HW6

第九組

謝愷昀、鄭琮寶、石苯源

第一題 (Problem 14.1)

14.1

(1)

$$dU = TdS - pdV + \mu dN$$

$$\Rightarrow \left(\frac{\partial \mu}{\partial V}\right)_{S,N} = \left(\frac{\partial(-p)}{\partial N}\right)_{V,S} \quad \#$$

(2)

$$dF = -SdT - pdV + \mu dN$$

$$\Rightarrow \left(\frac{\partial \mu}{\partial V}\right)_{T,N} = \left(\frac{\partial(-p)}{\partial N}\right)_{T,V} \quad \#$$

(3)

$$dG = -SdT + VdP + \mu dN$$

$$\Rightarrow \left(\frac{\partial S}{\partial P}\right)_{T,N} = \left(\frac{\partial(-V)}{\partial T}\right)_{P,N} \quad \#$$

(4)

$$dH = TdS + VdP + \mu dN$$

$$\Rightarrow \left(\frac{\partial V}{\partial S}\right)_{P,N} = \left(\frac{\partial T}{\partial P}\right)_{S,N} \quad \#$$

(5)

$$dK = TdS + VdP - Nd\mu \quad (K = U + PV - \mu N)$$

$$\Rightarrow \left(\frac{\partial N}{\partial P}\right)_{S,\mu} = \left(\frac{\partial(-V)}{\partial \mu}\right)_{S,P} \quad \#$$

(6)

$$dH = TdS + VdP + \mu dN$$

$$\left(\frac{\partial P}{\partial T}\right)_{S,N} = \frac{\partial(P,S,N)}{\partial(T,S,N)} = \frac{1}{\frac{\partial(T,S,N)}{\partial(P,S,N)}} = \frac{1}{\left(\frac{\partial T}{\partial P}\right)_{S,N}} = \frac{1}{\left(\frac{\partial V}{\partial S}\right)_{P,N}} \xlongequal[\text{Jacobians}]{\text{同理}} \left(\frac{\partial S}{\partial V}\right)_{P,N} \quad \#$$

(7)

$$dU = TdS - pdV + \mu dN$$

$$\left(\frac{\partial N}{\partial P}\right)_{S,V} = \frac{\partial(N,S,V)}{\partial(P,S,V)} = \frac{1}{\frac{\partial(P,S,V)}{\partial(N,S,V)}} = \frac{1}{\left(\frac{\partial P}{\partial N}\right)_{S,V}} = \frac{1}{\left(\frac{\partial(-\mu)}{\partial V}\right)_{N,S}} \xlongequal[\text{Jacobians}]{\text{同理}} \left(\frac{\partial(-V)}{\partial \mu}\right)_{N,S} \quad \#$$

第二題 (Problem 14.2)

14.2

$$\left(\frac{\partial T}{\partial P}\right)_{S,N} \xlongequal[\text{relation}]{\text{Maxwell}} \left(\frac{\partial V}{\partial S}\right)_{P,N} = \frac{\partial(V,P,N)}{\partial(S,P,N)} = \frac{\partial(V,P,N)}{\partial(T,P,N)} \cdot \frac{\partial(T,P,N)}{\partial(S,P,N)}$$

$$= \left(\frac{\partial V}{\partial T}\right)_{P,N} \cdot \left(\frac{\partial T}{\partial S}\right)_{P,N} = V\alpha \cdot \frac{T}{N \cdot C_P} = \frac{VT}{N} \frac{\alpha}{C_P} \quad \#$$

第三題 (Problem 14.3)

14.3

$$\left(\frac{\partial C_V}{\partial V}\right)_{T,N} = \left(\frac{\partial}{\partial V}\left(\frac{T}{N}\left(\frac{\partial S}{\partial T}\right)_{V,N}\right)\right)_{T,N} = \frac{T}{N}\left(\frac{\partial}{\partial V}\left(\frac{\partial S}{\partial T}\right)_{V,N}\right)_{T,N}$$

$$= \frac{T}{N}\left(\frac{\partial}{\partial T}\left(\frac{\partial S}{\partial V}\right)_{T,N}\right)_{V,N}$$

$$= \frac{T}{N}\left(\frac{\partial}{\partial T}\left(\frac{\partial P}{\partial T}\right)_{V,N}\right)_{V,N}, \text{ (By Maxwell relation)}$$

$$\Rightarrow \left(\frac{\partial C_V}{\partial V}\right)_{T,N} = \frac{T}{N}\left(\frac{\partial^2 P}{\partial T^2}\right)_{V,N} \quad \#$$

