Практичне заняття №8

Задача №1. Отримати відношення Максвела.

Для ідеального газу:

1) $dE = TdS - PdV$; – 1-й закон термодинаміки

$T = \frac{\partial E}{\partial S}\Big|_V$; $\quad P = -\frac{\partial E}{\partial V}\Big|_S$; $\quad E = E(S, V)$;

$\frac{\partial^2 E}{\partial S \partial V} = \frac{\partial^2 E}{\partial V \partial S} \Longrightarrow$ відношення Максвела

$$\frac{\partial^2 E}{\partial S \partial V} = \frac{\partial}{\partial S}\left(\frac{\partial E}{\partial V}\Big|_S\right)_V = -\frac{\partial P}{\partial S}\Big|_V;$$

$$\frac{\partial^2 E}{\partial V \partial S} = \frac{\partial}{\partial V}\left(\frac{\partial E}{\partial S}\Big|_V\right)_S = \frac{\partial T}{\partial V}\Big|_S;$$

$$\Longrightarrow \boxed{\frac{\partial T}{\partial V}\Big|_S = -\frac{\partial P}{\partial S}\Big|_V}$$

2) Ентальпія: $H = E + P \cdot V$;

$dH = dE + d(P \cdot V) = TdS - \cancel{PdV} + \cancel{PdV} + VdP = TdS + VdP$;

$H = H(S, P) \Longrightarrow$

$T = \frac{\partial H}{\partial S}\Big|_P$; $\quad V = \frac{\partial H}{\partial P}\Big|_S$; $\quad \frac{\partial^2 H}{\partial S \partial P} = \frac{\partial^2 H}{\partial P \partial S} \Longrightarrow$

$$\frac{\partial^2 H}{\partial S \partial P} = \frac{\partial}{\partial S}\left(\frac{\partial H}{\partial P}\Big|_S\right)_P = \frac{\partial V}{\partial S}\Big|_P;$$

$$\frac{\partial^2 H}{\partial P \partial S} = \frac{\partial}{\partial P}\left(\frac{\partial H}{\partial S}\Big|_P\right)_S = \frac{\partial T}{\partial P}\Big|_S;$$

$$\Longrightarrow \boxed{\frac{\partial T}{\partial P}\Big|_S = \frac{\partial V}{\partial S}\Big|_P}$$

3) Вільна енергія: $F = E - TS$;

$$dF = \cancel{TdS} - PdV - \cancel{TdS} - SdT = -SdT - PdV; \quad F = F(T,V)$$

$$S = -\frac{\partial F}{\partial T}\Big|_V; \quad P = -\frac{\partial F}{\partial V}\Big|_T;$$

$$\frac{\partial^2 F}{\partial T \partial V} = \frac{\partial}{\partial T}\left(\frac{\partial F}{\partial V}\Big|_T\right)_V = -\frac{\partial S}{\partial T}\Big|_V;$$

$$\frac{\partial^2 F}{\partial V \partial T} = \frac{\partial}{\partial V}\left(\frac{\partial F}{\partial T}\Big|_V\right)_T = -\frac{\partial P}{\partial V}\Big|_T;$$

$$\Rightarrow \boxed{\frac{\partial S}{\partial T}\Big|_V = \frac{\partial P}{\partial V}\Big|_T}$$

4) Вільна енергія Гіббса: $G = F + PV = E - TS + PV.$

$$dG = \cancel{TdS} - \cancel{PdV} - \cancel{TdS} - SdT + \cancel{PdV} + VdP = -SdT + VdP;$$

$G = G(T, P);$

$$S = -\frac{\partial G}{\partial T}\Big|_P; \quad V = \frac{\partial G}{\partial P}\Big|_T;$$

$$\frac{\partial^2 G}{\partial T \partial P} = \frac{\partial}{\partial T}\left(\frac{\partial G}{\partial P}\Big|_T\right)_P = \frac{\partial V}{\partial T}\Big|_P;$$

$$\frac{\partial^2 G}{\partial P \partial T} = \frac{\partial}{\partial P}\left(\frac{\partial G}{\partial T}\Big|_P\right)_T = -\frac{\partial S}{\partial P}\Big|_T;$$

$$\Rightarrow \boxed{\frac{\partial S}{\partial P}\Big|_T = -\frac{\partial V}{\partial T}\Big|_P}$$

Відношення Максвелла:

$\frac{\partial T}{\partial V}\Big\|_S = -\frac{\partial P}{\partial S}\Big\|_V;$	$\frac{\partial S}{\partial V}\Big\|_T = \frac{\partial P}{\partial T}\Big\|_V;$
$\frac{\partial T}{\partial P}\Big\|_S = \frac{\partial V}{\partial S}\Big\|_P;$	$\frac{\partial S}{\partial P}\Big\|_T = -\frac{\partial V}{\partial T}\Big\|_P;$

