26-01 van der Waals gas. Sýnið að κ_T fyrir $V = V_c$ uppfylli $\kappa_T = \frac{4b}{3R}(T - T_c)^{-1}$

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \qquad p = \frac{RT}{V-b} - \frac{a}{V^2}, \qquad V_c = 3b$$

$$T_c = \frac{8a}{27Rb}$$

$$p_c = \frac{a}{27b^2}$$

$$\left(\frac{\partial p}{\partial V}\right)_T = -\frac{RT}{(V-b)^2} + \frac{2a}{V^3}$$

þegar $V \to V_c = 3b$

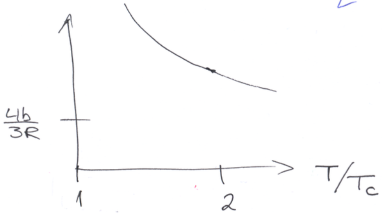
$$-\left(\frac{\partial V}{\partial p}\right)_T \frac{1}{V} = \frac{1}{\frac{RTV}{(V-b)^2} - \frac{2a}{V^2}} \longrightarrow \frac{1}{\frac{RT3b}{4b^2} - \frac{2a}{9b^2}}$$

$$\frac{1}{\frac{3RT}{4b} - \frac{2a}{9b^2}} = \frac{\frac{4b}{3R}}{T - \frac{8a}{27Rb}} = \frac{\frac{4b}{3R}}{T - T_c}$$

því fæst

$$K_T = \frac{4b}{3R}\left(\frac{1}{T-T_c}\right)$$ þegar $V = V_c$

þegar $T \to T_c^+$



Ef $T \to T_c^-$

þá er $K_T < 0$ og kerfið

er óstöðugt

26-02

Ef ástandsjafnan væri

$$P(V-b) = RT \quad , \quad b = \text{fasti}$$

jafnan er skrifuð fyrir 1 mole

Stærðargráða b?, sýna að $U = U(T)$:

Atóm gæti verið $1-3\ \mathring{A}$, $0{,}1-0{,}3$ nm

veljum $0{,}2\cdot 10^{-9}$ m $\to$ rúmmál $\sim 8\cdot 10^{-30}\ m^3 = V_{atóm}$

Eitt mól tekur þá $N_A \cdot V_{atóm} = 6\cdot 10^{23}\cdot 8\cdot 10^{-30} \simeq 4.8\cdot 10^{-6}\ m^3$

Fyrir 1 mól má því búast við að $b \lesssim 10^{-5}\ m^3$

$$p(V,T) = \frac{RT}{V-b}\ ,\quad \text{tökum } V,T \text{ sem breytur}$$

$$p = -\left(\frac{\partial F}{\partial V}\right)_T \to F = -RT\ln(V-b) + f(T)$$

enn fremur vitum við að $dF = -SdT - pdV$, 1. lögmálið

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = R\ln(V-b) - \frac{\partial f}{\partial T}$$

$$U = F + TS = -RT\ln(V-b) + f(T) + RT\ln(V-b) - T\frac{\partial f}{\partial T}$$

$$= f(T) - T\frac{\partial f}{\partial T}$$

aðeins háð T

26-03

Dieterici ástands jafnan er

$$p(V-b) = RT\exp\left\{-\frac{a}{RTV}\right\}$$

umrita með $\tilde{p} = \frac{p}{p_c}$, $\tilde{T} = \frac{T}{T_c}$, $\tilde{V} = \frac{V}{V_c}$

Notum (26.38)

$$T_c = \frac{a}{4Rb}, \quad p_c = \frac{a}{4e^2b^2}, \quad V_c = 2b$$

$$p_c\tilde{p}(V_c\tilde{V}-b) = RT_c\tilde{T}\exp\left\{-\frac{a}{RT_c\tilde{T}\,V_c\tilde{V}}\right\}$$

$$\frac{a}{4e^2b^2}\tilde{p}(2b\tilde{V}-b) = R\frac{a}{4Rb}\tilde{T}\exp\left\{-\frac{a\,4Rb}{Ra\tilde{T}2b\tilde{V}}\right\}$$

$$\frac{\tilde{p}\,(2\tilde{V}-1)}{e^2} = \frac{R}{R}\tilde{T}\exp\left\{-2\frac{1}{\tilde{T}\tilde{V}}\right\}$$

$$\rightarrow \tilde{p}(2\tilde{v}-1) = \tilde{T}\exp\left\{+2 - \frac{2}{\tilde{T}\tilde{v}}\right\} = \tilde{T}\exp\left\{2\left(1-\frac{1}{\tilde{T}\tilde{v}}\right)\right\}$$ 5

26-04 finna jafnþrýsti þenslu van der Waals gass

$$\beta_p = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \quad , \quad p = \frac{RT}{V-b} - \frac{a}{V^2}$$

$$\beta_p = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = -\frac{1}{V}\underbrace{\left(\frac{\partial V}{\partial p}\right)_T}\left(\frac{\partial p}{\partial T}\right)_V$$

$$\left.\begin{aligned}\left(\frac{\partial p}{\partial V}\right)_T &= -\frac{RT}{(V-b)^2} + \frac{2a}{V^3} \\ \left(\frac{\partial p}{\partial T}\right)_V &= \frac{R}{V-b}\end{aligned}\right\} \rightarrow \beta_p = -\frac{\frac{1}{V}\cdot\frac{R}{V-b}}{-\frac{RT}{(V-b)^2} + \frac{2a}{V^3}}$$

$$= \frac{1}{\frac{V(V-b)}{R}\left\{\frac{RT}{(V-b)^2} - \frac{2a}{V^3}\right\}} = \frac{1}{T\left\{\frac{V}{V-b} - \frac{2a(V-b)}{V^2\,RT}\right\}}$$

$$= \frac{1}{T\left\{1 + \frac{b}{V-b} - \frac{2a}{pV + a^2}\right\}}$$

nota ástandsjöfnuna

$$pV^2 + a = \frac{RTV^2}{V-b}$$

Í markpunkti

$$\left.\begin{aligned} V_c &= 3b \\ T_c &= \frac{8a}{27Rb} \\ p_c &= \frac{a}{27b^2} \end{aligned}\right\} \rightarrow \left.\begin{aligned} \frac{V}{V-b} &\rightarrow \frac{3}{2} \\ \frac{2a(V-b)}{V^2\,RT} &\rightarrow \frac{3}{2} \end{aligned}\right\} \rightarrow \beta_p \rightarrow \infty$$

26-06

Heildarorka eins móls van der Waals gass er

$$U = \frac{f}{2}RT - \frac{a}{V}$$

þar sem f er fjöldi frelsisgráða

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{f}{2}R \,,$$

Munum (11.25)

$$C_p - C_V = \underbrace{\left\{\underbrace{\left(\frac{\partial U}{\partial V}\right)_T}_{\frac{a}{V^2}} + p\right\}}_{\frac{RT}{V-b}} \underbrace{\left(\frac{\partial V}{\partial T}\right)_p}_{V\beta_p}$$

$\frac{RT}{V-b}$ ← frá ástandsjöfnunni

$$V\beta_p = \frac{\left(\frac{V}{T}\right)}{\frac{V}{V-b} - \frac{2a(V-b)}{V^2RT}}$$

dæmi 26-04

$$\rightarrow C_p - C_v = \frac{R}{1 - \frac{2a}{VRT}\frac{(V-b)^2}{V^2}}$$

gerum ráð fyrir að $V >> b$ $a << VTR$

$$\rightarrow C_p - C_v \simeq R\left\{1 + \frac{2a}{VRT}\right\} \simeq R + \frac{2a}{VT}$$