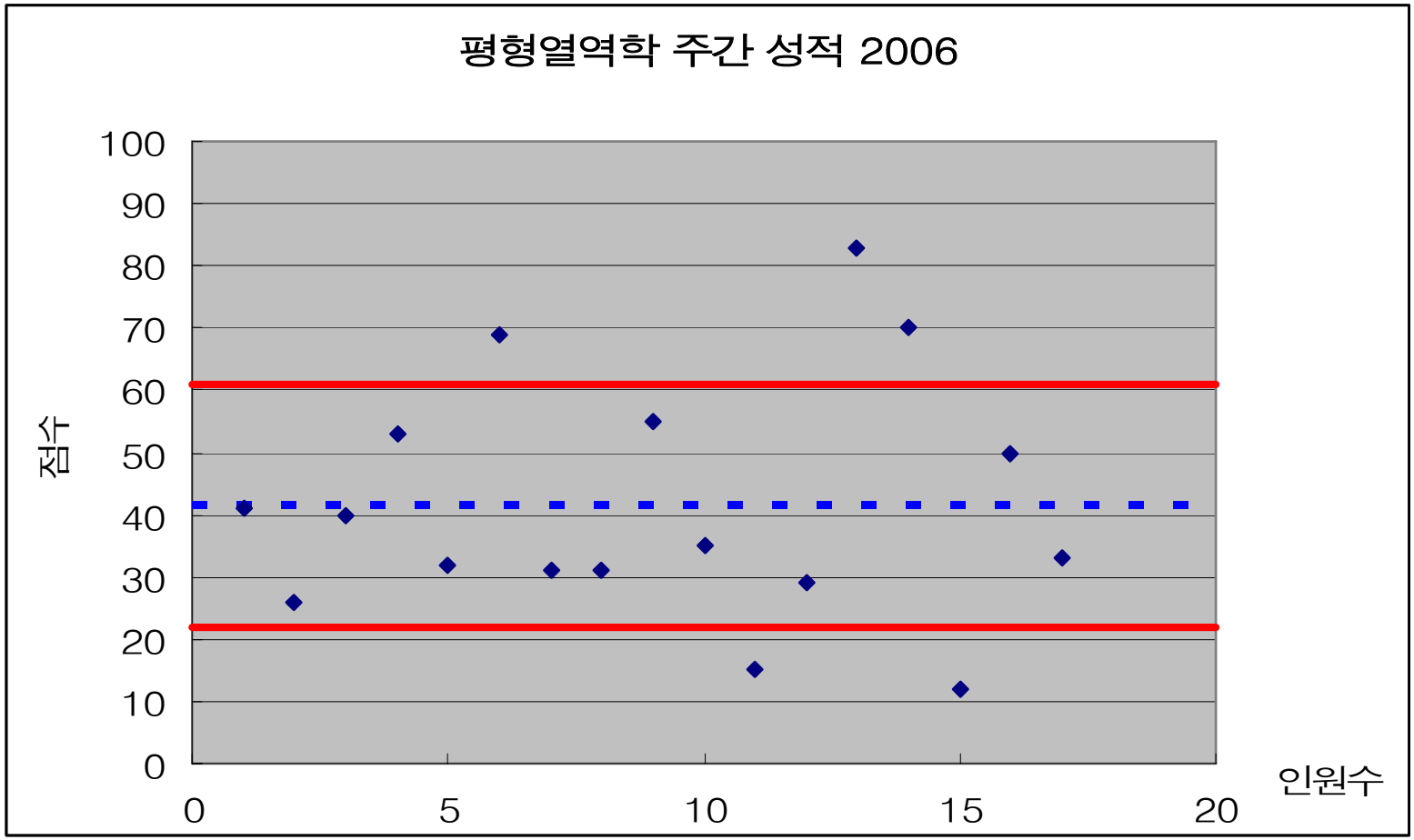
전산 평형열역학 강의계획

1. 개론 (1-2주)
2. Ch 3. (3-4주): 엔트로피
3. Ch 5. (5주): 깁스에너지
4. Ch 6. (5-7주): 상태방정식
5. Ch 9. (9-12주): 순수물질의 상평형
6. Ch 10. (13-14주): 혼합물질의 상평형

