Tæknileg skref

1. Skrifið varmafræðilegt mætti með viðeigandi breytum

2. Notið vensl Maxwells til að umrita hlutafleiður yfir í þægilegar

3. Munið eftir

$$\left(\frac{\partial x}{\partial z}\right)_y = \frac{1}{\left(\frac{\partial z}{\partial x}\right)_y}$$

4. Munið eftir

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$$

og

$$\left(\frac{\partial x}{\partial y}\right)_z = -\left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x$$

5. Takið eftir varmarýmd

$$\frac{C_V}{T} = \left(\frac{\partial S}{\partial T}\right)_V, \quad \frac{C_P}{T} = \left(\frac{\partial S}{\partial T}\right)_P$$

6. Takið eftir „viðtaki"

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

$$\beta_S = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_S$$ óvermin þensla

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

$$\kappa_S = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_S$$ övermün bjäppum

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Domi $\quad S = S(T,V) \longrightarrow$ sÿna det $\quad C_p - C_V = VT\dfrac{\beta_p^2}{\kappa_T}$

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

$$\underbrace{\left(\frac{\partial S}{\partial T}\right)_p}_{\frac{C_p}{T}} = \underbrace{\left(\frac{\partial S}{\partial T}\right)_V}_{\frac{C_V}{T}} + \underbrace{\left(\frac{\partial S}{\partial V}\right)_T}_{\underbrace{\left(\frac{\partial p}{\partial T}\right)_V}_{-\left(\frac{\partial p}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_p}} \left(\frac{\partial V}{\partial T}\right)_p$$

Maxwell

$$\underbrace{\frac{C_p}{T} - \frac{C_V}{T} = -\left(\frac{\partial p}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_p^2}$$

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

$$= VT\frac{\beta_p^2}{\kappa_T}$$

Dæmi   Óreiða eins móls kjörgass

$$\underbrace{pV = RT}, \quad \text{veljum } S = S(T,V)$$

Maxwell

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

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

$$= \frac{C_V}{T} dT + \underbrace{\left(\frac{\partial p}{\partial T}\right)_V}_{\frac{R}{V}} dV = \frac{C_V}{T} dT + \frac{R\,dV}{V}$$

fyrir kjörgas er C_V óháð T

$$\longrightarrow \quad S = C_V \int \frac{dT}{T} + R \int \frac{dV}{V}$$

$$= C_V \ln T + R \ln V + \text{fasti}$$

Finnum hlutfallið $\frac{\kappa_T}{\kappa_S}$

Samkvæmt skilgreiningu

$$\frac{\kappa_T}{\kappa_S} = \frac{\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T}{\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_S} = \frac{-\left(\frac{\partial V}{\partial T}\right)_p\left(\frac{\partial T}{\partial p}\right)_V}{-\left(\frac{\partial V}{\partial S}\right)_p\left(\frac{\partial S}{\partial p}\right)_V} = \frac{\left(\frac{\partial V}{\partial T}\right)_p\left(\frac{\partial S}{\partial V}\right)_p}{\left(\frac{\partial p}{\partial T}\right)_V\left(\frac{\partial S}{\partial p}\right)_V}$$

$$= \frac{\left(\frac{\partial S}{\partial T}\right)_p}{\left(\frac{\partial S}{\partial T}\right)_V} = \frac{C_p/T}{C_V/T} = \gamma$$

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fyrir kjörgas

$$pV \sim T \quad \rightarrow \quad \underbrace{\frac{dp}{dV} = -\frac{p}{V}}$$ eða $$\frac{dp}{p} = -\frac{dV}{V}$$

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

fyrir óvermið ferli $\quad p \sim V^{-\gamma} \longrightarrow \frac{dp}{dV} = -\gamma \frac{p}{V}$

$$K_S = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_S = \frac{1}{\gamma p}$$

$$\longrightarrow \frac{K_T}{K_S} = \frac{1}{p}\gamma p = \gamma$$

Þriðja lögmál varmafræðinnar

$$\boxed{S \to 0 \quad \text{þegar} \quad T \to 0}$$

notað til að reikna ΔS

$$C_p = T\left(\frac{\partial S}{\partial T}\right)_p \longrightarrow S(T) = S(T_0) + \int_{T_0}^{T} dT\, \frac{C_p}{T}$$

Afleiðingar

$$C = T\left(\frac{\partial S}{\partial T}\right) = \left(\frac{\partial S}{\partial \ln T}\right) \to 0 \quad , \quad \beta_p \to 0$$

Kemur ekki heim og saman við Kjörgas

Kjörgas er ekki til við lágt hitastig

Ekki er hægt að ná $T=0$ í endanlega mörgum skrefum

Víxlverkanir milli atóma og sameinda verða mikilvægar við lágt hitastig

og samhverfueiginleikar þeirra . . . .