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화공 열역학 과제

2019101074 안용상

6.2 (a) $dH = C_p dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_P \right] dP$

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

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

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

↳ 이상기체에서 $\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}$ ⇒ 상수이므로 $\left(\frac{\partial^2 V}{\partial T^2}\right)_P = 0$

$\therefore \left(\frac{\partial C_p}{\partial P}\right)_T = 0$ 이다.

(b)

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV = C_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

$$\left.\begin{aligned} dS &= C_V \frac{dT}{T} + \left(\frac{\partial P}{\partial T}\right)_V dV \\ dS &= C_P \frac{dT}{T} - \left(\frac{\partial V}{\partial T}\right)_P dP \end{aligned}\right] \text{같다.}$$

$$C_P \frac{dT}{T} - \left(\frac{\partial V}{\partial T}\right)_P dP = C_V \frac{dT}{T} + \left(\frac{\partial P}{\partial T}\right)_V dV$$

$$(C_P - C_V)\frac{dT}{T} = \left(\frac{\partial P}{\partial T}\right)_V dV + \left(\frac{\partial V}{\partial T}\right)_P dP$$

$$= \frac{\beta}{\kappa} dV + \beta V dP$$

$$(C_P - C_V)\frac{dT}{T} = \frac{\beta}{\kappa} dV + \beta V dP$$

$$(C_P - C_V) = T \beta V \left(\frac{\partial P}{\partial T}\right)_V \Rightarrow C_P = C_V + T\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial T}\right)_V$$

6.7 $d\left(\frac{G}{RT}\right) = \frac{1}{RT} dG - \frac{G}{RT^2} dT$

$$= \frac{1}{RT}(V dP - S dT) - \frac{dT}{RT^2}(H - TS)$$

$$= \frac{V}{RT} dP - \frac{H}{RT^2} dT$$

$\hookrightarrow \left(\frac{\partial \left(\frac{G}{RT}\right)}{\partial P}\right)_T = \frac{V}{RT} \cdots ①$ $\quad \frac{H}{RT^2} = -\left(\frac{\partial}{\partial T}\left(\frac{G}{RT}\right)\right)_P \cdots ②$

$G = \Gamma(T) + RT \ln P$ 에서 $\frac{G}{RT} = \frac{\Gamma(T)}{RT} + \ln P$ 이고

①에서 $\frac{V}{RT} = \left(\frac{\partial}{\partial P}\left(\frac{\Gamma(T)}{RT} + \ln P\right)\right)_T \Rightarrow \frac{V}{RT} = \frac{1}{P} \Rightarrow \boxed{V = \frac{RT}{P}}$ ①

②에서 $\frac{H}{RT^2} = -\left(\frac{\partial}{\partial T}\left(\frac{\Gamma(T)}{RT} + \ln P\right)\right)_P = +\frac{\Gamma(T)}{RT^2} - \frac{1}{RT}\frac{d\Gamma(T)}{dT} \Rightarrow \boxed{H = \Gamma(T) - T\frac{d\Gamma(T)}{dT}}$ ②

③ $G = H - TS$

$S = \frac{1}{T}(H - G)$

$S = \frac{1}{T}\left(J(T) - T\frac{dJ(T)}{dT} - J(T) - RT\ln P\right)$

$S = -\frac{dJ(T)}{dT} - R\ln P$

④ $H = U + PV$

$U = H - PV = J(T) - T\frac{dJ(T)}{dT} - RT$

⑤ $C_V = \left(\frac{\partial U}{\partial T}\right)_V$

$C_V = \frac{\partial}{\partial T}\left(J(T) - T\frac{dJ(T)}{dT} - RT\right)$

$= -T\frac{d^2J(T)}{dT^2} - R$ $\qquad C_V = -\frac{T\,d^2J(T)}{dT^2} - R$

17. $dH = TdS + VdP$ $\qquad \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$ $\qquad dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$

$dU = TdS - PdV$ $\qquad \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$ $\qquad = C_P dT + \left(-T\left(\frac{\partial V}{\partial T}\right)_P + V\right) dP$

$dA = -SdT - PdV$ $\qquad +\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

$dG = -SdT + VdP$ $\qquad -\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$ $\qquad \left(\frac{\partial H}{\partial P}\right)_{\cancel{T}} = T\left(\frac{\partial S}{\partial P}\right)_T + V$

$= -T\left(\frac{\partial V}{\partial T}\right)_P + V$

$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$

$= \frac{C_P}{T}dT - \left(\frac{\partial V}{\partial T}\right)_P dP = \frac{C_P}{T}dT - \beta V dP$

