

0.1 10, 11, 12, 13 Gaiak

0.1.1 Oinarrizko Ekuazioa eta egoera-ekuazioak

1. Zenbait sistema termodinamikori dagokion oinarrizko ekuazioa agertuko da ondoren. Dena den, horietariko bost, II, III eta IV postulatuetatik baten edo gehiagoren aurka dago; eta, ondorioz, fisikoki onartezinak dira. Adieraz itzazu aipatu bostak, eta betegabeko postulatu(k). v_0 , θ eta R konstante positiboak dira. Onartu ezazu erro positibo erreala soilik, berredura frakzionarioa ageri den guztietan. (C 1.9.1)

$$\begin{aligned}
 S &= \left(\frac{R^2}{v_0\theta}\right)^{\frac{1}{3}} [NVU]^{\frac{1}{3}} \\
 S &= \left(\frac{R}{\theta^2}\right)^{\frac{1}{3}} \left[\frac{NU}{V}\right]^{\frac{2}{3}} \\
 S &= \left(\frac{R}{\theta}\right)^{\frac{1}{2}} \left[NU - \frac{R\theta V^2}{v_0^2}\right]^{\frac{1}{2}} \\
 S &= \left(\frac{R^2\theta}{v_0^3}\right)^{\frac{1}{5}} \frac{V^3}{NU} \\
 S &= \left(\frac{R^3}{v_0\theta^2}\right)^{\frac{1}{5}} [N^2 V U^2]^{\frac{1}{5}} \\
 S &= NR \ln \left(\frac{UV}{N^2 R \theta v_0}\right) \\
 S &= \left(\frac{R}{\theta}\right)^{\frac{1}{2}} [NU]^{\frac{1}{2}} \exp\left(-\frac{V^2}{2N^2 v_0^2}\right) \\
 S &= \left(\frac{R}{\theta}\right)^{\frac{1}{2}} [NU]^{\frac{1}{2}} \exp\left(-\frac{UV}{NR\theta v_0}\right) \\
 U &= \left(\frac{v_0\theta}{R}\right) \frac{S^2}{V} \exp\left(\frac{S}{NR}\right) \\
 U &= \left(\frac{R\theta}{v_0}\right) NV \left(1 + \frac{S}{NR}\right) \exp\left(-\frac{S}{NR}\right)
 \end{aligned}$$

Ebazpena

2. Lortu U barne-energia S , V eta N aldagaien funtzioan, aurrerko ariketako fisikoki onargarriak diren oinarrizko ekuazioen kasuetarako. (C 1.9.2)

Ebazpena

3. A sistemaren oinarrizko ekuazioa ondokoa da:

$$S_A = \left(\frac{R^2}{v_0\theta}\right)^{\frac{1}{3}} [N_A V_A U_A]^{\frac{1}{3}}$$

B sistemarena, berriz:

$$S_B = \left(\frac{R^2}{v_0\theta}\right)^{\frac{1}{3}} [N_B V_B U_B]^{\frac{1}{3}}$$

Zein da A + B sistema konposatuari dagokion oinarrizko ekuazioa ? (C 1.9.3)

Ebazpena

4. Onartu aurreko ariketan deskribatutako A eta B azpisistemen arteko bereizte-horma finkoa, iragaztezina eta energia trukatzeari utziko duena dela. Modu berean, demagun A sistemaren bolumena 3 cm^3 -koa dela, eta mol-kopurua 3. B sistemaren kasuan, bolumena 4 cm^3 -koa da, eta mol-kopurua 2. Sistema konposatuaren energia osoa 20 cal -koa da. Adieraz ezazu entropia A sistemari dagokion $\frac{U_A}{(U_A + U_B)}$ energia-frakzioaren funtzioan. Zenbatekoa da azpisistema bakoitzari dagokion barne-energia, sistemak oreka lortu duen kasurako ? (C 1.9.4)

Ebazpena

5. Lortu ondoko oinarrizko ekuazioko sistemari dagozkion hiru egoera-ekuazioak. (C 2.2.1)

$$U = \left(\frac{v_0 \theta}{R^2}\right) \frac{S^3}{NV}$$

Ebazpena

6. Lortu aurreko sistemari dagokion μ potentzial kimikoa; adieraz ezazu emaitza T , V eta N parametroen funtzioan. (C 2.2.2)

Ebazpena

7. Lortu aurreko sistemaren kasuan, eta tenperatura finkoa denean, presioak bolumenarekiko duen mendekotasuna, hautazkoa den eskalako diagraman. Irudikatu itzazu bi tenperatura desberdini dagozkion lerro isoterminoak; eta adieraz ezazu zein den bietatik tenperatura handienari dagokiona. (C 2.2.3)

Ebazpena

8. Lortu ondoko oinarritzko ekuazioko sistemari dagozkion hiru egoera-ekuazioak. (C 2.2.4)

$$U = \left(\frac{\theta}{R}\right) s^2 - \left(\frac{R\theta}{v_0^2}\right) v^2$$

Ebazpena

9. Lortu aurreko sistemari dagokion μ potentzial kimikoa; adieraz ezazu emaitza T , V eta N parametroen funtzioan. (C 2.2.5)

Ebazpena

10. Lortu ondoko oinarritzko ekuazioko sistemari dagozkion hiru egoera-ekuazioak. (C 2.2.6)

$$u = \left(\frac{v_0 \theta}{R}\right) \frac{s^2}{v} \exp\left(\frac{s}{R}\right)$$

Ebazpena

11. Adieraz ezazu eskematikoki, aurreko ariketako sistemaren kasuan, kuasiestatikoa den espantsio adiabatikoan zehar ($dS = 0$), tenperaturak bolumenarekiko duen mendekotasuna. (C 2.2.7)

Ebazpena

12. Lortu, adierazpen entropikoan, ondoko oinarritzko ekuazioko sistemari dagozkion hiru egoera-ekuazioak. (C 2.3.1)

$$u = \left(\frac{\frac{1}{2} \theta}{\frac{v_0^2}{R^2}}\right) \frac{s^{\frac{5}{2}}}{v^{\frac{1}{2}}}$$

Ebazpena

13. Lortu aurreko sistemaren kasuan, eta presioa finkoa den kasuan, tenperaturak bolumenarekiko duen mendekotasuna, hautazkoa den eskalako diagraman. Irudikatu itzazu bi presio desberdini dagozkion lerro isobaroak eta adierazi zein den bietatik presio handienari dagokiona. (C 2.3.2)

Ebazpena

14. Lortu, adierazpen entropikoan, ondoko oinarritzko ekuazioko sistemari dagozkion hiru egoera-ekuazioak: (C 2.3.3)

$$u = \left(\frac{\theta}{R}\right) s^2 \exp\left(\frac{v^2}{v_0^2}\right)$$

Ebazpena

15. Bi sistemari dagozkion egoera-ekuazioak ondokoak dira,

$$\frac{1}{T^{(1)}} = \frac{3}{2} R \frac{N^{(1)}}{U^{(1)}} \quad \frac{1}{T^{(2)}} = \frac{5}{2} R \frac{N^{(2)}}{U^{(2)}}$$

non $R = 1.986$ cal/mol K balioko konstantea den. Lehenengo sistemaren mol-kopurua $N^{(1)} = 2$ da, eta bigarrenarena $N^{(2)} = 3$. Sistema horiek diatermanoak den bereizte-hormak banatu ditu. Sistema konposatuaren energia 6000 cal-koa da. Oreka lortutakoan, zenbatekoa da sistema bakoitzari dagokion barne-energia ? (C 2.6.3)

Ebazpena

16. Aurreko ariketako azpisistemak, diatermanoak den bereizte-hormaren bidez banatuta daude. Mol-kopuruen balioak ondokoak dira: $N^{(1)} = 2$ eta $N^{(2)} = 3$. Hasierako tenperaturak $T^{(1)} = 250$ K eta $T^{(2)} = 350$ K-ekoak dira. Oreka lortutakoan, zein dira $U^{(1)}$ eta $U^{(2)}$ parametroen balioak ? Zein da oreka-tenperatura ? (C 2.6.4)

Ebazpena

17. Bi sistemari dagozkion egoera-ekuazioak ondokoak dira,

$$\frac{1}{T^{(1)}} = \frac{3}{2} R \frac{N^{(1)}}{U^{(1)}}, \frac{p^{(1)}}{T^{(1)}} = R \frac{N^{(1)}}{V^{(1)}} \quad \frac{1}{T^{(2)}} = \frac{5}{2} R \frac{N^{(2)}}{U^{(2)}}, \frac{p^{(2)}}{T^{(2)}} = R \frac{N^{(2)}}{V^{(2)}}$$

non $R = 1.986$ cal/mol K den. $N^{(1)} = 0.5$ eta $N^{(2)} = 0.75$ dira. Sistema biak isolaturiko zilindroaren barnean daude, higikorra den pistoi isoterminoak banandurik. Hasierako tenperaturak $T^{(1)} = 200$ K eta $T^{(2)} = 300$ K-ekoak dira, eta bolumen osoa 20 l-koa. Oreka lortutakoan, zein dira sistema bakoitzari dagozkion energia eta bolumena ? Zein dira presioa eta tenperatura ? (C 2.7.1)

Ebazpena

18. Bi osagaiko sistemari dagokion oinarritzko ekuazioa ondokoa da,

$$S = NA + NR \ln \left(\frac{U^{\frac{3}{2}} V}{N^{\frac{5}{2}}} \right) - N_1 R \ln \left(\frac{N_1}{N} \right) - N_2 R \ln \left(\frac{N_2}{N} \right)$$

$$N \equiv N_1 + N_2$$

non $R = 1.986$ cal/mol K den, eta A finkatugabeko konstantea. Lehenengo osagaiarekiko iragazkorra baina bigarrenarekiko ez den mintz diatermanoak bi gunetan zatitu du 10 l-ko bolumeneko eta itxita dagoen zilindro zurruna. Lehenengo gunean ondoko parametroez ezaugarritutako lagina kokatu da: $N_1^{(1)} = 0.5$, $N_2^{(1)} = 0.75$, $V^{(1)} = 5$ l eta $T^{(1)} = 300$ K. Bigarrenean, berriz, ondokoen bidez: $N_1^{(2)} = 0.5$, $N_2^{(2)} = 0.5$, $V^{(2)} = 5$ l eta $T^{(2)} = 250$ K. Oreka lortutakoan, zein dira $N_1^{(1)}$, $N_1^{(2)}$, T , $p^{(1)}$ eta $p^{(2)} = 300$ K parametroen balioak ? (C 2.8.1)