중간고사 성적 (야간)



Ch. 5.
깁스 자유에너지

Entropy, enthalpy, 내부에너지

- 엔트로피와 내부에너지

  $dU=dQ - dW$

  $dS=dQ/T,\ dW=FdL=PAdL=PdV$

  $dU = TdS - PdV$

- 엔트로피와 엔탈피

  $H = U + PV$

  $dH = dU + PdV + VdP$

  $= TdS + VdP$

- Gibbs free energy 와 엔트로피

  $G = H - TS$

  $dG = -SdT + VdP$

Gibbs free energy 계산

FACS
Functional analysis of complex systems

For ideal gas

$dG = -SdT + VdP$

1. Isotherm, dT=0

$dG = VdP = nRT\, dP/P$

$dS = dH/T = C_p dT/T$

2. Isobaric, dP=0

$dG = -SdT$, where $S = S_0 + \Delta H/T = S_0 + \int_0^T C_P \frac{dT}{T}$

3. Isotherm and isobaric, dT= dP=0

$dG=0$

$dS = dU/T = C_v dT/T$

4. Isometric, dV=0

$\Delta G = V\Delta P - \int SdT$, where $S=S_0+ \Delta U/T=S_0+ \int_{T_1}^{T_2} C_V \frac{dT}{T}$

과제 4

- 다음 그림에서 주어진 5단계에서의 깁스에너지 변화량 (ΔG) 을 구하시오.

