Facit Teor. fys. I D
Mandag 6/6-1977

I

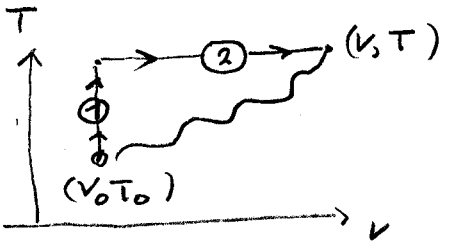
a) De oppgitte funksjoner er konsistente d.v.s:

$$\frac{\partial}{\partial T}\frac{\partial U}{\partial V} = \frac{\partial}{\partial V} C_V = -\frac{2\alpha}{T^2 V^2}$$

Vi kan derfor integrere et totalt differensial:

$$dU = \left(\frac{3}{2}R + \frac{2\alpha}{T^2 V}\right) dT + \left(\frac{2\alpha}{V^2 T} - \frac{\beta}{V^2}\right) dV$$

f.ex. langs veien ① – ② i V-T diagrammet



På ①: $dV = 0$, $V = V_0$: $\int_{T_0 V_0}^{T V_0} = \frac{3}{2}R(T - T_0) - \frac{2\alpha}{V_0}\left(\cancel{\frac{1}{T}} - \frac{1}{T_0}\right)$

På ②: $dT = 0$ $T = T$: $\int_{T V_0}^{T V} = -\frac{2\alpha}{T}\left(\frac{1}{V} - \cancel{\frac{1}{V_0}}\right) + \beta\left(\frac{1}{V} - \frac{1}{V_0}\right)$

$$U - U_0 = \frac{3}{2}RT + \left(\beta - \frac{2\alpha}{T}\right)\frac{1}{V} - \frac{3}{2}RT_0 \cdots$$

$$\therefore \quad U = \frac{3}{2}RT + \left(\beta - \frac{2\alpha}{T}\right)\frac{1}{V}$$

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b) I Gay-Lussacforsøket vil fryser systemet inket arbeid. Det vil si: $U(V_0 T_0) = U(2V_0, T)$

$$\frac{3}{2}RT_0 + \left(\beta - \frac{2\alpha}{T_0}\right)\frac{1}{V_0} = \frac{3}{2}RT + \left(\beta - \frac{2\alpha}{T}\right)\frac{1}{2V_0}$$

$$T = T_0(1 - \Delta) \; ; \quad \frac{1}{T} = \frac{1}{T_0}(1 + \Delta) + O(\Delta^2) \quad \Rightarrow$$

$$\text{h.s.} = \cancel{\frac{3}{2}RT_0} - \frac{3}{2}RT_0\Delta + \frac{\beta}{2V_0} - \frac{\alpha}{T_0 V_0}(1 + \Delta)$$

$$\text{v.s} = \cancel{\frac{3}{2}RT_0} + \frac{\beta}{V_0} - \frac{2\alpha}{T_0 V_0}$$

$$0 = -\frac{\beta}{2V_0} - \left(\frac{3}{2}RT_0 + \frac{\alpha}{T_0V_0}\right)\Delta + \frac{\alpha}{T_0V_0}$$

$$\Delta = \frac{\frac{\alpha}{T_0V_0} - \frac{\beta}{2V_0}}{\frac{3}{2}RT_0 + \frac{\alpha}{T_0V_0}} = \frac{\delta T}{T_0}$$

Tallverdier:

$$\tfrac{3}{2}RT_0 = 1{,}5 \times 0{,}082 \times 273 = 33{,}5$$

$$\frac{\alpha}{V_0T_0} = \frac{491}{273 \cdot 22{,}4} = 0{,}08$$

$$\frac{\beta}{2V_0} = \frac{0{,}96}{44{,}8} = 0{,}02$$

$$\Delta = \frac{0{,}06}{33{,}5 + 0{,}08} = 1{,}79 \cdot 10^{-3}$$

$$\delta T = T_0\Delta = \frac{273 \times 0{,}06}{33{,}58} = 0{,}48\,^\circ K$$

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c) Skriv den termodynamiske tilstandsligning:

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

ifflg. oppgaven $= \left(\frac{2\alpha}{T} - \beta\right)\frac{1}{V^2} = -''-$

$$\therefore \quad \frac{P}{T} = \left(-\frac{\alpha}{T^2} + \frac{\beta}{T}\right)\frac{1}{V^2} + f(V)$$

$$\frac{PV}{T} = \left(-\frac{\alpha}{T^2} + \frac{\beta}{T}\right)\cdot\frac{1}{V} + V\cdot f(V) = \cancel{C} + g(V)$$