$dH = C_P dT + (-TV\beta + V)dP$

$\Delta H = (1 - \beta T)V\Delta P = 0.55117\ \mathrm{kJ/kg \cdot K}$

$\Delta S = -\beta V\Delta P \qquad = -2.6612\times10^{-3}\ \mathrm{kJ/kg \cdot K}$

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6.10 $\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \rightarrow \beta dT = \frac{1}{V}dV$

$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \rightarrow \kappa dP = -\frac{1}{V}dV$

$\rightarrow \beta dT = \kappa dP$

$\frac{dV}{V} = \beta dT - \kappa dP \quad \frac{\beta}{\kappa} = \left(\frac{dT}{dP}\right)_V \Rightarrow \underline{\beta dT = \kappa dP}$

$\beta(T_2 - T_1) = \kappa(P_2 - P_1) \Rightarrow P_2 = \frac{\beta(T_2 - T_1)}{\kappa} + P_1$

$T_1 = 298 \rightarrow 323K \quad \beta = 36.2 \times 10^{-5}/K \quad \kappa = 4.42 \times 10^{-5}/bar$

$P_1 = 1 bar \rightarrow P_2 = ?$

$P_2 = \frac{36.2 \times 10^{-5} \times (323 - 298)}{4.42 \times 10^{-5}} + 1 = 205.751 bar$

14. $T = 50°C = 323K$

$\ln P^{sat}/kPa = 13.8858 - \frac{2788}{50 + 220.7} = 3.588$

$P^{sat} = 36.166 kPa$

(a) $\Delta V^{lv} = V^v - V^l \quad V^v = \frac{RT}{P}\left(1 + (B_0 + \omega B_1)\frac{P_r}{T_r}\right)$

$= \frac{83.6 \times 323}{0.357}\left(1 + \left(-0.944 + 0.21 \times (-1.679)\right)\frac{7.28 \times 10^{-3}}{0.575}\right)$

$= 74247.14 cm^3/mol$

$V^l = V_c Z_c^{(1-T_r)^{0.2857}} = 259 cm^3/mol \times (0.271)^{(1-0.575)^{0.2857}} = 93.163 cm^3/mol$

$\Delta V^{lv} = 74247.14 cm^3/mol - 93.163 cm^3/mol = 74153.977 cm^3/mol$

$\frac{1}{P^{sat}}dP = \frac{2788.51}{(t + 220.79)^2}dT \rightarrow \frac{dP}{dT} = 36.166 kPa \times \frac{2788.51}{(50 + 220.79)^2} = 1.3597 kPa/K$

$\boxed{\Delta S = \frac{dP}{dT} \times \Delta V = 101.962 J/mol \cdot K}$

(b) $\Delta H^{lv} = R\frac{dP^{sat}}{d(1/T)} = -R\frac{1}{P}(-T)\frac{dP}{dT} \rightarrow \boxed{\Delta S = \frac{\Delta H^{lv}}{T} = \frac{RT}{P}\frac{dP}{dT} = 102.1 J/mol \cdot K}$

morning glory

117. $q = C_p\Delta T + x\Delta H = 0$

$C_p\Delta T + x\Delta H_{fusion} = 0$

$x = -\dfrac{C_p\Delta T}{\Delta H}$

$= -\dfrac{4.226 \times 6}{-333.7} = 0.076$

$\Delta S = C_p \ln\dfrac{T_2}{T_1} + \dfrac{x\Delta H}{T_2} = 4.226 \times \ln\dfrac{273}{267} + \dfrac{0.076 \times (-333.4)}{273}$

$= 1.1 \times 10^{-3}\ J/g\cdot K$

$T = 0°C$, $x = 0.076$.

$\Delta S = 1.1 \times 10^{-3}\ J/g\cdot K$

물이 어는 과정은 비가역적이다.

6.19 8000 kPa, 액체 V, 기체 V

$V^l = \dfrac{1.388-1.381}{8118.9-7884.7} = \dfrac{V^l-1.381}{8000-7884.7} \rightarrow V^l = 1.3844\ cm^3/g$

$V^v = \dfrac{23.13-23.9}{8118.9-7884.7} = \dfrac{V^v-23.9}{8000-7884.7} \rightarrow V^v = 23.53\ cm^3/g$

$V_{total} = 0.15\ m^3$ 액체 V = 기체 V $= 0.075\ m^3$

$M_l = 0.075 \times 10^6 / 1.3844 = 54175.09\ g$

$M_g = 3187.42\ g$

$H^l = \dfrac{1322.8-1311.8}{8118.9-7884.7} = \dfrac{H^l-1311.8}{8000-7884.7} \rightarrow H^l = 1317.01\ kJ/kg$

$H^v = \dfrac{2758.2-2761.5}{8118.9-7884.7} = \dfrac{H^v-2761.5}{8000-7884.7} \rightarrow H^v = 2759.91\ kJ/kg$