$dG = VdP = nRT\, dP/P$

a) isotherm, dT=0

$\Delta G = RT \ln(P_2/P_1)$

$= -9363$ kJ

b) Isometric, dV=0

$\Delta G = V\Delta P - \int SdT$

=

c) Isobaric, dP=0

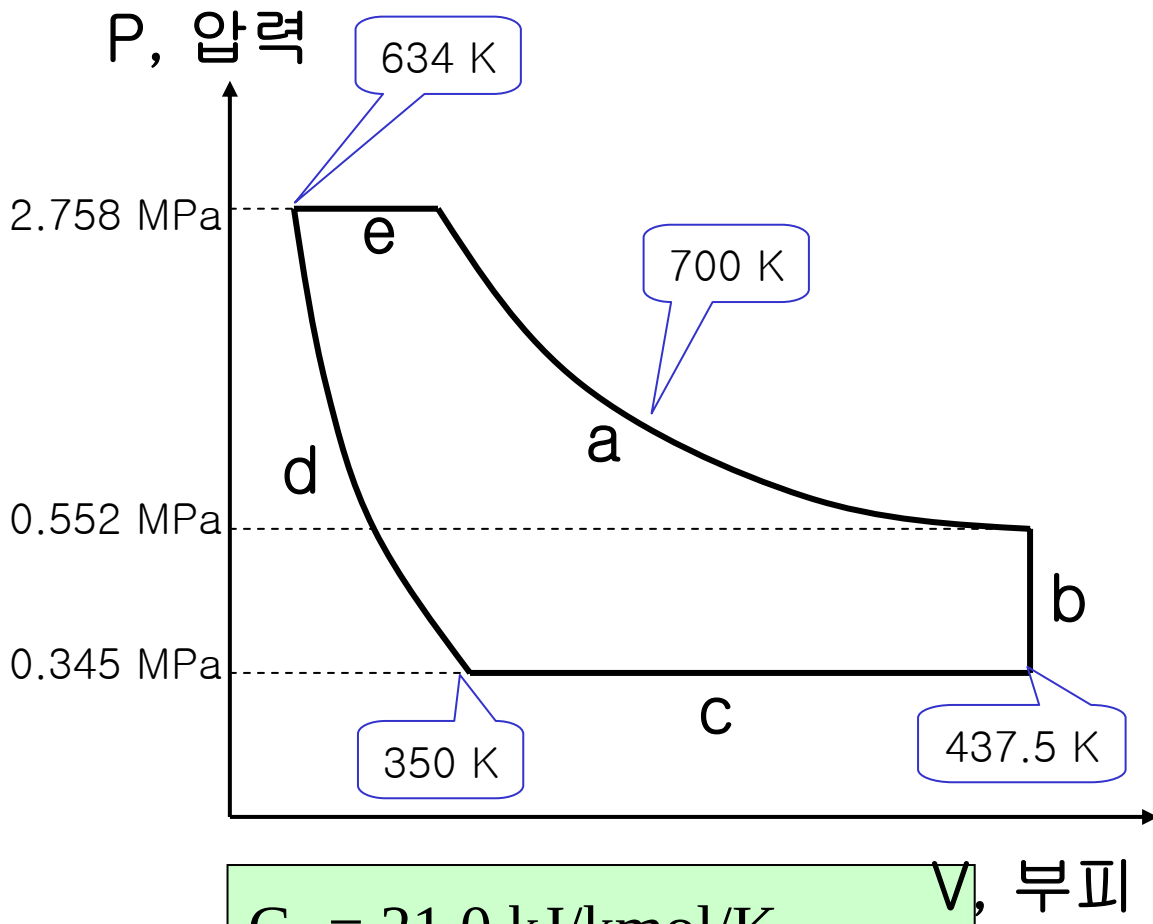
$\Delta G = -\int_{437.5}^{350} SdT$

d) adiabatic, dQ=0

$\Delta G = \int_{0.345}^{2.758} VdP - \int_{350}^{634} SdT$

e) Isobaric, dP=0

$\Delta G = -\int_{634}^{700} SdT$



$C_v = 21.0$ kJ/kmol/K

$C_p = 29.3$ kJ/kmol/K

$R = 8.314$ kJ/kmol/K

n = 1 kmol

$S_{1atm,\ 25\ ^oC} = 198.0$kJ/kmol/K

Entropy, enthalpy, 내부에너지

FACS
Functional analysis of complex systems

- 엔트로피와 내부에너지

$$dU = TdS - PdV$$

$$dU = dQ - dW$$

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

- 엔트로피와 엔탈피

$$dH = TdS + VdP$$

$$H = U + PV$$

$$dH = \left(\frac{\partial H}{\partial S}\right)_P dS + \left(\frac{\partial H}{\partial P}\right)_S dP$$

- Gibbs free energy 와 엔트로피

$$G = H - TS$$

$$dG = -SdT + VdP$$

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

Maxwell relations

- Gibbs free energy 와 엔트로피

$$G = H - TS$$

$$dG = -SdT + VdP$$

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

$$S = -(\partial G/\partial T)_p,\ V = =(\partial G/\partial P)_T$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\frac{\partial^2 G}{\partial P \partial T} \qquad \left(\frac{\partial V}{\partial T}\right)_P = \frac{\partial^2 G}{\partial T \partial P}$$

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

Maxwell relations

- 엔트로피와 엔탈피

$$dH = TdS + VdP$$

$$H = U + PV$$

$$\left(\frac{\partial H}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P + V\left(\frac{\partial P}{\partial T}\right)_P$$