第四題 (Problem 14.4)

14.4

$$dF = -SdT - PdV + \mu dN$$

$$\Rightarrow \left(\frac{\partial F}{\partial S}\right)_{T,N} = -S\left(\frac{\partial T}{\partial S}\right)_{T,N} - P\left(\frac{\partial V}{\partial S}\right)_{T,N} + \mu\left(\frac{\partial N}{\partial S}\right)_{T,N}$$

$$= -P\left(\frac{\partial V}{\partial S}\right)_{T,N} = -P\left(\frac{\partial V}{\partial P}\right)_{T,N}\left(\frac{\partial P}{\partial S}\right)_{T,N} \quad \text{(By Jacobians)}$$

$$= -P\left(\frac{\partial V}{\partial P}\right)_{T,N}\left[-\left(\frac{\partial T}{\partial V}\right)_{P,N}\right] \quad \text{(By Maxwell relation)}$$

$$= -P\cdot(-V\kappa_T)\left(\frac{-1}{V\alpha}\right) = -P\frac{\kappa_T}{\alpha} \quad \#$$

第五題 (Problem 14.5)

14.5

$$C_V = \frac{T}{N}\left(\frac{\partial S}{\partial T}\right)_{V,N} = \frac{T}{N}\left(\frac{\partial P}{\partial T}\right)_{V,N}\left(\frac{\partial S}{\partial P}\right)_{V,N} \quad \text{(By Jacobians)}$$

$$= \frac{T}{N}\left(\frac{\partial P}{\partial T}\right)_{V,N}\left[-\left(\frac{\partial V}{\partial T}\right)_{S,N}\right] \quad \text{(By Maxwell relation)}$$

$$= -\frac{T}{N}\left(\frac{\partial P}{\partial T}\right)_{V,N}\left(\frac{\partial V}{\partial T}\right)_{S,N} \quad \#$$

第六題 (Problem 14.6)

14.6

$$K_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,N} \qquad K_S = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{S,N}$$

$$\left(\frac{\partial V}{\partial P}\right)_{S,N} = \frac{\partial(V,S,N)}{\partial(P,S,N)} = \frac{\dfrac{\partial(V,S,N)}{\partial(T,P,N)}}{\dfrac{\partial(P,S,N)}{\partial(T,P,N)}} = \frac{\left(\frac{\partial V}{\partial T}\right)_{P,N}\left(\frac{\partial S}{\partial P}\right)_{T,N} - \left(\frac{\partial V}{\partial P}\right)_{T,N}\left(\frac{\partial S}{\partial T}\right)_{P,N}}{-\left(\frac{\partial S}{\partial T}\right)_{P,N}}$$

$$= \frac{-V\alpha\cdot V\alpha}{-\frac{N}{T}C_P} + (-VK_T) = -V\left(\frac{-TV\alpha^2}{NC_P} + K_T\right)$$

$$\Rightarrow K_S = K_T - \frac{TV\alpha^2}{NC_P}$$

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第七題 (Problem 14.7)

14.7

$$\left(\frac{\partial P}{\partial U}\right)_{G,N} = \left(\frac{\dfrac{\partial(P,G)}{\partial(T,P)}}{\dfrac{\partial(U,G)}{\partial(T,P)}}\right)_N = \frac{-\left(\frac{\partial G}{\partial T}\right)_{P,N}}{\left(\frac{\partial U}{\partial T}\right)_{P,N}\left(\frac{\partial G}{\partial P}\right)_{T,N} - \left(\frac{\partial U}{\partial P}\right)_{T,N}\left(\frac{\partial G}{\partial T}\right)_{P,N}}$$

$$dU = TdS - PdV + \mu dN$$

$$dG = -SdT + VdP + \mu dN$$

$$\left(\frac{\partial U}{\partial T}\right)_{P,N} = T\left(\frac{\partial S}{\partial T}\right)_{P,N} - P\left(\frac{\partial V}{\partial T}\right)_{P,N} = NC_P - PV\alpha$$

$$\left(\frac{\partial U}{\partial P}\right)_{T,N} = T\left(\frac{\partial S}{\partial P}\right)_{T,N} - P\left(\frac{\partial V}{\partial P}\right)_{T,N} = -TV\alpha + VK_T$$

$$\left(\frac{\partial P}{\partial U}\right)_{G,N} = \frac{S}{V(NC_P - PV\alpha) + S(-TV\alpha + VK_T)} = \frac{S}{VNC_P + VSK_T - (PV^2 + STV)\alpha}$$