$S^l = 3.2075\ kJ/kg\cdot K$ $S^v = 5.7471\ kJ/kg\cdot K$

$$\boxed{\begin{aligned} H^T &= 1317.01 \times 54.175 + 2759.9 \times 3.187 = 80144.18\ kJ \\ S^T &= 3.2075 \times 54.175 + 5.7471 \times 3.187 \\ &= 192.08\ kJ/K \end{aligned}}$$

25. 증기 2100kPa, 260°C → 125kPa (H는 일정)

P		250°C	275°C
2100kPa	V	105.64	112.59
	U	2676.1	2725.4
	H	2897.9	2961.9
	S	6.5162	6.6356

$$H = \frac{2961.9-2897.9}{275-250} = \frac{x-2897.9}{260-250}$$

$$= 2923.5\ kJ/kg$$

$$S = 6.5638\ kJ/kg \cdot K$$

H유지, P=125kPa, T는?

P		200°C	225°C
125kPa	H	2874.2	2923.4
	S	7.73	7.8324

$$T = \frac{225-200}{2923.4-2874.2} = \frac{T-200}{2923.5-2874.2}$$

$$T_2 = 224.777$$

$$S_2 = 7.8316\ kJ/kg \cdot K$$

$T_2 = 224.799°C$

$\Delta S = 1.2678\ kJ/kg \cdot K$

이상기체에서

$\Delta H = C_p \Delta T$ 이므로 T_2는 260°C이다

$$\Delta S = C_p \ln\frac{T_2}{T_1} - R\ln\frac{P_2}{P_1} = -R\ln\frac{P_2}{P_1}$$

$$= 23.45\ J/mol \cdot K$$

31. 총부피 $2m^3 \rightarrow 0.02m^3$ $H_2O(l)$ + $1.98m^3$ $H_2O(g)$

$P=101.33kPa$

P		liq.sat	vap.sat
101.33kPa	V	1.044	1673.0
	U	418.599	2506.5

$m_{liq} = \frac{0.02}{1.044} \times 10^6 = 19157.088g$

$m_{vap} = \frac{1.98}{1673} \times 10^6 = 1183.5g$

$m_{total} = 20340.588g$

$X^v = \frac{m_{va}}{m_{total}} = \frac{1183.5}{20340.588} = 0.0581$

$V_1 = (1-X^v)V^l + X^v V^v$

$= (1-0.0581) \times 1.044 + 0.0581 \times 1673$

$= 98.185\ cm^3/g$

$U_1 = (1-X^v)U^l + X^v U^v$

$= 539.91J/g$

전체부피 일정, 질량 일정

최종상태의 Saturator 기체의 부피는 $98.185\ cm^3/g$

Table E.1의 t, V, U 표를 보고 U_2을 구한다

$\frac{2598.7-2598}{96.46-100.26} = \frac{U_2-2598}{98.185-100.26} \Rightarrow U_2 = 2598.382J/g$

$\Rightarrow Q = m_T(U_2-U_1) = 41870530.86J$

6.35 $x=0.9$

가역 단열 팽창 일정부피가열

$P_1 = 2100\,kPa \xRightarrow{\text{팽창}} 400\,kPa \rightarrow$ 압력증가 (포화증기)

Q? W?

① $\Delta U = Q + W$ ② $\Delta U = Q + W$

$W = U_2 - U_1$ $Q = U_3 - U_2$

$\Rightarrow Q = U_3 - U_2 \quad W = U_2 - U_1$

$U_1 = (1-x)U^l + xU^v$

$= (1-0.9) \times 977.968\,J/g + 0.9 \times 2601.8\,J/g$

$= 2439.417\,J/g$

$S_1 = (1-x)S^l + xS^v$

$= 5.86127\,J/g \cdot K$

$S_2 = S_1 = 5.86127\,J/g \cdot K$

$= (1-x_2)S^l + x_2 S^v$

$x_2 = 0.7981$

$U_2 = (1-x_2)U^l + xU^v$

$= 2159.31\,J/g$

$V_2 = (1-x_2)V^l + xV^v$

$= (1-0.7981) \times 1.084 + 0.7981 * 462.22$

$= 369.117\,cm^3/g$

$V_3 = V_2 = 369.117\,cm^3/g$

$$\frac{2561.8 - 2560.2}{357.84 - 374.68} = \frac{U_3 - 2560.2}{364.117 - 374.68} \Rightarrow U_3 = 2560.73\,J/g$$

$Q = U_3 - U_2 = 401.42\,J/g$

$W = U_2 - U_1 = -280.107\,J/g$

$$\boxed{\begin{aligned} Q &= 401.42\,J/g \\ W &= -280.107\,J/g \end{aligned}}$$