Ebazpena

$$S = NA + NR \ln \left[\frac{U^{\frac{3}{2}} V}{N^{\frac{5}{2}}} \right] - N_1 R \ln \left[\frac{N_1}{N} \right] - N_2 R \ln \left[\frac{N_2}{N} \right]$$

$$N = N_1 + N_2$$

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U} \right)_{V, N_1, N_2} \Rightarrow \frac{1}{T} = NR \frac{3}{2} \frac{1}{U}$$

$$\frac{p}{T} = \left(\frac{\partial U}{\partial V} \right)_{S, N_1, N_2} \Rightarrow \frac{p}{T} = NR \frac{1}{V}$$

$$\frac{\mu_1}{T} = - \left(\frac{\partial U}{\partial N_1} \right)_{S, V, N_2} \Rightarrow \frac{\mu_1}{T} = -A + \frac{5}{2} R - R \ln \left[\frac{U^{\frac{3}{2}} V}{N^{\frac{3}{2}} N_1} \right]$$

$$\frac{\mu_2}{T} = - \left(\frac{\partial U}{\partial N_2} \right)_{S, V, N_1} \Rightarrow \frac{\mu_2}{T} = -A + \frac{5}{2} R - R \ln \left[\frac{U^{\frac{3}{2}} V}{N^{\frac{3}{2}} N_2} \right]$$

$$\left\{ \begin{array}{l} S = NA + NR \ln \left[\frac{U^{\frac{3}{2}} V}{N^{\frac{5}{2}}} \right] - N_1 R \ln \left[\frac{N_1}{N} \right] - N_2 R \ln \left[\frac{N_2}{N} \right] \\ N = N_1 + N_2 \\ U = U_1 + U_2 \end{array} \right\}^{(i)} \quad i = 1, 2 \Rightarrow$$

$$\left. \begin{array}{l} S^{(i)} = N^{(i)} A + N^{(i)} R \ln \left[\frac{U^{(i)\frac{3}{2}} V^{(i)}}{N^{(i)\frac{5}{2}}} \right] - N_1^{(i)} R \ln \left[\frac{N_1^{(i)}}{N} \right] - N_2^{(i)} R \ln \left[\frac{N_2^{(i)}}{N} \right] \\ N^{(i)} = N_1^{(i)} + N_2^{(i)} \\ U^{(i)} = U_1^{(i)} + U_2^{(i)} \end{array} \right\} i = 1, 2 \Rightarrow$$

$$S^{(i)} = \left(N_1^{(i)} + N_2^{(i)} \right) A + N^{(i)} R \ln \left[\frac{\left(U_1^{(i)} + U_2^{(i)} \right)^{\frac{3}{2}} V^{(i)}}{\left(N_1^{(i)} + N_2^{(i)} \right)^{\frac{5}{2}}} \right] - N_1^{(i)} R \ln \left[\frac{N_1^{(i)}}{\left(N_1^{(i)} + N_2^{(i)} \right)} \right] - N_2^{(i)} R \ln \left[\frac{N_2^{(i)}}{\left(N_1^{(i)} + N_2^{(i)} \right)} \right]$$

$$i = 1, 2$$

$$\left(\frac{1}{T} \right)^{(i)} = \left(\frac{\partial S^{(i)}}{\partial U^{(i)}} \right)_{V, N_1^{(i)}, N_2^{(i)}} \Rightarrow \left(\frac{1}{T} \right)^{(i)} = N^{(i)} R \frac{3}{2} \frac{1}{U^{(i)}}$$

$$\left(\frac{p}{T} \right)^{(i)} = \left(\frac{\partial U^{(i)}}{\partial V^{(i)}} \right)_{S, N_1^{(i)}, N_2^{(i)}} \Rightarrow \left(\frac{p}{T} \right)^{(i)} = N^{(i)} R \frac{1}{V^{(i)}}$$

$$\left(\frac{\mu_1}{T} \right)^{(i)} = - \left(\frac{\partial U^{(i)}}{\partial N_1^{(i)}} \right)_{S, V, N_2^{(i)}} \Rightarrow \left(\frac{\mu_1}{T} \right)^{(i)} = -A + \frac{5}{2} R - R \ln \left[\frac{U^{(i)\frac{3}{2}} V^{(i)}}{\left(N_1^{(i)} + N_2^{(i)} \right)^{\frac{3}{2}} N_1^{(i)}} \right]$$

$$\left(\frac{\mu_2}{T} \right)^{(i)} = - \left(\frac{\partial U^{(i)}}{\partial N_2^{(i)}} \right)_{S, V, N_1^{(i)}} \Rightarrow \left(\frac{\mu_2}{T} \right)^{(i)} = -A + \frac{5}{2} R - R \ln \left[\frac{U^{(i)\frac{3}{2}} V^{(i)}}{\left(N_1^{(i)} + N_2^{(i)} \right)^{\frac{3}{2}} N_2^{(i)}} \right]$$

$$\left. \begin{array}{l} dS^{\text{osoa}} = 0 \\ dS^{\text{osoa}} = dS^{(1)} + dS^{(2)} \end{array} \right\} \Rightarrow dS^{(1)} + dS^{(2)} = 0$$

$$\begin{aligned}
dS^{(1)} &= \left(\frac{1}{T}\right)^{(1)} dU^{(1)} + \left(\frac{p}{T}\right)^{(1)} dV^{(1)} - \left(\frac{\mu_1}{T}\right)^{(1)} dN_1^{(1)} - \left(\frac{\mu_2}{T}\right)^{(1)} dN_2^{(1)} \\
&+ \\
dS^{(2)} &= \left(\frac{1}{T}\right)^{(2)} dU^{(2)} + \left(\frac{p}{T}\right)^{(2)} dV^{(2)} - \left(\frac{\mu_1}{T}\right)^{(2)} dN_1^{(2)} - \left(\frac{\mu_2}{T}\right)^{(2)} dN_2^{(2)}
\end{aligned}$$

$$\begin{aligned}
dS^{\text{osoa}} &= \left\{ \left(\frac{1}{T}\right)^{(1)} - \left(\frac{1}{T}\right)^{(2)} \right\} dU^{(1)} + \left\{ \left(\frac{p}{T}\right)^{(1)} - \left(\frac{p}{T}\right)^{(2)} \right\} dV^{(1)} - \\
&- \left\{ \left(\frac{\mu_1}{T}\right)^{(1)} - \left(\frac{\mu_1}{T}\right)^{(2)} \right\} dN_1^{(1)} - \left\{ \left(\frac{\mu_2}{T}\right)^{(1)} - \left(\frac{\mu_2}{T}\right)^{(2)} \right\} dN_2^{(1)}
\end{aligned}$$

$$U^{(1)} + U^{(2)} = \text{Konst.} \Rightarrow dU^{(1)} + dU^{(2)} = 0 \Rightarrow dU^{(2)} = -dU^{(1)}$$

$$V^{(1)} + V^{(2)} = \text{Konst.} \Rightarrow dV^{(1)} + dV^{(2)} = 0 \Rightarrow dV^{(2)} = -dV^{(1)}$$

$$N_1^{(1)} + N_1^{(2)} = \text{Konst.} \Rightarrow dN_1^{(1)} + dN_1^{(2)} = 0 \Rightarrow dN_1^{(2)} = -dN_1^{(1)}$$

$$N_2^{(1)} + N_2^{(2)} = \text{Konst.} \Rightarrow dN_2^{(1)} + dN_2^{(2)} = 0 \Rightarrow dN_2^{(1)} = -dN_2^{(2)}$$

$$\left\{ \left(\frac{1}{T}\right)^{(1)} - \left(\frac{1}{T}\right)^{(2)} \right\} = 0 \Rightarrow \left(\frac{1}{T}\right)^{(1)} = \left(\frac{1}{T}\right)^{(2)} \Rightarrow N^{(1)} R_2^{\frac{3}{2}} \frac{1}{U^{(1)}} = N^{(2)} R_2^{\frac{3}{2}} \frac{1}{U^{(2)}} \Rightarrow \boxed{\frac{N^{(1)}}{U^{(1)}} = \frac{N^{(2)}}{U^{(2)}}}$$

$$\left\{ \left(\frac{p}{T}\right)^{(1)} - \left(\frac{p}{T}\right)^{(2)} \right\} = 0 \Rightarrow \left(\frac{p}{T}\right)^{(1)} = \left(\frac{p}{T}\right)^{(2)} \Rightarrow N^{(1)} R \frac{1}{V^{(1)}} = N^{(2)} R \frac{1}{V^{(2)}} \Rightarrow \boxed{\frac{N^{(1)}}{V^{(1)}} = \frac{N^{(2)}}{V^{(2)}}}$$

$$\left\{ \left(\frac{\mu_1}{T}\right)^{(1)} - \left(\frac{\mu_1}{T}\right)^{(2)} \right\} = 0 \Rightarrow \left(\frac{\mu_1}{T}\right)^{(1)} = \left(\frac{\mu_1}{T}\right)^{(2)} \Rightarrow$$

$$-A + \frac{5}{2}R - R \ln \left[\frac{U^{(1)\frac{3}{2}} V^{(1)}}{(N_1^{(1)} + N_2^{(1)})^{\frac{3}{2}} N_1^{(1)}} \right] = -A + \frac{5}{2}R - R \ln \left[\frac{U^{(2)\frac{3}{2}} V^{(2)}}{(N_1^{(2)} + N_2^{(2)})^{\frac{3}{2}} N_1^{(2)}} \right] \Rightarrow$$

$$\frac{U^{(1)\frac{3}{2}} V^{(1)}}{(N_1^{(1)} + N_2^{(1)})^{\frac{3}{2}} N_1^{(1)}} = \frac{U^{(2)\frac{3}{2}} V^{(2)}}{(N_1^{(2)} + N_2^{(2)})^{\frac{3}{2}} N_1^{(2)}} \Rightarrow \boxed{\frac{U^{(1)\frac{3}{2}} V^{(1)}}{N_1^{(1)}} = \frac{U^{(2)\frac{3}{2}} V^{(2)}}{N_1^{(2)}}}$$

$$\left\{ \left(\frac{\mu_2}{T}\right)^{(1)} - \left(\frac{\mu_2}{T}\right)^{(2)} \right\} = 0 \Rightarrow \left(\frac{\mu_2}{T}\right)^{(1)} = \left(\frac{\mu_2}{T}\right)^{(2)} \Rightarrow$$

$$-A + \frac{5}{2}R - R \ln \left[\frac{U^{(1)\frac{3}{2}} V^{(1)}}{(N_1^{(1)} + N_2^{(1)})^{\frac{3}{2}} N_2^{(1)}} \right] = -A + \frac{5}{2}R - R \ln \left[\frac{U^{(2)\frac{3}{2}} V^{(2)}}{(N_1^{(2)} + N_2^{(2)})^{\frac{3}{2}} N_2^{(2)}} \right]$$

$$\frac{U^{(1)\frac{3}{2}} V^{(1)}}{(N_1^{(1)} + N_2^{(1)})^{\frac{3}{2}} N_2^{(1)}} = \frac{U^{(2)\frac{3}{2}} V^{(2)}}{(N_1^{(2)} + N_2^{(2)})^{\frac{3}{2}} N_2^{(2)}} \Rightarrow \boxed{\frac{U^{(1)\frac{3}{2}} V^{(1)}}{N_2^{(1)}} = \frac{U^{(2)\frac{3}{2}} V^{(2)}}{N_2^{(2)}}}$$

$$\begin{aligned}
dS^{(1)} &= \left(\frac{1}{T}\right)^{(1)} dU^{(1)} + \left(\frac{p}{T}\right)^{(1)} dV^{(1)} - \left(\frac{\mu_1}{T}\right)^{(1)} dN_1^{(1)} - \left(\frac{\mu_2}{T}\right)^{(1)} dN_2^{(1)} \\
&+ \\
dS^{(2)} &= \left(\frac{1}{T}\right)^{(2)} dU^{(2)} + \left(\frac{p}{T}\right)^{(2)} dV^{(2)} - \left(\frac{\mu_1}{T}\right)^{(2)} dN_1^{(2)} - \left(\frac{\mu_2}{T}\right)^{(2)} dN_2^{(2)}
\end{aligned}$$