Задача №2. Довести тотожність:

$$\frac{\partial S}{\partial T}\Big|_P = \frac{\partial S}{\partial T}\Big|_V + \frac{\partial S}{\partial V}\Big|_T \cdot \frac{\partial V}{\partial T}\Big|_P ;$$

$$\frac{\partial S}{\partial T}\Big|_P - \frac{\partial S}{\partial T}\Big|_V \quad - ?$$

$$\frac{\partial S}{\partial T}\Big|_P = \frac{\partial}{\partial T}\left(-\frac{\partial F}{\partial T}\Big|_V\right)_P = -\frac{\partial^2 F}{\partial T^2}\Big|_{P,V} ;$$

$$\frac{\partial S}{\partial T}\Big|_V = \frac{\partial}{\partial T}\left(-\frac{\partial G}{\partial T}\Big|_P\right)_V = -\frac{\partial^2 G}{\partial T^2}\Big|_{V,P} ;$$

$$\frac{\partial S}{\partial T}\Big|_P - \frac{\partial S}{\partial T}\Big|_V = -\frac{\partial^2 F}{\partial T^2}\Big|_{P,V} + \frac{\partial^2 G}{\partial T^2}\Big|_{P,V} = \frac{\partial^2 (G-F)}{\partial T^2}\Big|_{P,V} ;$$

$$G - F = F + PV - F = PV ;$$

$$\frac{\partial^2 (PV)}{\partial T^2}\Big|_{P,V} = \frac{\partial}{\partial T}\left(\frac{\partial (PV)}{\partial T}\Big|_V\right)_P = \frac{\partial}{\partial T}\left(V\frac{\partial P}{\partial T}\Big|_V\right)_P \Rightarrow$$

$$\frac{\partial S}{\partial T}\Big|_P - \frac{\partial S}{\partial T}\Big|_V = \frac{\partial V}{\partial T}\Big|_P \cdot \frac{\partial P}{\partial T}\Big|_V = \frac{\partial S}{\partial V}\Big|_T \cdot \frac{\partial V}{\partial T}\Big|_P ;$$

Задача №3. Розглянемо ідеальний газ з постійною теплоємністю $C_V = Nk_B\alpha$, $\alpha = const$.

a) Показати, що $C_P = Nk_B(\alpha+1)$

b) Показати, що ентропія: $S = Nk_B \ln\left(\frac{V}{N}\right) + Nk_B\alpha \ln T + const$

c) Показати, що для адіабатичного процесу $VT^{\alpha} = const$ та $PV^{\gamma} = const$, де $\gamma = C_P/C_V$.

a) $C_P - C_V = T\frac{\partial V}{\partial T}\Big|_P \cdot \frac{\partial P}{\partial T}\Big|_V$; (– тотожність)

$$PV = Nk_BT ;$$

$$\frac{\partial}{\partial T}[PV]_V = \frac{\partial}{\partial T}[Nk_BT]_V \Rightarrow V\frac{\partial P}{\partial T}\Big|_V = Nk_B ;$$

$$\frac{\partial}{\partial T}\left[PV\right]_P = \frac{\partial}{\partial T}\left[Nk_BT\right]_P \Rightarrow P\frac{\partial V}{\partial T}\Big|_P = Nk_B;$$

$$C_P - C_V = T\frac{Nk_B}{P}\cdot\frac{Nk_B}{V} = \frac{T}{PV}\cdot(Nk_B)^2 = \frac{(Nk_B)^2}{Nk_B} = Nk_B;$$

$$C_P = C_V + Nk_B = Nk_B\alpha + Nk_B = Nk_B(\alpha+1).$$

b) $$đQ = TdS; \quad dS = \frac{đQ}{T} = \frac{dH - VdP}{T} = \frac{dH}{T} - V\frac{dP}{T};$$

$$C_P = \frac{\partial H}{\partial T}\Big|_P \Rightarrow dH = C_P dT \Rightarrow$$

$$dS = C_P\frac{dT}{T} - V\frac{dP}{T} = C_P\frac{dT}{T} - Nk_B\frac{dP}{P};$$

$$S_2 - S_1 = C_P\int_1^2\frac{dT}{T} - Nk_B\int_1^2\frac{dP}{P};$$

$$S = C_P\ln T - Nk_B\ln P + \text{const};$$

$$\ln P = \left\{P = \frac{Nk_BT}{V}\right\} = \ln k_B + \ln T + \ln\left(\frac{N}{V}\right) =$$

$$= \ln k_B + \ln T - \ln\left(\frac{V}{N}\right);$$

$$S = (C_P - Nk_B)\ln T + Nk_B\ln\left(\frac{V}{N}\right) + \text{const};$$

$$S = Nk_B\ln\left(\frac{V}{N}\right) + Nk_B\alpha\ln T + \text{const};$$

c) $$đQ = 0 \Rightarrow dS = 0;$$

$$d\left[Nk_B\ln\left(\frac{V}{N}\right) + Nk_B\alpha\ln T\right] = 0;$$

$$\cancel{Nk_B}\cdot d\left[\ln\left(\frac{V}{N}\right) + \ln T^\alpha\right] = 0;$$

$$\ln\left(\frac{VT^\alpha}{N}\right) = \text{const} \Rightarrow VT^\alpha = \text{const};$$

$$T = \frac{PV}{Nk_B}; \quad V\frac{P^\alpha V^\alpha}{(Nk_B)^\alpha} = \text{const}; \quad \left[P^\alpha V^{\alpha+1} = \text{const};\right]^{1/\alpha}$$

$$\Rightarrow PV^{\frac{\alpha+1}{\alpha}} = \text{const} \; ; \qquad \frac{\alpha+1}{\alpha} = \frac{Nk_B(\alpha+1)}{Nk_B\alpha} = \frac{c_p}{c_v} = \gamma \; ;$$

$$PV^{\gamma} = \text{const} .$$