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第八題 (Problem 14.8)

14.8

$$\frac{\partial(V,S)}{\partial(T,P)} = \frac{\frac{\partial(V,S)}{\partial(T,V)}}{\frac{\partial(T,P)}{\partial(T,V)}} = \frac{-\left(\frac{\partial S}{\partial T}\right)_V}{\left(\frac{\partial P}{\partial V}\right)_T} = \frac{-\frac{N}{T}C_V}{\frac{-1}{K_T V}} = \frac{NVC_VK_T}{T} \quad \#$$

第九題 (Problem 14.9)

14.9

(1)

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{N}{T}C_V, \quad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V = \frac{\partial(P,V)}{\partial(T,V)} = \frac{\frac{\partial(P,V)}{\partial(T,P)}}{\frac{\partial(T,V)}{\partial(T,P)}}$$

$$= \frac{-\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial P}\right)_T} = \frac{-V\alpha}{-VK_T} = \frac{\alpha}{K_T}$$

$$\Rightarrow dS = \frac{N}{T}C_V dT + \frac{\alpha}{K_T} dV$$

$$\Rightarrow TdS = NC_V dT + \frac{T\alpha}{K_T} dV \quad \#$$

(2)

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{N}{T}C_P, \quad \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P = -\alpha V$$

$$\Rightarrow dS = \frac{N}{T}C_P dT - \alpha V dP$$

$$\Rightarrow TdS = NC_P dT - TV\alpha dP \quad \#$$

(3)

$$\left(\frac{\partial S}{\partial V}\right)_P = \frac{\partial(S,P)}{\partial(V,P)} = \frac{\frac{\partial(S,P)}{\partial(T,P)}}{\frac{\partial(V,P)}{\partial(T,P)}} = \frac{\left(\frac{\partial S}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial T}\right)_P} = \frac{\frac{N}{T}C_P}{V\alpha} = \frac{NC_P}{TV\alpha}$$

$$\left(\frac{\partial S}{\partial P}\right)_V = \frac{\partial(S,V)}{\partial(P,V)} = \frac{\frac{\partial(S,V)}{\partial(T,V)}}{\frac{\partial(P,V)}{\partial(T,V)}} = \frac{\frac{\partial(S,V)}{\partial(T,V)}}{\frac{\partial(P,V)}{\partial(P,T)}\frac{\partial(P,T)}{\partial(T,V)}} = \frac{\left(\frac{\partial S}{\partial T}\right)_V}{\left(\frac{\partial V}{\partial T}\right)_P\left[-\left(\frac{\partial P}{\partial V}\right)_T\right]}$$

$$= \frac{\frac{N}{T}C_V}{V\alpha \cdot \frac{1}{VK_T}} = \frac{NC_VK_T}{T\alpha}$$

$$\Rightarrow dS = \frac{NC_P}{TV\alpha} dV + \frac{NC_VK_T}{T\alpha} dP$$

$$\Rightarrow TS = \frac{NC_P}{V\alpha} dV + \frac{NC_VK_T}{\alpha} dP \quad \#$$

第十題 (Problem 14.10)

14.10

$$F = U - TS$$

$$\Rightarrow \beta F = \beta U - \beta TS = \beta U - \frac{1}{K_B T} TS$$

$$= \beta U - \frac{S}{K_B}$$

$$\Rightarrow d(\beta F) = \beta dU + U d\beta - \frac{1}{K_B} dS$$

$$= \beta(TdS - PdV + \mu dN) + U d\beta - \frac{1}{K_B} dS$$

$$= -\beta P dV + \beta\mu dN + U d\beta + \frac{1}{K_B T} TdS - \frac{1}{K_B} dS$$

$$= -\beta P dV + \beta\mu dN + U d\beta$$

$$\Rightarrow \left(\frac{\partial(\beta F)}{\partial \beta}\right)_{VN} = U \quad \#$$