$V \to \infty$ $T \to \infty$, (V/T) fast $\Rightarrow$

$$R = \lim V f(V)$$

$$\therefore f = \frac{R}{V} + \frac{g(V)}{V}$$

Gyldig: $g \equiv 0$

$$P = \frac{RT}{V} + \left(\beta - \frac{\alpha}{T}\right)\frac{1}{V^2}$$

d) Joule-Thomsonkoeffisienten er:

$$(\partial H/\partial P)_T \,/\, C_p$$

$$H = U + PV$$

$$U = \frac{3}{2}RT + \left(\beta - \frac{2\alpha}{T}\right)\cdot\frac{1}{V}$$

$$PV = RT + \left(\beta - \frac{\alpha}{T}\right)\cdot\frac{1}{V}$$

$$H = \frac{5}{2}RT + \left(2\beta - \frac{3\alpha}{T}\right)\cdot\frac{1}{V}$$

$$\frac{\partial H}{\partial P} = \left(2\beta - \frac{3\alpha}{T}\right)\left(\frac{-1}{V^2}\right)\frac{\partial V}{\partial P}$$

$= 0$ ved inversjonstemperaturen

$$T_i = \frac{3}{2}\frac{\alpha}{\beta} = \frac{3}{2}\,\frac{491}{0{,}96} = 753\,^\circ K = \underline{\underline{480\,^\circ C}}.$$

Dette er høyt til man ser på hva kunnet finne eksperimentelle data, så T_i er formodentlig meget høy.

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II

a) I dette tilf. isoterm rev. utvidelse:

$$L_{rev} = \int_{V_0}^{V} P\,dV \quad , \quad P = \frac{RT_0}{V}$$

$$= \underline{\underline{RT_0 \log \frac{V}{V_0}}}$$

Ingen grense $V \to \infty \Rightarrow L \to \infty$!

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b) Adiab. rev. $\therefore PV^{\varkappa} = \text{konst}$

$$L_{rev} = P_0 V_0^{\varkappa} \int_{V_0}^{V} \frac{dV}{V^{\varkappa}} = \frac{P_0 V_0^{\varkappa}}{\varkappa - 1}\left[\frac{1}{V_0^{\varkappa-1}} - \frac{1}{V^{\varkappa-1}}\right]$$

$$= \underline{\underline{\frac{P_0 V_0}{\varkappa - 1}\left[1 - \left(\frac{V_0}{V}\right)^{\varkappa-1}\right]}}$$

Øvre grense $V \to \infty \Rightarrow L = \underline{\underline{\frac{P_0 V_0}{\varkappa - 1}}}$. Hvorfor?

For en-atomig gas $\varkappa = 5/3$ $\quad L = \frac{RT_0}{5/3 - 1} = \underline{\frac{3}{2} RT_0}$

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c) For å få en varmekraftmaskin må arbeids-substansen periodisk bringes tilbake til utgangstilstanden. Dersom vi ikke forlanger dette kan en arbeidssubstans (som f.ex. gassen i (a) og (b) ovenfor) — godt omsette varmeenergi direkte i arbeid. I tilfelle (a) endog ubegrenset. Men en slik aperiodisk prosess kan naturligvis ikke danne grunnlag for noen maskin.

III

$$U = F - T\frac{\partial F}{\partial T} \quad \therefore$$

Betrakt: $\boxed{\frac{\partial F}{\partial T} = \frac{F-U}{T}}$ for $T \to 0$

Da må h. side bli et null-nulltedels uttrykk — såfremt vi forutsetter at v. side ikke kan vokse ubegrenset. (I virkeligheten går $\partial F/\partial T = -S$ mot 0 i Planck's formulering av 3. Hovedsetning men vi skal altså ikke gjøre nødvendigvis bruk av 3. H. ktn.)

Grenseverdiene i $\boxed{}$ må da beregnes v. hj. av l'Hopital's regel:

$$\lim_{T\to 0} \frac{F-U}{T} = \lim_{T\to 0}\left(\frac{\partial F}{\partial T} - \frac{\partial U}{\partial T}\right)\Big/ 1$$

Ledet $\partial F/\partial T$ faller bort mot v. side:

$$\lim\left(\cancel{\frac{\partial F}{\partial T}} = \cancel{\frac{\partial F}{\partial T}} - \frac{\partial U}{\partial T}\right);$$

$$\therefore \lim_{T\to 0} \frac{\partial U}{\partial T} = \lim C_v = 0 \qquad \text{q. e. d.}$$

Tilsvarende for C_p.

Dette teorem, som vistnok skyldes Odd Hassel i Oslo, er merkelig nok lite kjent.