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P, \left(\frac{\partial P}{\partial T}\right)_P = 0$$

$$\frac{C_P}{T} = \left(\frac{\partial S}{\partial T}\right)_P$$

Entropy 의 온도/압력에 대한 영향

FACS
Functional analysis of complex systems

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

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

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

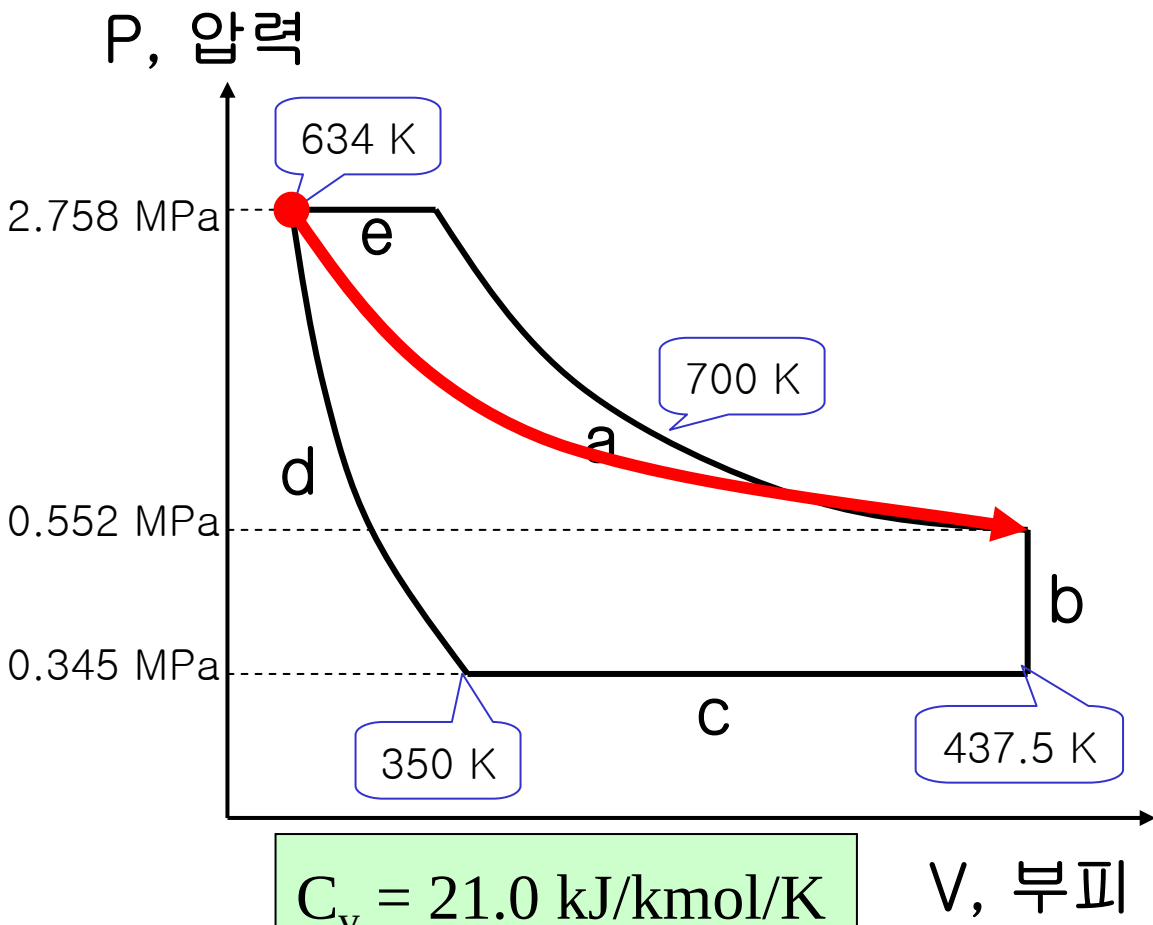
$$\Delta S = \int C_P d \ln T - \int \left(\frac{\partial V}{\partial T}\right)_P dP$$

만일, 이상기체식을 따른다면, $(\partial V/\partial T)_P$ = ?