$$dS^{\text{osoa}} = \left\{ \left(\frac{1}{T} \right)^{(1)} - \left(\frac{1}{T} \right)^{(2)} \right\} dU^{(1)} + \left\{ \left(\frac{p}{T} \right)^{(1)} - \left(\frac{p}{T} \right)^{(2)} \right\} dV^{(1)} - \\ - \left\{ \left(\frac{\mu_1}{T} \right)^{(1)} - \left(\frac{\mu_1}{T} \right)^{(2)} \right\} dN_1^{(1)} - \left\{ \left(\frac{\mu_2}{T} \right)^{(1)} - \left(\frac{\mu_2}{T} \right)^{(2)} \right\} dN_2^{(1)}$$

$$U^{(1)} + U^{(2)} = \text{Konst.} \Rightarrow dU^{(1)} + dU^{(2)} = 0 \Rightarrow dU^{(2)} = -dU^{(1)}$$

$$\left\{ U^{(1)} + U^{(2)} \right\}^{(i)} = \left\{ \left(N_1^{(1)} + \frac{3}{4} \right) R \frac{3}{2} T^{(1)} + \left(N_1^{(2)} + \frac{1}{2} \right) R \frac{3}{2} T^{(2)} \right\}^{(i)}$$

$$\left\{ U^{(1)} + U^{(2)} \right\} = \left\{ \left(\frac{1}{2} + \frac{3}{4} \right) R \frac{3}{2} 300 + \left(1 + \frac{1}{2} \right) R \frac{3}{2} 250 \right\} \Rightarrow U^{(1)} + U^{(2)} = R \frac{3}{2} \left(\frac{5}{4} 300 + \frac{3}{2} 250 \right) = 1125R$$

$$U^{(1)} + U^{(2)} = 1125R$$

$$V^{(1)} = \text{Konst.} \Rightarrow dV^{(1)} = 0$$

$$V^{(2)} = \text{Konst.} \Rightarrow dV^{(2)} = 0$$

$$V^{(1)} = V^{(2)} = V$$

$$N_1^{(1)} + N_1^{(2)} = \text{Konst.} \Rightarrow dN_1^{(1)} + dN_1^{(2)} = 0 \Rightarrow dN_1^{(2)} = -dN_1^{(1)}$$

$$N_2^{(1)} = \text{Konst.} \Rightarrow dN_2^{(1)} = 0$$

$$N_2^{(2)} = \text{Konst.} \Rightarrow dN_2^{(2)} = 0$$

$$N_2^{(1)} = \frac{3}{4}$$

$$N_2^{(2)} = \frac{1}{2}$$

$$\left. \begin{aligned} \left\{ \left(\frac{1}{T} \right)^{(1)} - \left(\frac{1}{T} \right)^{(2)} \right\} = 0 &\Rightarrow \left(\frac{1}{T} \right)^{(1)} = \left(\frac{1}{T} \right)^{(2)} \Rightarrow \frac{\left(N_1^{(1)} + \frac{3}{4} \right)}{U^{(1)}} = \frac{\left(N_1^{(2)} + \frac{1}{2} \right)}{U^{(2)}} \\ \left\{ \left(\frac{\mu_1}{T} \right)^{(1)} - \left(\frac{\mu_1}{T} \right)^{(2)} \right\} = 0 &\Rightarrow \left(\frac{\mu_1}{T} \right)^{(1)} = \left(\frac{\mu_1}{T} \right)^{(2)} \Rightarrow \frac{U^{(1) \frac{3}{2}}}{\left(N_1^{(1)} + \frac{3}{4} \right)^{\frac{3}{2}} N_1^{(1)}} = \frac{U^{(2) \frac{3}{2}}}{\left(N_1^{(2)} + \frac{1}{2} \right)^{\frac{3}{2}} N_1^{(2)}} \\ U^{(1)} + U^{(2)} &= 1125R \\ N_1^{(1)} + N_1^{(2)} &= \frac{3}{2} \end{aligned} \right\} \Rightarrow$$

$N_1^{(1)} = N_1^{(2)} = \frac{3}{4}$ $U^{(1)} = \frac{6}{5} U^{(2)} \Rightarrow U^{(2)} = \frac{5}{11} U^{(\text{osoa})} \Rightarrow U^{(1)} = \frac{6}{11} U^{(\text{osoa})}$ $T = \frac{8}{33} \frac{1}{R} U^{(\text{osoa})}$ $\left(\frac{p}{T} \right)^{(1)} = \frac{4}{55} U^{(\text{osoa})}$ $\left(\frac{p}{T} \right)^{(2)} = \frac{2}{33} U^{(\text{osoa})}$
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19. He gasa duen gordailuak 1000 l-ko bolumeneko da. Gasa 0.5 atm-n eta 20 °C-ko tenperaturan dago. Bolumen berdineko bigarren gordailuan dagoen He gasa 1 atm-n eta 80 °C-ko tenperaturan dago. Gordailu biak loturik dituen balbula ireki da. Demagun aipatu gasa monoatomikoa eta ideala dela, eta gordailuen hormak finkoak eta adiabatikoak. Lortu sistemari dagozkion amaierako tenperatura eta presioa. Kontura zaitenez energia osoa konstantea dela. (C 3.4.4)

0.1.2 Maxwell-en erlazioak eta Kalkulu Termodinamikoa

Ebazpena

20. Aztertuko dugun sistema alboko irudian ageri dena da; 1 eta 2 zilindroek osatu dute. Irudian ikus daitekeenez lehenengoa bigarrenaren barnean higi daiteke. Bien artean ez dago marruskadurarik. Irudiko marrazturiko hormak adiabatikoak dira; eta besteak, aldiz, diatermanoak. Hasiera batean sistema osoa oreka-egoeran dago. 1 zilindroa T tenperaturako eta p presioko iturriarekin kontaktuan jarri dugu. Efizientzia maximoko punpa dugu, zeinak eskura dugun iturritik beroa ateraz, 1 zilindrotik ateratako bero osoa 2 zilindroari emango dion. Prozesu honek iturriarekiko oreka lortu arte iraungo du. Lortu:

- (a) zilindroen bukaerako tenperaturak eta 2 zilindroaren bukaerako bolumena,
- (b) bi sistemetako entropia-aldakuntzak,
- (c) punpak egindako lana eta
- (d) inguruneari dagokion entropia-aldakuntza.
- (e) Eztabaidatu kualitatiboki zenbatekoa izango den sistema osoaren entropia-aldakuntza.

Ebazpena

21. Lortu $\left(\frac{\partial T}{\partial v}\right)_h$ koefizienteari dagokion adierazpena, (C_p, α, κ_T) sortaren funtzioan. (C 7.4.1)

Ebazpena

$$\left(\frac{\partial T}{\partial v}\right)_h = -\frac{\left(\frac{\partial h}{\partial v}\right)_T}{\left(\frac{\partial h}{\partial T}\right)_v}$$

$$dh = Tds + vdp$$

$$\left(\frac{\partial h}{\partial v}\right)_T = \left(\frac{\partial(Tds + vdp)}{\partial v}\right)_T = T\left(\frac{\partial s}{\partial v}\right)_T + v\left(\frac{\partial p}{\partial v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v + v\frac{1}{\left(\frac{\partial v}{\partial p}\right)_T} = T\frac{\alpha}{\kappa_T} - \frac{1}{\kappa_T} = \frac{1}{\kappa_T}(T\alpha - 1)$$

$$\left(\frac{\partial h}{\partial T}\right)_v = \left(\frac{\partial(Tds + vdp)}{\partial T}\right)_v = T\left(\frac{\partial s}{\partial T}\right)_v + v\left(\frac{\partial p}{\partial T}\right)_v = c_V + v\frac{\alpha}{\kappa_T}$$

$$\left. \begin{aligned} c_p - c_V &= \frac{Tv\alpha^2}{\kappa_T} \\ \left(\frac{\partial T}{\partial v}\right)_h &= -\frac{\frac{1}{\kappa_T}(T\alpha - 1)}{Tc_V + v\frac{\alpha}{\kappa_T}} \end{aligned} \right\} \Rightarrow \left(\frac{\partial T}{\partial v}\right)_h = -\frac{(T\alpha - 1)}{\kappa_T c_V + v\alpha}$$

22. Esku artean dugun gas errealearen bi molekulak 100 K-eko tenperaturan eta 2 MPa-eko presioan litro bateko gordailua bete dute. 10 cm³-ko balioko bolumenera era askean espantsionatu dadila utzi diogu gasari. Lortu entalpia-aldakuntza. Hasierako egoerari dagozkion datuak honako hauek dira: $C_p = 0.8$ J/mol K, $\kappa_T = 3 \times 10^6$ Pa⁻¹ eta $\alpha = 0.002$ K⁻¹. (C 7.4.6)

Ebazpena Espantsioa askea denez, $U = \text{konst.}$ -ko prozesua da; eta aldagai independentea V bolumena; beraz, kalkulatu beharreko koefizientea ondoko hau da: $\left(\frac{\partial h}{\partial v}\right)_u$

$$dh = Tds + vdp$$

$$\left(\frac{\partial h}{\partial v}\right)_u = \left(\frac{\partial(Tds + vdp)}{\partial v}\right)_u \Rightarrow \left(\frac{\partial h}{\partial v}\right)_u = T\left(\frac{\partial s}{\partial v}\right)_u + v\left(\frac{\partial p}{\partial v}\right)_u = -T\left(\frac{\partial u}{\partial s}\right)_v - v\left(\frac{\partial u}{\partial p}\right)_v$$

$$du = sdT - pdv$$

$$\left. \begin{aligned} \left(\frac{\partial u}{\partial v}\right)_s &= \left(\frac{\partial(Tds - pdv)}{\partial v}\right)_s = T\left(\frac{\partial s}{\partial v}\right)_s - p\left(\frac{\partial v}{\partial v}\right)_s = -p \\ \left(\frac{\partial u}{\partial s}\right)_v &= \left(\frac{\partial(Tds - pdv)}{\partial s}\right)_v = T\left(\frac{\partial s}{\partial s}\right)_v - p\left(\frac{\partial v}{\partial s}\right)_v = T \end{aligned} \right\} \Rightarrow -T\left(\frac{\partial u}{\partial s}\right)_v = p$$

$$\left. \begin{aligned} \left(\frac{\partial u}{\partial v}\right)_p &= \left(\frac{\partial(Tds - pdv)}{\partial v}\right)_p = T\left(\frac{\partial s}{\partial v}\right)_p - p\left(\frac{\partial v}{\partial v}\right)_p = T\left(\frac{\partial s}{\partial T}\right)_p\left(\frac{\partial T}{\partial v}\right)_p - p = c_p\frac{1}{v\alpha} - p \\ \left(\frac{\partial u}{\partial p}\right)_v &= \left(\frac{\partial(Tds - pdv)}{\partial p}\right)_v = T\left(\frac{\partial s}{\partial p}\right)_v - p\left(\frac{\partial v}{\partial p}\right)_v = T\left(\frac{\partial s}{\partial T}\right)_v\left(\frac{\partial T}{\partial p}\right)_v = c_V\frac{\kappa_T}{\alpha} \end{aligned} \right\} \Rightarrow$$

$$-v\left(\frac{\partial u}{\partial p}\right)_v = -v\frac{c_p\frac{1}{v\alpha} - p}{c_V\frac{\kappa_T}{\alpha}}$$

$$\left(\frac{\partial h}{\partial v}\right)_u = p - v\frac{c_p\frac{1}{v\alpha} - p}{c_V\frac{\kappa_T}{\alpha}} \Rightarrow \left(\frac{\partial h}{\partial v}\right)_u = p - \frac{v\alpha(c_p - p)}{c_V\kappa_T}$$

