partial T}\right)_P^2\left(\frac{\partial P}{\partial V}\right)_T$$

Heat-capacity Equations

This is one of the most important equations of thermodynamics, and it shows that:

Remarks

$$C_P - C_v = -T\left(\frac{\partial V}{\partial T}\right)_P^2\left(\frac{\partial P}{\partial V}\right)_T$$

Heat-capacity Equations

- Since $\left(\frac{\partial P}{\partial V}\right)_T$ is always negative for all known substances and $\left(\frac{\partial V}{\partial T}\right)_P^2$ must be positive, then $C_P - C_v$ can never be negative, or C_P can never be less than C_v
- As $T \to 0$, $C_P \to C_v$; or at absolute zero, the two heat capacities are equal.
- $C_P = C_v$ when $\left(\frac{\partial V}{\partial T}\right)_P = 0$. For example at 4°C, the temperature at which the density of water is maximum, $C_P = C_v$.

Remarks

- Laboratory measurements of the heat capacity of solids and liquids usually take place at constant pressure and therefore yield values of C_p.
- It would be extremely difficult to measure with any degree of accuracy the C_V of a solid or liquid.
- Values of C_V, however, must be known for purposes of comparison with theory. The equation for the difference in the heat capacities is very useful in calculating C_V in terms of C_P and other measurable quantities. **Remembering that**

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \qquad \kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

Volume expansivity **Isothermal compressibility**

Heat-capacity Equations (Practical form)

Heat-capacity Equations

$$C_P - C_v = -T\left(\frac{\partial V}{\partial T}\right)_P^2\left(\frac{\partial P}{\partial V}\right)_T$$

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

$$C_P - C_v = \frac{TV\left[\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P\right]^2}{-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T}$$

$$C_P - C_v = \frac{TV\beta^2}{\kappa}$$

Example

Calculate C_V of mercury at 20°C and atmospheric pressure, where C_P=139J/kg.K, T=293K, $V = 7.38 \times 10^{-5} m^3/kg.\ \beta = 1.81 \times 10^{-4} K^{-1},\ \kappa = 4.01 \times 10^{-11} Pa^{-1}$

$$C_P - C_v = \frac{TV\beta^2}{\kappa}$$

$$139 - C_v = \frac{(293)(7.38 \times 10^{-5})(1.81 \times 10^{-4})^2}{4.01 \times 10^{-11}}$$

$$= 17.7.3 J/kg.K$$

$$C_v = 121.3 J/kg.K$$

The ratio $\frac{C_P}{C_v} = \gamma$,

$$\gamma = \frac{C_P}{C_v} = \frac{139}{121.3} = 1.15$$

Heat-capacity in adiabatic compressibility

The two TdS equations are

$$TdS = C_v\, dT + T\left(\frac{\partial P}{\partial T}\right)_V dV$$ The first Tds equation

$$TdS = C_P\, dT - T\left(\frac{\partial V}{\partial T}\right)_P dP$$ The second Tds equation

At constant S

$$C_P\, dT_S = T\left(\frac{\partial V}{\partial T}\right)_P dP_S$$

$$C_V\, dT_S = -T\left(\frac{\partial P}{\partial T}\right)_V dV_S$$

→

$$\frac{C_P}{C_V} = -\left[\frac{\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial P}{\partial T}\right)_V}\right]\left(\frac{\partial P}{\partial V}\right)_S$$

$$\frac{C_P}{C_V} = -\left[\frac{\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial P}{\partial T}\right)_V}\right]\left(\frac{\partial P}{\partial V}\right)_S$$

But

$$\left[\frac{\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial P}{\partial T}\right)_V}\right] = -\left(\frac{\partial V}{\partial P}\right)_T$$

And

$$\kappa_S = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S \qquad \kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

Isentropic compressibility **Isothermal compressibility**

Therefore

$$\gamma = \frac{C_P}{C_v} = \frac{\kappa}{\kappa_S}$$

From which κ_S can be calculated

إلى اللقاء في سلسلة محاضرات

فيزيائية اخرى

مع خالص دعواتي لكم بالتوفيق