Daubert (1985), Chemical engineering thermodynamics, McGRAW-HILL, p203

ΔS_e=+2.9 kJ/kmol/K

ΔS_a=+13.37 kJ/kmol/K



$$\Delta S = \int C_P d\ln T - \int \left(\frac{\partial V}{\partial T}\right)_P dP$$

$$\Delta S = 29.6 \ln \frac{700}{634} - R \ln \frac{0.552}{2.758}$$

$$= 16.306\, kJ / K$$

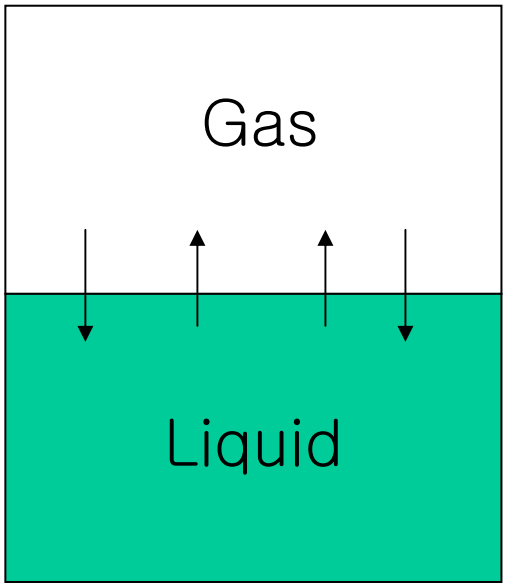
C_v = 21.0 kJ/kmol/K

C_p = 29.3 kJ/kmol/K

R = 8.314 kJ/kmol/K

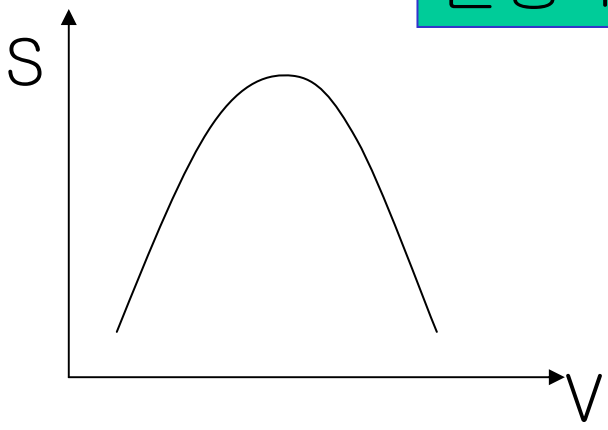
n = 1 kmol

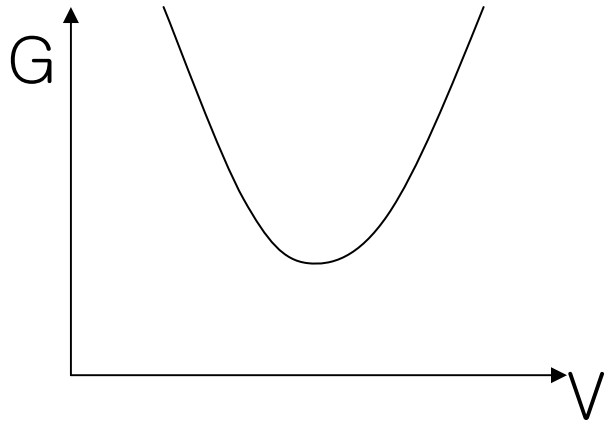
평형과 엔트로피



- 평형상태란 주어진 열린계에서 엔트로피의 전체 변화량이 dS=0 라고 정의한다.
- 평형상태란 주어진 닫힌계에서 엔트로피가 T, P or V 의 변화에 따라 최대일 때를 말한다.
- 평형상태에서 자유에너지는 일정 T, P에서 부피에 따라 최저값을 보여준다.

일정 T, P





상평형

- 상변화시 온도와 압력은 일정하다.

$$dG = VdP - SdT = 0$$

- 평형상태에서 공존하는 순수물질의 두상은 같은 Gibbs 자유에너지를 갖는다.

$$G^{vapor} = G^{liquid}$$