23. Frogatu ondoko berdintza beteko dela; eta lortu horri dagokion adierazpena *van der Waals*-en gasaren kasurako: (C 7.4.7)

$$\left(\frac{\partial c_v}{\partial v}\right)_T = T\left(\frac{\partial^2 p}{\partial T^2}\right)_v$$

Ebazpena

$$\left(\frac{\partial c_v}{\partial v}\right)_T = \left(\frac{\partial\left\{T\left(\frac{\partial s}{\partial T}\right)_v\right\}}{\partial v}\right)_T \Rightarrow \left(\frac{\partial c_v}{\partial v}\right)_T = \left(\frac{\partial T}{\partial v}\right)_T\left(\frac{\partial s}{\partial T}\right)_v + T\left(\frac{\partial^2 s}{\partial v\partial T}\right) \Rightarrow \left(\frac{\partial c_v}{\partial v}\right)_T = T\left(\frac{\partial^2 s}{\partial T\partial v}\right) \Rightarrow$$

$$\left(\frac{\partial c_v}{\partial v}\right)_T = T\left(\frac{\partial\left(\frac{\partial s}{\partial T}\right)_v}{\partial T}\right)_v \Rightarrow \left(\frac{\partial c_v}{\partial v}\right)_T = T\left(\frac{\partial\left(\frac{\partial p}{\partial T}\right)_v}{\partial T}\right)_v \Rightarrow \boxed{\left(\frac{\partial c_v}{\partial v}\right)_T = T\left(\frac{\partial^2 p}{\partial T^2}\right)_v}$$

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT \Rightarrow p = \frac{RT}{(v-b)} - \frac{a}{v^2}$$

$$\left(\frac{\partial^2 p}{\partial T^2}\right)_v = \left(\frac{\partial^2\left(\frac{RT}{(v-b)} - \frac{a}{v^2}\right)}{\partial T^2}\right)_v \Rightarrow \left(\frac{\partial^2 p}{\partial T^2}\right)_v = \left(\frac{\partial\left(\frac{RT}{(v-b)}\right)}{\partial T}\right)_v \Rightarrow \left(\frac{\partial^2 p}{\partial T^2}\right)_v = 0$$

24. Frogatu ondoko berdintza beteko dela:

$$\left(\frac{\partial c_p}{\partial p}\right)_T = -Tv\left[\alpha^2 + \left(\frac{\partial \alpha}{\partial T}\right)_p\right]$$

Lortu berdintza horri dagokion adierazpena ondoko egoera-ekuazioa beteko duen sistemaren kasurako: (C 7.4.8)

$$p\left(v + \frac{A}{T^2}\right) = RT$$

Ebazpena

$$\begin{aligned}
\left(\frac{\partial c_p}{\partial p}\right)_T &= \left(\frac{\partial \left\{T \left(\frac{\partial s}{\partial T}\right)_p\right\}}{\partial p}\right)_T \Rightarrow \left(\frac{\partial c_p}{\partial p}\right)_T = \left(\frac{\partial T}{\partial p}\right)_T \left(\frac{\partial s}{\partial T}\right)_p + T \left(\frac{\partial^2 s}{\partial p \partial T}\right) \Rightarrow \left(\frac{\partial c_p}{\partial p}\right)_T = T \left(\frac{\partial^2 s}{\partial T \partial p}\right) \Rightarrow \\
\left(\frac{\partial c_p}{\partial p}\right)_T &= T \left(\frac{\partial \left(\frac{\partial s}{\partial T}\right)_T}{\partial T}\right)_p \Rightarrow \left(\frac{\partial c_p}{\partial p}\right)_T = T \left(\frac{\partial \left(-\frac{\partial v}{\partial T}\right)_p}{\partial T}\right)_p \Rightarrow \left(\frac{\partial c_p}{\partial p}\right)_T = T \left(\frac{\partial (-v\alpha)_p}{\partial T}\right)_p \Rightarrow \\
\left(\frac{\partial c_p}{\partial p}\right)_T &= -T \left(\left(\frac{\partial v}{\partial T}\right)_p \alpha + v \left(\frac{\partial \alpha}{\partial T}\right)_p\right)_p \Rightarrow \left(\frac{\partial c_p}{\partial p}\right)_T = -T \left(v\alpha^2 + v \left(\frac{\partial \alpha}{\partial T}\right)_p\right)_p \Rightarrow \\
\boxed{\left(\frac{\partial c_p}{\partial p}\right)_T} &= -T v \left(\alpha^2 + \left(\frac{\partial \alpha}{\partial T}\right)_p\right)_p
\end{aligned}$$

$$p \left(v + \frac{A}{T^2}\right) = RT \Rightarrow v = \frac{RT}{p} - \frac{A}{T^2}$$

$$\alpha = \frac{1}{v} \left(\frac{\partial v}{\partial T}\right)_p \Rightarrow \alpha = \frac{1}{\left(\frac{RT}{p} - \frac{A}{T^2}\right)} \left(\frac{\partial \left(\frac{RT}{p} - \frac{A}{T^2}\right)}{\partial T}\right)_p \Rightarrow \alpha = \frac{1}{\left(\frac{RT}{p} - \frac{A}{T^2}\right)} \left(\frac{R}{p} + \frac{2A}{T^3}\right)$$

$$\alpha^2 = \left(\frac{1}{\left(\frac{RT}{p} - \frac{A}{T^2}\right)} \left(\frac{R}{p} + \frac{2A}{T^3}\right)\right)^2$$

$$\left(\frac{\partial \alpha}{\partial T}\right)_p = \left(\frac{\partial \left(\frac{1}{\left(\frac{RT}{p} - \frac{A}{T^2}\right)} \left(\frac{R}{p} + \frac{2A}{T^3}\right)\right)}{\partial T}\right)_p$$

25. Aurreko ariketako mol bati p_0 hasierako presiotik p_f bukaerako presiorainoko espantsio isotermaoa eragin diogu. Lortu prozesuan sistemak trukatu duen bero-kantitatea. (C 7.4.9)

Ebazpena Sistemari, presioa aldatuz, espantsioa eragin diogu; beraz, aldagai independentea p presioa da. Beroaz galdatu dutenez, tenperatura konstanteko prozesuan, ondokoa adierazpena erabil dezakegu: $\delta Q = T dS$. Orduan, ondokoa da kalkulatu beharreko koefizientea: $\left(\frac{\partial S}{\partial p}\right)_T$.

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p \Rightarrow \left(\frac{\partial S}{\partial p}\right)_T = -V\alpha$$

$$dS = \left(\frac{\partial S}{\partial p}\right)_T dp \Rightarrow dS = (-V\alpha) dp \Rightarrow \int dS = \int (-V\alpha) dp$$

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p \Rightarrow \left(\frac{\partial S}{\partial p}\right)_T = -V\alpha$$

$$dS = \left(\frac{\partial S}{\partial p}\right)_T dp \Rightarrow dS = (-V\alpha) dp \Rightarrow \int dS = \int (-V\alpha) dp$$

$$\left. \begin{aligned} \alpha &= \frac{1}{\left(\frac{RT}{p} - \frac{A}{T^2}\right)} \left(\frac{R}{p} + \frac{2A}{T^3}\right) \\ v &= \frac{RT}{p} - \frac{A}{T^2} \end{aligned} \right\} \Rightarrow -V\alpha = -\left(\frac{R}{p} + \frac{2A}{T^3}\right)$$

$$\left. \begin{aligned} \Delta S &= \int -\left(\frac{R}{p} + \frac{2A}{T^3}\right) dp \Rightarrow \Delta S = -\left\{R \ln \frac{p_f}{p_i} + \frac{2A}{T^3} \Delta p\right\} \\ Q &= T \Delta S \end{aligned} \right\} \Rightarrow \boxed{Q = -T \left\{R \ln \frac{p_f}{p_i} + \frac{2A}{T^3} \Delta p\right\}}$$

26. *van der Waals*-en egoera-ekuazioa esleitu zaion 1 mol-eko sistemari v_0 hasierako bolumenetik v_f bukaerako bolumenerako espantsio isotermaoa eragin diogu. Lortu prozesuan trukaturiko bero-kantitatea. (C 7.4.10)

Ebazpena Sistemari, bolumena aldatuz, espantsioa eragin diogu; beraz, aldagai independentea v bolumena da. Berroaz galdatu dutenez, temperatura konstanteko prozesuan, ondokoa adierazpena erabil dezakegu: $\delta Q = TdS$. Orduan, ondokoa da kalkulatu beharreko koefizientea: $\left(\frac{\partial S}{\partial V}\right)_T$.

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

$$dS = \left(\frac{\partial S}{\partial V}\right)_T dV \Rightarrow dS = \frac{\alpha}{\kappa_T} dV \Rightarrow \int dS = \int \frac{\alpha}{\kappa_T} dV$$

van der Waals-en fluidoaren kasuan, hobea da $\left(\frac{\partial p}{\partial T}\right)_V$ koefizientea kalkulatzeko: egoera-ekuazioa hirugarren graduko polinomioa, bolumenean, baita. Orduan,

$$p = \frac{RT}{(v-b)} - \frac{a}{v^2}$$

$$-\left(\frac{\partial p}{\partial T}\right)_V = -\left(\frac{\partial \left(\frac{RT}{(v-b)} - \frac{a}{v^2}\right)}{\partial T}\right)_V \Rightarrow -\left(\frac{\partial p}{\partial T}\right)_V = -\frac{R}{(v-b)}$$

$$dS = -\left(\frac{\partial p}{\partial T}\right)_V dV \Rightarrow dS = -\frac{R}{(v-b)} dV \Rightarrow \int dS = \int \left(-\frac{R}{(v-b)}\right) dV$$

$$\left. \begin{array}{l} \Delta S = -R \ln \frac{(v_f - b)}{(v_i - b)} \\ Q = T \Delta S \end{array} \right\} \Rightarrow \boxed{Q = -RT \ln \frac{(v_f - b)}{(v_i - b)}}$$

27. Esku artean dugun oxigenoaren bi molak 0°C -ko tenperaturan eta 10^5 Pa-eko presioan daude. Konpresio adiabatikoaren bidez bukaerako tenperatura 300°C -ko balioraino eraman da. Lortu bukaerako presioaren balioa ondoko ekuazioa integratuz:

$$dT = \frac{T v \alpha}{c_p} dp$$

Onartu oxigenoa ondoko bero-ahalmeneko gas ideala dela: (C 7.4.11)

$$c_p = 26.20 + 11.49 \times 10^{-3} T - 3.223 \times 10^{-6} T^2$$

Ebazpena Lehenengo eta behin, kalkulatu dezagun ondoko koefizientea: $\left(\frac{\partial T}{\partial p}\right)_S$, aurreko adierazpenaren berdina dela konprobatzeko.

$$\left(\frac{\partial T}{\partial p}\right)_S = -\frac{\left(\frac{\partial S}{\partial p}\right)_T}{\left(\frac{\partial S}{\partial T}\right)_p} = -\frac{-\left(\frac{\partial V}{\partial T}\right)_p}{\frac{c_p}{T}} = \frac{T}{c_p} V \alpha \Rightarrow \left(\frac{\partial T}{\partial p}\right)_S = \frac{T v \alpha}{c_p}$$

$$\left. \begin{array}{l} dT = \left(\frac{\partial T}{\partial p}\right)_S dp \Rightarrow dT = \frac{T v \alpha}{c_p} dp \\ c_p = a + bT + cT^2 \end{array} \right\} \Rightarrow \frac{c_p dT}{T} = v \alpha dp \Rightarrow \frac{(a+bT+cT^2)dT}{T} = v \alpha dp$$

$$\Delta p = \frac{1}{v \alpha} \int \left(\frac{a}{T} + b + cT\right) dT \Rightarrow \Delta p = \frac{1}{v \alpha} \left\{ a \ln \frac{T_f}{T_i} + b(T_f - T_i) + \frac{1}{2} c(T_f^2 - T_i^2) \right\}$$

$$\boxed{p_f = p_i + \frac{1}{v \alpha} \left\{ a \ln \frac{T_f}{T_i} + b(T_f - T_i) + \frac{1}{2} c(T_f^2 - T_i^2) \right\}}$$

28. Sinplifikatu ondoko adierazpena: $\left(\frac{\partial u}{\partial p}\right)_h$. (C 7.4.13)

Ebazpena

$$du = Tds - pdv$$

$$\left(\frac{\partial u}{\partial p}\right)_h = \left(\frac{\partial(Tds - pdv)}{\partial p}\right)_h = T\left(\frac{\partial s}{\partial p}\right)_h - p\left(\frac{\partial v}{\partial p}\right)_h$$

$$\left(\frac{\partial s}{\partial p}\right)_h = -\left(\frac{\frac{\partial h}{\partial p}}{\left(\frac{\partial h}{\partial s}\right)_p}\right)_s = -\left(\frac{\frac{\partial(Tds + vdp)}{\partial p}}{\left(\frac{\partial(Tds + vdp)}{\partial s}\right)_p}\right)_s = -\frac{T\left(\frac{\partial s}{\partial p}\right)_s + v\left(\frac{\partial p}{\partial p}\right)_s}{T\left(\frac{\partial s}{\partial s}\right)_p + v\left(\frac{\partial p}{\partial s}\right)_p} = -\frac{v}{T}$$

$$\left(\frac{\partial v}{\partial p}\right)_h = -\left(\frac{\frac{\partial h}{\partial p}}{\left(\frac{\partial h}{\partial v}\right)_p}\right)_v = -\left(\frac{\frac{\partial(Tds + vdp)}{\partial p}}{\left(\frac{\partial(Tds + vdp)}{\partial v}\right)_p}\right)_v = -\frac{T\left(\frac{\partial s}{\partial p}\right)_v + v\left(\frac{\partial p}{\partial p}\right)_v}{T\left(\frac{\partial s}{\partial v}\right)_p + v\left(\frac{\partial p}{\partial v}\right)_p} = -\frac{T\left(\frac{\partial s}{\partial p}\right)_v + v}{T\left(\frac{\partial s}{\partial v}\right)_p} = -\frac{T\left(\frac{\partial s}{\partial T}\right)_v\left(\frac{\partial T}{\partial p}\right)_v + v}{T\left(\frac{\partial s}{\partial T}\right)_p\left(\frac{\partial T}{\partial v}\right)_p}$$

$$\left(\frac{\partial v}{\partial p}\right)_h = -\frac{c_V \frac{\kappa_T}{\alpha} + v}{c_p \frac{1}{v\alpha}} = -\frac{v\alpha}{c_p} (c_V \frac{\kappa_T}{\alpha} + v)$$

29. Espantsio askearen ondorioz esku artean dugun gasaren temperatura-aldakuntza dT da. Lortu presio-aldakuntza. (C 7.4.14)

Ebazpena Sistemari, bolumena aldatuz, espantsio askea eragin diogu; beraz, aldagai independentea v bolumena da. Espantsioa askea denez, U konstanteko prozesua da; eta presioaz galdetu dute, baina temperatura-aldakuntza ezagututa; orduan, ondokoa da kalkulatu beharreko koefizientea: $\left(\frac{\partial p}{\partial T}\right)_u$.

$$du = Tds - pdv$$

$$\left(\frac{\partial p}{\partial T}\right)_u = -\frac{\left(\frac{\partial u}{\partial T}\right)_p}{\left(\frac{\partial u}{\partial p}\right)_T} = -\frac{\left(\frac{\partial(Tds - pdv)}{\partial T}\right)_p}{\left(\frac{\partial(Tds - pdv)}{\partial p}\right)_T} = -\frac{T\left(\frac{\partial s}{\partial T}\right)_p - p\left(\frac{\partial v}{\partial T}\right)_p}{T\left(\frac{\partial s}{\partial p}\right)_T - p\left(\frac{\partial v}{\partial p}\right)_T} = -\frac{c_p - pv\alpha}{-T\left(\frac{\partial v}{\partial T}\right)_p - p\left(\frac{\partial v}{\partial p}\right)_T} = -\frac{c_p - pv\alpha}{-Tv\alpha + pv\kappa_T}$$

$$dp = \left(\frac{\partial p}{\partial T}\right)_u dT \Rightarrow dp = \left\{ -\frac{c_p - pv\alpha}{-Tv\alpha + pv\kappa_T} \right\} dT$$

30. Esku artean *van der Waals*-en fluidoaren 1 mol dugu: T_i temperaturan, eta V_i bolumena betez. Balbula bat irekiz gasa dagoen gordailua hasieran hutsik zegoen beste gordailu batekin konektatu dugu, gasa V_f bolumen osora hedatuz. Gordailuen hormak adiabatikoak dira. Lortu T_f bukaerako temperatura. (C 7.4.15)

Ebazpena Sistemari, bolumena aldatuz, espantsio askea eragin diogu; beraz, aldagai independentea v bolumena da. Espantsioa askea denez, U konstanteko prozesua da; eta temperaturaz galdetu dute; orduan, ondokoa da kalkulatu beharreko koefizientea: $\left(\frac{\partial T}{\partial v}\right)_u$.

$$du = Tds - pdv$$

$$\left(\frac{\partial T}{\partial v}\right)_u = -\frac{\left(\frac{\partial u}{\partial v}\right)_T}{\left(\frac{\partial u}{\partial T}\right)_v} = -\frac{\left(\frac{\partial(Tds - pdv)}{\partial v}\right)_T}{\left(\frac{\partial(Tds - pdv)}{\partial T}\right)_v} = -\frac{T\left(\frac{\partial s}{\partial v}\right)_T - p\left(\frac{\partial v}{\partial v}\right)_T}{T\left(\frac{\partial s}{\partial T}\right)_v - p\left(\frac{\partial v}{\partial T}\right)_v} = -\frac{T\left(\frac{\partial p}{\partial T}\right)_v - p}{T\left(\frac{\partial s}{\partial T}\right)_v} = -\frac{1}{c_V} \left(T \frac{\alpha}{\kappa_T} - p \right)$$

$$dT = \left(\frac{\partial T}{\partial v}\right)_u dv \Rightarrow dT = \left\{ -\frac{1}{c_V} \left(T \frac{\alpha}{\kappa_T} - p \right) \right\} dv$$

$$\begin{aligned}
& \left. \begin{aligned} (p + \frac{a}{v^2})(v - b) &= RT \Rightarrow p = \frac{RT}{(v-b)} - \frac{a}{v^2} \\ \alpha = \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_p &= -\frac{1}{v} \frac{\left(\frac{\partial p}{\partial T} \right)_v}{\left(\frac{\partial p}{\partial v} \right)_T} \\ \kappa_T = -\frac{1}{v} \left(\frac{\partial v}{\partial p} \right)_T &= -\frac{1}{v} \frac{1}{\left(\frac{\partial p}{\partial v} \right)_T} \end{aligned} \right\} \Rightarrow \frac{\alpha}{\kappa_T} = \frac{\left(-\frac{1}{v} \frac{\left(\frac{\partial p}{\partial T} \right)_v}{\left(\frac{\partial p}{\partial v} \right)_T} \right)}{\left(-\frac{1}{v} \frac{1}{\left(\frac{\partial p}{\partial v} \right)_T} \right)} \Rightarrow \frac{\alpha}{\kappa_T} = \left(\frac{\partial p}{\partial T} \right)_v \Rightarrow \frac{\alpha}{\kappa_T} = \frac{R}{(v-b)} \Rightarrow \\
& dT = \left\{ -\frac{1}{c_V} \left(T \frac{R}{(v-b)} - p \right) \right\} dv \Rightarrow dT = \left\{ -\frac{1}{c_V} \frac{a}{v^2} \right\} dv \Rightarrow \int dT = \int \left\{ -\frac{1}{c_V} \frac{a}{v^2} \right\} dv \Rightarrow \\
& \Delta T = \frac{a}{c_V} \left(\frac{1}{v_f} - \frac{1}{v_i} \right) \Rightarrow \boxed{T_f = T_i + \frac{a}{c_V} \left(\frac{1}{v_f} - \frac{1}{v_i} \right)}
\end{aligned}$$

31. Ebatz ezazu aurreko ariketa berbera baina kasu honetan espantsioa adiabatikoa izateaz gain kuasiestatikoa dela onartuz. (C 7.4.16)

Ebazpena Sistemari, bolumena aldatuz, espantsio aske kuasiestatikoa eragin diogu; beraz, aldagai independentea v bolumena da. Espantsioa aske kuasiestatikoa denez, s konstanteko prozesua da; eta tenperaturaz galdetu dute; orduan, ondokoa da kalkulatu beharreko koefizienteak: $\left(\frac{\partial T}{\partial v} \right)_s$.

$$\begin{aligned}
& \left(\frac{\partial T}{\partial v} \right)_s = -\frac{\left(\frac{\partial s}{\partial v} \right)_T}{\left(\frac{\partial s}{\partial T} \right)_v} = -\frac{\left(\frac{\partial p}{\partial T} \right)_v}{T \left(\frac{\partial s}{\partial T} \right)_v} = -\frac{1}{T} \frac{\alpha}{\kappa_T} = -\frac{T}{c_V} \frac{\alpha}{\kappa_T} \\
& dT = \left(\frac{\partial T}{\partial v} \right)_s dv \Rightarrow dT = \left\{ -\frac{T}{c_V} \frac{\alpha}{\kappa_T} \right\} dv \\
& \left. \begin{aligned} (p + \frac{a}{v^2})(v - b) &= RT \Rightarrow p = \frac{RT}{(v-b)} - \frac{a}{v^2} \\ \alpha = \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_p &= -\frac{1}{v} \frac{\left(\frac{\partial p}{\partial T} \right)_v}{\left(\frac{\partial p}{\partial v} \right)_T} \\ \kappa_T = -\frac{1}{v} \left(\frac{\partial v}{\partial p} \right)_T &= -\frac{1}{v} \frac{1}{\left(\frac{\partial p}{\partial v} \right)_T} \end{aligned} \right\} \Rightarrow \frac{\alpha}{\kappa_T} = \frac{\left(-\frac{1}{v} \frac{\left(\frac{\partial p}{\partial T} \right)_v}{\left(\frac{\partial p}{\partial v} \right)_T} \right)}{\left(-\frac{1}{v} \frac{1}{\left(\frac{\partial p}{\partial v} \right)_T} \right)} \Rightarrow \frac{\alpha}{\kappa_T} = \left(\frac{\partial p}{\partial T} \right)_v \Rightarrow \frac{\alpha}{\kappa_T} = \frac{R}{(v-b)} \Rightarrow \\
& dT = \left(\frac{\partial T}{\partial v} \right)_s dv \Rightarrow dT = \left\{ -\frac{T}{c_V} \frac{\alpha}{\kappa_T} \right\} dv \Rightarrow dT = -\frac{TR}{c_V(v-b)} dv \Rightarrow \frac{dT}{T} = -\frac{R}{c_V(v-b)} dv \Rightarrow \\
& \ln \frac{T_f}{T_i} = -\frac{R}{c_V} \ln \left(\frac{v_f - b}{v_i - b} \right) \Rightarrow \boxed{T_f = T_i \left[\frac{(v_f - b)}{(v_i - b)} \right]^{-\frac{R}{c_V}}}
\end{aligned}$$

32. Bolumenaren %1-eko beherakuntza adiabatikoak μ potentzial kimikoaren gainean aldakuntza jakina eragin du. Zein bolumen-portzentajek izango du eragin berbera beherakuntza isotermanoa bada? (C 7.4.17)

Ebazpena Ondoko bi koefiziente hauek kalkulatu eta alderatu behar ditugu: $\left(\frac{\partial \mu}{\partial v} \right)_s$ eta $\left(\frac{\partial \mu}{\partial v} \right)_T$.

$$d\mu = -sdT + vdp$$

$$\left(\frac{\partial \mu}{\partial v}\right)_s = \left(\frac{\partial(-sdT + vdp)}{\partial v}\right)_s = -s\left(\frac{\partial T}{\partial v}\right)_s + v\left(\frac{\partial p}{\partial v}\right)_s = -s\left(-\left(\frac{\partial s}{\partial v}\right)_T\right) + v\left(-\left(\frac{\partial s}{\partial p}\right)_v\right) \Rightarrow$$

$$\left(\frac{\partial \mu}{\partial v}\right)_s = s\frac{\left(\frac{\partial p}{\partial T}\right)_v}{\frac{c_V}{T}} - v\frac{\left(\frac{\partial s}{\partial T}\right)_p\left(\frac{\partial T}{\partial v}\right)_p}{\left(\frac{\partial s}{\partial T}\right)_v\left(\frac{\partial T}{\partial p}\right)_v} = s\frac{T}{c_V}\frac{\alpha}{\kappa_T} - v\frac{c_P\frac{1}{\left(\frac{\partial v}{\partial T}\right)_p}}{c_V\left(-\left(\frac{\partial p}{\partial T}\right)_p\right)} = s\frac{T}{c_V}\frac{\alpha}{\kappa_T} - \frac{c_P}{c_V\kappa_T} = -\frac{1}{c_V\kappa_T}(T\alpha s - c_P)$$

$$\left(\frac{\partial \mu}{\partial v}\right)_T = \left(\frac{\partial(-sdT + vdp)}{\partial v}\right)_T = -s\left(\frac{\partial T}{\partial v}\right)_T + v\left(\frac{\partial p}{\partial v}\right)_T = v\left(\frac{\partial p}{\partial v}\right)_T = v\frac{1}{\left(\frac{\partial v}{\partial p}\right)_T} = -\frac{1}{\kappa_T}$$

$$\left.\begin{aligned} \left(\frac{\partial \mu}{\partial v}\right)_s &= -\frac{1}{\kappa_T} \left\{ \frac{1}{c_V} (T\alpha s - c_P) \right\} \Rightarrow \left(\frac{\partial \mu}{\partial v}\right)_s = \left(\frac{\partial \mu}{\partial v}\right)_T \left\{ \frac{1}{c_V} (T\alpha s - c_P) \right\} \\ \left.\begin{aligned} d\mu &= \left(\frac{\partial \mu}{\partial v}\right)_s dv \\ d\mu &= \left(\frac{\partial \mu}{\partial v}\right)_T dv \end{aligned} \right\} \Rightarrow (d\mu)_s = (d\mu)_T \Rightarrow \left(\frac{\partial \mu}{\partial v}\right)_s = \left(\frac{\partial \mu}{\partial v}\right)_T \frac{dv}{v_o} 100 \Rightarrow \frac{dv}{v_o} 100 = \frac{\left(\frac{\partial \mu}{\partial v}\right)_s}{\left(\frac{\partial \mu}{\partial v}\right)_T} \Rightarrow \end{aligned}$$

$$\boxed{\frac{dv}{v_o} 100 = \left\{ \frac{1}{c_V} (T\alpha s - c_P) \right\}}$$

Ondoko bi ariketak elkarrekin aztertuko ditugu.

33. Helio gasa erabiliz beteriko zilindroa pistoi batek itxi du. Zilindroaren aldeko horma adiabatikoa, higiezina eta helioarekiko iragaztezina da. Zilindroaren beheko aldea, berriz, isotermaoa, higiezina eta helioarekiko iragazkorra da. Horma horren bidez, zilindroa T tenperaturako bero-iturriarekin eta μ_{He} potentzial kimiko-k materia-iturriarekin kontaktuan dago. Lortu sistemari dagokion $(-\frac{1}{V}\frac{dV}{dp})$ konpresibilitatea; frogatu ezazu konpresibilitateak dibergentzia izango duela. Zein da dibergentzia horren jatorri fisikoa? (C 7.4.18)
34. Aurreko ariketako zilindroa Ne gasa erabiliz bete dugu: $\frac{1}{10}$ mol sartuz. Aipatu zilindroaren beheko horma ez da neonarekiko iragazkorra. Lortu zilindroko presioaren balioa eta sistemaren konpresibilitatea. (C 7.4.19)

Ebazpena Baldintza esperimentalen arabera, sistemaren tenperatura eta sisteman dagoen helioaren potentzial kimikoaren balioak finkoak dira: bero-iturri batekin eta materia-iturri batekin kontaktuan baitago sistema. Beraz, ondorioz, enuntziatuan aipaturiko $-\frac{1}{V}\frac{dV}{dp}$ konpresibilitatea tenperatura konstantekoa eta μ_{He} potentzial kimiko konstantekoa da; hots, ondoko hau: $-\frac{1}{V}\frac{dV}{dp} \rightarrow -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{T, \mu_{He}}$.

Kasu honetan, edozer kalkulatzeko, potentzial termodinamikorik erabilgarriena ondoko hau da: $U[T, \mu_{He}] = U[T, \mu_{He}](T, V, \mu_{He})$; hots, aldagai independenteen sorta naturala $\{T, V, \mu_{He}\}$ duena. Orduan, *Legendre*-ren bi transformazio burutu behar dugu U barne-energiaren adierazpenetik $U[T, \mu_{He}]$ potentzial termodinamikoa lortzeko: S -ren ordez T tenperatura ordezkatzeko duena, lehenik; eta, ondoren, N_{He} -ren ordez μ_{He} ordezkatzeko duena.

Jakina, abiapuntua U izan beharrean F bada, *Legendre*-ren transformazio bakarra burutu behar da, $N_{He} \rightarrow \mu_{He}$; baina, horrez gain, aldagai-aldaketa bat egin behar da: $F = F(T, V, N) \rightarrow F = F(T, V, N(T, V, \mu_{He}))$.

Abiatu gaitezen F potentzial termodinamikitik; ondokoa da adierazpena:

$$F = -N_{He}RT \ln \left[\frac{T^{\frac{3}{2}}V}{N_{He}} \right]$$

Lortu dezagun $F[\mu_{He}](=U[T, \mu_{He}])$. Horretarako, μ_{He} lortuko dugu.

$$\mu_{He} \equiv \left(\frac{\partial F}{\partial N_{He}}\right)_{T, V} \Rightarrow \mu_{He} = \left(\frac{\partial \left(-N_{He}RT \ln \left[\frac{T^{\frac{3}{2}}V}{N_{He}}\right]\right)}{\partial N_{He}}\right)_{T, V} \Rightarrow \mu_{He} = -RT \ln \left[\frac{T^{\frac{3}{2}}V}{N_{He}}\right] + RT$$

$$\begin{aligned}
\mu_{\text{He}} &= RT \left\{ 1 - \ln \left[\frac{T^{\frac{3}{2}} V}{N_{\text{He}}} \right] \right\} \\
\frac{\mu_{\text{He}}}{RT} &= 1 - \ln \left[\frac{T^{\frac{3}{2}} V}{N_{\text{He}}} \right] \Rightarrow \ln \left[\frac{T^{\frac{3}{2}} V}{N_{\text{He}}} \right] = 1 - \frac{\mu_{\text{He}}}{RT} \Rightarrow \frac{T^{\frac{3}{2}} V}{N_{\text{He}}} = e^{(1 - \frac{\mu_{\text{He}}}{RT})} \Rightarrow N_{\text{He}} = \frac{T^{\frac{3}{2}} V}{e^{(1 - \frac{\mu_{\text{He}}}{RT})}} \\
F[\mu_{\text{He}}] &= F - N_{\text{He}} \mu_{\text{He}} \Rightarrow F[\mu_{\text{He}}] = F(T, V, \mu_{\text{He}}) - N_{\text{He}}(T, V, \mu_{\text{He}}) \mu_{\text{He}} \\
F[\mu_{\text{He}}] &= \left\{ - \left(\frac{T^{\frac{3}{2}} V}{e^{(1 - \frac{\mu_{\text{He}}}{RT})}} \right) RT \ln \left[\frac{T^{\frac{3}{2}} V}{\left(\frac{T^{\frac{3}{2}} V}{e^{(1 - \frac{\mu_{\text{He}}}{RT})}} \right)} \right] \right\} - \left\{ \frac{T^{\frac{3}{2}} V}{e^{(1 - \frac{\mu_{\text{He}}}{RT})}} \mu_{\text{He}} \right\} \Rightarrow \\
F[\mu_{\text{He}}] &= \left\{ - \left(\frac{T^{\frac{3}{2}} V}{e^{(1 - \frac{\mu_{\text{He}}}{RT})}} \right) RT \ln \left[e^{(1 - \frac{\mu_{\text{He}}}{RT})} \right] \right\} - \left\{ \frac{T^{\frac{3}{2}} V}{e^{(1 - \frac{\mu_{\text{He}}}{RT})}} \mu_{\text{He}} \right\} \Rightarrow \\
F[\mu_{\text{He}}] &= \left\{ - \left(\frac{T^{\frac{3}{2}} V}{e^{(1 - \frac{\mu_{\text{He}}}{RT})}} \right) RT \left(1 - \frac{\mu_{\text{He}}}{RT} \right) \right\} - \left\{ T^{\frac{3}{2}} V \mu_{\text{He}} e^{-(1 - \frac{\mu_{\text{He}}}{RT})} \right\} \Rightarrow \\
F[\mu_{\text{He}}] &= -RT^{\frac{5}{2}} V e^{-(1 - \frac{\mu_{\text{He}}}{RT})} \\
p &\equiv - \left(\frac{\partial F[\mu_{\text{He}}]}{\partial V} \right)_{T, \mu_{\text{He}}} \Rightarrow p = - \left(\frac{\partial \left(-RT^{\frac{5}{2}} V e^{-(1 - \frac{\mu_{\text{He}}}{RT})} \right)}{\partial V} \right)_{T, \mu_{\text{He}}} \Rightarrow p = RT^{\frac{5}{2}} e^{-(1 - \frac{\mu_{\text{He}}}{RT})} \\
p &= p(T, \mu_{\text{He}}) \Rightarrow \left(\frac{\partial p}{\partial V} \right)_{T, \mu_{\text{He}}} = 0 \Rightarrow \left(\frac{\partial V}{\partial p} \right)_{T, \mu_{\text{He}}} = \infty
\end{aligned}$$

Badago beste modu bat ariketa ebazteko, hainbesteko kalkulu egin gabe:

$$\left(\frac{\partial V}{\partial p} \right)_{T, \mu_{\text{He}}} = - \left(\frac{\frac{\partial \mu_{\text{He}}}{\partial p}}{\left(\frac{\partial \mu_{\text{He}}}{\partial V} \right)_{T, p}} \right)_{T, V} = \frac{v}{0} = \infty$$

$$\left(\frac{\partial \mu_{\text{He}}}{\partial p} \right)_{T, V} = v \text{ eta } \left(\frac{\partial \mu_{\text{He}}}{\partial V} \right)_{T, p} = 0 \text{ definizioak baino ez dira.}$$

He eta Ne gasen arteko nahastura dugunean, sistema konposatuak konpresibilitatea izango du: Ne-ak ezin baitu zilindrotik atera. Oraingo honetan, kalkulatu beharreko potentzial termodinamikoa ondoko hau da: $F[\mu_{\text{He}}] = F(T, V, \mu_{\text{He}}, N_{\text{Ne}}) (= U[T, \mu_{\text{He}}, N_{\text{Ne}}])$. Jakina, sistema koposatuari, nahasturari, dagokion $F[\mu]$ potentzial termodinamiko, azpisistema bakoitzari dagokionaren batura da: $F = F_{\text{He}} + F_{\text{Ne}}$. Orduan, F -ren aurreko adierazpenetik abiatuz, ondokoa izango dugu:

$$\begin{aligned}
F &= F_{\text{He}} + F_{\text{Ne}} \\
F &= -N_{\text{He}} RT \ln \left[\frac{T^{\frac{3}{2}} V}{N_{\text{He}}} \right] - N_{\text{Ne}} RT \ln \left[\frac{T^{\frac{3}{2}} V}{N_{\text{Ne}}} \right] \\
F[\mu_{\text{He}}] &= -RT^{\frac{5}{2}} V e^{-(1 - \frac{\mu_{\text{He}}}{RT})} - N_{\text{Ne}} RT \ln \left[\frac{T^{\frac{3}{2}} V}{N_{\text{Ne}}} \right] \\
p &\equiv - \left(\frac{\partial F[\mu_{\text{He}}]}{\partial V} \right)_{T, \mu_{\text{He}}, N_{\text{Ne}}} \Rightarrow p = - \left(\frac{\partial \left(-RT^{\frac{5}{2}} V e^{-(1 - \frac{\mu_{\text{He}}}{RT})} - N_{\text{Ne}} RT \ln \left[\frac{T^{\frac{3}{2}} V}{N_{\text{Ne}}} \right] \right)}{\partial V} \right)_{T, \mu_{\text{He}}} \Rightarrow \\
p &= RT^{\frac{5}{2}} e^{-(1 - \frac{\mu_{\text{He}}}{RT})} + \left[\frac{N_{\text{Ne}} RT}{V} \right] \\
p &= p(T, V, \mu_{\text{He}}, N_{\text{Ne}}) \Rightarrow \left(\frac{\partial p}{\partial V} \right)_{T, \mu_{\text{He}}, N_{\text{Ne}}} = - \frac{V^2}{N_{\text{Ne}} RT} \Rightarrow - \frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_{T, \mu_{\text{He}}, N_{\text{Ne}}} = \frac{V^2}{N_{\text{Ne}} RT} \Rightarrow \\
- \frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_{T, \mu_{\text{He}}, N_{\text{Ne}}} &= \frac{1}{p_{\text{Ne}}}
\end{aligned}$$

Ondorengo bi ariketak modu berean abatzi behar dira. Lehenengo eta behin, ebazketan erabiliko diren aldagaiak finkatu behar dira; printzipioz, enuntziatuek berek finkatuko dute: bien kasuan, p/v diagraman gertatuko

den prozesua dugu; beraz, aldagai independenteak p eta v dira. Gainera, bietan ere bai, prozesua bera nola gertatuko den ere aipatuta dago: p/v diagramako kurba baten adierazpenaren bidez; hots, aldagaien arteko lotura baten bidez (aldakuntzak ere lotuta daude). Beraz, aldagaietatik bat baino ez da independentea, gure esku dago zein. Horrez gain, ariketa bietan, hasierako zein bukaerako oreka-egoerak ezagunak dira: A eta B etiketen bidez adierazita. Azkenik, A eta B egoerak lotuko dituen kurban zehar ezagunak dira (c_p , α , κ_T) sortako koefiziente esperimentalak; orduan, kalkulu termodinamikoaren bidez lortuko ditugun adierazpenetan ezagunak diren funtzioak ordezkatu ondoren, integrazioz, kalkulatu beharreko parametroen aldakuntzak lortu ahal izango ditugu.

Prozedura laburbilduz:

- (a) Identifikatu aldagai independenteak
 - (b) Identifikatu hasierako eta bukaerako oreka-egoerak
 - (c) Identifikatu prozesuaren adierazpena: aldagai independenteen arteko lotura
Lortu aldagien aldakuntza diferentzialen arteko lotura
 - (d) Identifikatu kalkulatu beharreko koefizientea
Kalkulatu koefizientea: lortu adierazpen orokorra
 - (e) Ordezkatu adierazpen orokorrean enuntziatuko datuak Integratu
35. Esku artean substantzia baten mol bakarra dugu. p/V diagramako A eta B puntuak $pv^2 = \text{konstantea}$ lerroko puntuak dira. Aipatu lerroan zehar ezagunak dira sistemari dagozkion ondoko ezaugarriak: $C_p = Cv^2$, $\alpha = \frac{D}{v}$ eta $\kappa_T = Ev$. C , D eta E konstanteak dira. Lortu T_B temperatura (T_A , p_A , v_A , v_B , C , D , E) sortaren funtzioan. (C 7.4.20)

Ebazpena (a) Identifikatu aldagai independenteak:

$$p/v \Rightarrow p, v$$

- (b) Identifikatu hasierako eta bukaerako oreka-egoerak:
 A, B

- (c) Identifikatu prozesuaren adierazpena: aldagai independenteen arteko lotura
Lortu aldagien aldakuntza diferentzialen arteko lotura

$$pv^2 = \text{konst.} \Rightarrow v^2 dp + 2p dv = 0 \Rightarrow \frac{dp}{p} = -2 \frac{dv}{v^2}$$

$$dp = -2(p_A v_A^2) \frac{dv}{v^3}$$

- (d) Identifikatu kalkulatu beharreko koefizientea
Kalkulatu koefizientea: lortu adierazpen orokorra

$$T = T(p, v)$$

$$dT = \left(\frac{\partial T}{\partial p} \right)_v dp + \left(\frac{\partial T}{\partial v} \right)_p dv \Rightarrow dT = \frac{\kappa_T}{\alpha} dp + \frac{1}{v\alpha} dv$$

- (e) Ordezkatu adierazpen orokorrean enuntziatuko datuak
Integratu

$$\left. \begin{aligned} dT &= \frac{\kappa_T}{\alpha} \left(-2p_A v_A^2 \frac{dv}{v^3} \right) + \frac{1}{v\alpha} dv \\ \alpha &= \frac{D}{v} \\ \kappa_T &= Ev \end{aligned} \right\} \Rightarrow dT = \frac{Ev}{\left(\frac{D}{v} \right)} \left(-2p_A v_A^2 \frac{dv}{v^3} \right) + \frac{1}{v \left(\frac{D}{v} \right)} dv \Rightarrow$$

$$dT = -\frac{2E}{D} p_A v_A^2 \frac{dv}{v} + \frac{1}{D} dv \Rightarrow dT = \left\{ -\frac{2E}{D} p_A v_A^2 \frac{1}{v} + \frac{1}{D} \right\} dv \Rightarrow \int dT = \int \left\{ -\frac{2E}{D} p_A v_A^2 \frac{1}{v} + \frac{1}{D} \right\} dv \Rightarrow$$

$$\Delta T = -\frac{2E}{D} p_A v_A^2 \ln \frac{v_B}{v_A} + \frac{1}{D} (v_B - v_A) \Rightarrow \boxed{T_B = T_A - \frac{2E}{D} p_A v_A^2 \ln \frac{v_B}{v_A} + \frac{1}{D} (v_B - v_A)}$$

36. Esku artean substantzia baten mol bakarra dugu. p/V diagramako A eta B puntuak $pv = \text{konstantea}$ lerroko puntuak dira. Aipatu lerroan zehar ezagunak dira sistemari dagozkion ondoko ezaugarriak: $C_p = Cv$, $\alpha = \frac{D}{v^2}$ eta $\kappa_T = Ev$. C , D eta E konstanteak dira. Lortu $(u_A - u_B)$ kendura (T_A , p_A , v_A , v_B , C , D , E) sortaren funtzioan. (C 7.4.21)

Ebazpena (a) Identifikatu aldagai independenteak:

$$p/v \Rightarrow p, v$$

(b) Identifikatu hasierako eta bukaerako oreka-egoerak:
 A, B

(c) Identifikatu prozesuaren adierazpena: aldagai independenteen arteko lotura
 Lortu aldagien aldakuntza diferentzialen arteko lotura

$$pv = \text{konst.} \Rightarrow vdp + pdv = 0 \Rightarrow \frac{dp}{p} = -\frac{dv}{v}$$

$$dp = -2(p_A v_A) \frac{dv}{v^2}$$

(d) Identifikatu kalkulatu beharreko koefizientea
 Kalkulatu koefizientea: lortu adierazpen orokorra

$$u = u(p, v) \Rightarrow du = \left(\frac{\partial u}{\partial p} \right)_v dp + \left(\frac{\partial u}{\partial v} \right)_p dv$$

$$du = Tds - pdv$$

$$\left. \begin{aligned} \left(\frac{\partial u}{\partial p} \right)_v &= \left(\frac{\partial(Tds - pdv)}{\partial p} \right)_v = T \left(\frac{\partial s}{\partial p} \right)_v - p \left(\frac{\partial v}{\partial p} \right)_v = T \left(\frac{\partial s}{\partial T} \right)_v \left(\frac{\partial T}{\partial p} \right)_v = c_V \frac{\kappa_T}{\alpha} \\ \left(\frac{\partial u}{\partial v} \right)_p &= \left(\frac{\partial(Tds - pdv)}{\partial v} \right)_p = T \left(\frac{\partial s}{\partial v} \right)_p - p \left(\frac{\partial v}{\partial v} \right)_p = T \left(\frac{\partial s}{\partial T} \right)_p \left(\frac{\partial T}{\partial v} \right)_p - p = c_p \frac{1}{v\alpha} - p \end{aligned} \right\} \Rightarrow$$

$$du = \left(c_V \frac{\kappa_T}{\alpha} \right) dp + \left(c_p \frac{1}{v\alpha} - p \right) dv$$

(e) Ordezkatu adierazpen orokorrean enuntziatuko datuak
 Integratu

$$\left. \begin{aligned} du &= \left(c_V \frac{\kappa_T}{\alpha} \right) \left(-p_A v_A \frac{dv}{v^2} \right) + \left(c_p \frac{1}{v\alpha} - p \right) dv \Rightarrow du = \left(c_V \frac{\kappa_T}{\alpha} \right) \left(-p_A v_A \frac{dv}{v^2} \right) + \left(c_p \frac{1}{v\alpha} - p \right) dv \\ \alpha &= \frac{D}{v^2} \\ \kappa_T &= Ev \end{aligned} \right\} \Rightarrow \frac{\kappa_T}{\alpha} = \frac{(Ev)}{\left(\frac{D}{v^2} \right)} = \frac{E}{D} v^3$$

$$\left. \begin{aligned} c_p &= Cv \\ c_p - c_V &= \frac{Tv\alpha^2}{\kappa_T} \Rightarrow c_V = c_p - \frac{Tv\alpha^2}{\kappa_T} \end{aligned} \right\} \Rightarrow c_V = Cv - \frac{Tv \left(\frac{D}{v^2} \right)^2}{(Ev)} \Rightarrow c_V = Cv - T \left(\frac{D}{E} \right)^2 \frac{1}{v^3}$$

$$du = \left(c_V \frac{\kappa_T}{\alpha} \right) \left(-p_A v_A \frac{dv}{v^2} \right) + \left(c_p \frac{1}{v\alpha} - p \right) dv$$

$$du = \left\{ \left(Cv - Tv \frac{1}{Ev} \left(\frac{D}{v^2} \right)^2 \right) \left(\frac{E}{D} v^3 \right) \right\} \left(-p_A v_A \right) \frac{dv}{v^2} + \left(Cv \frac{1}{v \left(\frac{D}{v^2} \right)} - \frac{p_A v_A}{v} \right) dv$$

$$du = \left\{ \left(\frac{CE}{D} v^2 - T \frac{1}{v^3} D \right) \right\} \left(-p_A v_A \right) dv + \left(\frac{C}{D} v^2 - \frac{p_A v_A}{v} \right) dv$$

$$du = \left(\frac{C}{D} (1 - p_A v_A E) v^2 + TD p_A v_A \frac{1}{v^3} - \frac{p_A v_A}{v} \right) dv$$

$$dT = \frac{\kappa_T}{\alpha} \left(-p_A v_A \frac{dv}{v^2} \right) + \frac{1}{v\alpha} dv$$

$$dT = \frac{E}{D} v^3 \left(-p_A v_A \frac{dv}{v^2} \right) + \frac{1}{v \left(\frac{D}{v^2} \right)} dv \Rightarrow dT = -p_A v_A \frac{E}{D} v dv + \frac{1}{D} v dv \Rightarrow dT = (1 - p_A v_A E) \frac{1}{D} v dv \Rightarrow$$

$$\int dT = \int (1 - p_A v_A E) \frac{1}{D} v dv \Rightarrow T = (1 - p_A v_A E) \frac{1}{D} v^2 \Rightarrow$$

$$du = \left\{ \frac{C}{D} (1 - p_A v_A E) v^2 + \left((1 - p_A v_A E) \frac{1}{D} v^2 \right) D p_A v_A \frac{1}{v^3} - \frac{p_A v_A}{v} \right\} dv$$

37. Esku artean dugun sistemaren kasuan ezagunak dira ondoko bi propietate hauek:

$$C_V = AT^3$$

$$(v - v_0)p = B(T)$$

non A konstantea den eta $B(T)$ tenperaturaren funtzio ezezaguna. Eztabaidatu zer forma har dezakeen $B(T)$ funtzioak. Lortu (C_p, α, κ_T) sortakoak, T eta v -ren funtzioan. Laguntza: aztertu $\left(\frac{\partial^2 s}{\partial T \partial v}\right)$ deribatua. (C 7.4.22)

Ebazpena (a) $B(T)$ funtzioaren formaz.

Aurreko ariketaren emaitza erabiliko dugu $B(T)$ funtzioaren forma finkatzeko. Beraz, jakina da ondoko adierazpena beteko dela: $\left(\frac{\partial c_V}{\partial v}\right)_T = T \left(\frac{\partial^2 p}{\partial T^2}\right)_v$. Orduan, berdintzako atal biak, bakoitza bere aldetik, kalkulatu egingo dugu; eta, ondoren, alderatu.

$$\begin{aligned} \left(\frac{\partial c_V}{\partial v}\right)_T &= T \left(\frac{\partial^2 p}{\partial T^2}\right)_v \\ \left(\frac{\partial c_V}{\partial v}\right)_T &= \left(\frac{\partial(AT^3)}{\partial v}\right)_T \Rightarrow \left(\frac{\partial c_V}{\partial v}\right)_T = 0 \\ (v - v_o)p &= B(T) \Rightarrow p = \frac{B(T)}{(v-v_o)} \\ \left(\frac{\partial^2 p}{\partial T^2}\right)_v &= \left(\frac{\partial^2 \left(\frac{B(T)}{(v-v_o)}\right)}{\partial T^2}\right)_v = \frac{1}{(v-v_o)} \left(\frac{\partial^2 (B(T))}{\partial T^2}\right)_v = \frac{1}{(v-v_o)} B''(T) \end{aligned} \left. \vphantom{\begin{aligned} \left(\frac{\partial c_V}{\partial v}\right)_T &= T \left(\frac{\partial^2 p}{\partial T^2}\right)_v \\ \left(\frac{\partial c_V}{\partial v}\right)_T &= \left(\frac{\partial(AT^3)}{\partial v}\right)_T \Rightarrow \left(\frac{\partial c_V}{\partial v}\right)_T = 0 \\ (v - v_o)p &= B(T) \Rightarrow p = \frac{B(T)}{(v-v_o)} \\ \left(\frac{\partial^2 p}{\partial T^2}\right)_v &= \left(\frac{\partial^2 \left(\frac{B(T)}{(v-v_o)}\right)}{\partial T^2}\right)_v = \frac{1}{(v-v_o)} \left(\frac{\partial^2 (B(T))}{\partial T^2}\right)_v = \frac{1}{(v-v_o)} B''(T) \end{aligned}} \right\} \Rightarrow$$

$$T \left(\frac{\partial^2 p}{\partial T^2}\right)_v = T \frac{1}{(v-v_o)} B''(T) \Rightarrow$$

$$0 = T \frac{1}{(v-v_o)} B''(T) \Rightarrow 0 = TB''(T) \Rightarrow B''(T) = 0 \Rightarrow \boxed{B(T) = B_1 T + B_2}$$

(b) (C_p, α, κ_T) sortakoak.

i. α

$$\begin{aligned} p &= \frac{B_1 T + B_2}{(v-v_o)} \Rightarrow (v - v_o) = \frac{B_1 T + B_2}{p} \\ \alpha &= \frac{1}{v} \left(\frac{\partial v}{\partial T}\right)_p \Rightarrow \alpha = \frac{1}{(v-v_o)} \left(\frac{\partial(v-v_o)}{\partial T}\right)_p \Rightarrow \\ \left(\frac{\partial(v-v_o)}{\partial T}\right)_p &= \left(\frac{\partial \left(\frac{B_1 T + B_2}{p}\right)}{\partial T}\right)_p = \frac{1}{p} B_1 \end{aligned} \left. \vphantom{\begin{aligned} p &= \frac{B_1 T + B_2}{(v-v_o)} \Rightarrow (v - v_o) = \frac{B_1 T + B_2}{p} \\ \alpha &= \frac{1}{v} \left(\frac{\partial v}{\partial T}\right)_p \Rightarrow \alpha = \frac{1}{(v-v_o)} \left(\frac{\partial(v-v_o)}{\partial T}\right)_p \Rightarrow \\ \left(\frac{\partial(v-v_o)}{\partial T}\right)_p &= \left(\frac{\partial \left(\frac{B_1 T + B_2}{p}\right)}{\partial T}\right)_p = \frac{1}{p} B_1 \end{aligned}} \right\} \Rightarrow \alpha = \frac{1}{(v-v_o)} \frac{1}{p} B_1$$

ii. κ_T

$$\begin{aligned} \kappa_T &= -\frac{1}{v} \left(\frac{\partial v}{\partial p}\right)_T \Rightarrow \kappa_T = -\frac{1}{(v-v_o)} \left(\frac{\partial(v-v_o)}{\partial p}\right)_T \Rightarrow \\ \left(\frac{\partial(v-v_o)}{\partial p}\right)_T &= \left(\frac{\partial \left(\frac{B_1 T + B_2}{p}\right)}{\partial p}\right)_T = -\frac{B_1 T + B_2}{p^2} = -\frac{B_1 T + B_2}{\left(\frac{B_1 T + B_2}{(v-v_o)}\right)^2} = -\frac{(v-v_o)^2}{(B_1 T + B_2)} = -\frac{(v-v_o)}{p} \end{aligned} \left. \vphantom{\begin{aligned} \kappa_T &= -\frac{1}{v} \left(\frac{\partial v}{\partial p}\right)_T \Rightarrow \kappa_T = -\frac{1}{(v-v_o)} \left(\frac{\partial(v-v_o)}{\partial p}\right)_T \Rightarrow \\ \left(\frac{\partial(v-v_o)}{\partial p}\right)_T &= \left(\frac{\partial \left(\frac{B_1 T + B_2}{p}\right)}{\partial p}\right)_T = -\frac{B_1 T + B_2}{p^2} = -\frac{B_1 T + B_2}{\left(\frac{B_1 T + B_2}{(v-v_o)}\right)^2} = -\frac{(v-v_o)^2}{(B_1 T + B_2)} = -\frac{(v-v_o)}{p} \end{aligned}} \right\} \Rightarrow$$

$$\kappa_T = -\frac{1}{(v-v_o)} \left\{ -\frac{(v-v_o)}{p} \right\} \Rightarrow \kappa_T = \frac{1}{p}$$

iii. C_p

$$\begin{aligned}
& \left. \begin{aligned} c_p - c_V &= \frac{T v \alpha^2}{\kappa_T} \Rightarrow c_p = c_V + \frac{T v \alpha^2}{\kappa_T} \Rightarrow c_p = c_V + \frac{T(v-v_o)\alpha^2}{\kappa_T} \\ \frac{T(v-v_o)\alpha^2}{\kappa_T} &= T(v-v_o) \frac{\left(\frac{1}{(v-v_o)} \frac{1}{p} B_1\right)^2}{\left(\frac{1}{p}\right)} = T \left(\frac{1}{(v-v_o)} \frac{1}{p} B_1^2\right) = T B_1^2 (B_1 T + B_2) \end{aligned} \right\} \Rightarrow \\
& c_p = c_V + T B_1^2 (B_1 T + B_2) \\
& \left(\frac{\partial c_p}{\partial p}\right)_T = -T v \left\{ \alpha^2 + \left(\frac{\partial \alpha}{\partial T}\right)_p \right\} \Rightarrow \left(\frac{\partial c_p}{\partial p}\right)_T = -T(v-v_o) \left\{ \alpha^2 + \left(\frac{\partial \alpha}{\partial T}\right)_p \right\} \\
& \left. \begin{aligned} \alpha &= \frac{1}{(v-v_o)} \frac{1}{p} B_1 \Rightarrow \alpha^2 = \left(\frac{1}{(v-v_o)} \frac{1}{p} B_1\right)^2 \\ \left(\frac{\partial \alpha}{\partial T}\right)_p &= \left(\frac{\partial \left(\frac{1}{(v-v_o)} \frac{1}{p} B_1\right)}{\partial T}\right)_p = 0 \end{aligned} \right\} \Rightarrow \left(\frac{\partial c_p}{\partial p}\right)_T = -T(v-v_o) \left(\frac{1}{(v-v_o)} \frac{1}{p} B_1\right)^2 \Rightarrow \\
& \left(\frac{\partial c_p}{\partial p}\right)_T = -T \frac{1}{(v-v_o)} \left(\frac{1}{(B_1 T + B_2)} B_1\right)^2
\end{aligned}$$

38. Esku artean dugun sistemaren kasuan, p/v diagramako lerro zuzenean zeharreko espantsioak (p_0, v_0) eta (p_f, v_f) egoerak lotu ditu. (c_p, α, κ_T) sortako parametroak $v = v_0$ lerro isokoroan zehar eta $p = p_f$ lerro isobaroan zehar soilik ezagunak dira; $\frac{c_p \kappa_T}{\alpha} = A p$ ($v = v_0$), $\frac{c_p}{v \alpha} = B v$ ($p = p_f$). Lortu prozesuan trukaturiko beroa. (C 7.4.23)

Ebazpena