

Advanced Thermodynamics (Midterm Exam)

M2794.007900-001

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1. Equation of State (EOS): $\left(P + \frac{a}{v^2}\right)(v - b) = RT$

$$P = \frac{RT}{v - b} - \frac{a}{v^2}$$

The critical point is identical to inflection point of isothermal line in pressure-specific volume graph.

$$\left(\frac{\partial P}{\partial v}\right)_T = -\frac{RT_c}{(v_c - b)^2} + \frac{2a}{v_c^3} = 0$$

$$\left(\frac{\partial^2 P}{\partial v^2}\right)_T = \frac{2RT_c}{(v_c - b)^3} - \frac{6a}{v_c^4} = 0$$

Solving the simultaneous equation

$$\frac{2RT_c}{(v_c - b)^3} = \frac{RT_c}{(v_c - b)^2} \times \frac{2}{v_c - b} = \frac{2a}{v_c^3} \times \frac{2}{v_c - b} = \frac{6a}{v_c^4}$$

$$v_c = 3b$$

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

Substituting the above critical values into EOS

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

(Answer)

(1) Critical temperature: $T_c = \frac{8a}{27Rb}$

(2) Critical specific volume: $v_c = 3b$

(3) Critical pressure: $P_c = \frac{a}{27b^2}$

2. (1) Joule-Thomson coefficient $\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_h$

Using cyclical relation

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

From a definition of isobaric heat capacity

$$c_p \equiv \left(\frac{\partial h}{\partial T}\right)_P$$

Another derivative term is obtained from the first law of thermodynamics

$$\begin{aligned} dh &= Tds + vdP = T\left(\frac{\partial s}{\partial T}\right)_P dT + \left[T\left(\frac{\partial s}{\partial P}\right)_T + v\right]dP = \left(\frac{\partial h}{\partial T}\right)_P dT + \left(\frac{\partial h}{\partial P}\right)_T dP \\ \left(\frac{\partial h}{\partial P}\right)_T &= T\left(\frac{\partial s}{\partial P}\right)_T + v \end{aligned}$$

Using Maxwell relations

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

So Joule-Thomson coefficient can be expressed as follows.

$$\left(\frac{\partial T}{\partial P}\right)_h = \frac{1}{c_p} \left[T\left(\frac{\partial v}{\partial T}\right)_P - v \right]$$

EOS of the problem

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

$$Pv - bP + \frac{a}{Tv} - \frac{ab}{Tv^2} = RT$$

Differentiating all of the terms with temperature and specific volume in constant pressure

$$P \partial v + a \left(\frac{1}{v} \times \frac{-1}{T^2} \partial T + \frac{1}{T} \times \frac{-1}{v^2} \partial v \right) - ab \left(\frac{1}{v^2} \times \frac{-1}{T^2} \partial T + \frac{1}{T} \times \frac{-2}{v^3} \partial v \right) = R \partial T$$

$$\left(P - \frac{a}{Tv^2} + \frac{2ab}{Tv^3} \right) \left(\frac{\partial v}{\partial T} \right)_P = R + \frac{a}{vT^2} - \frac{ab}{v^2T^2}$$

$$\left(\frac{\partial v}{\partial T} \right)_P = \frac{R + \frac{a}{vT^2} - \frac{ab}{v^2T^2}}{P - \frac{a}{Tv^2} + \frac{2ab}{Tv^3}} = \frac{Rv^3T^2 + av^3 - abv}{Pv^3T^2 - avT + 2abT}$$

(Answer)

$$\left(\frac{\partial T}{\partial P}\right)_h = \frac{1}{c_p} \left[\frac{Rv^3T^2 + av^3 - abv}{Pv^3T - av + 2ab} - v \right]$$

Or

$$\left(\frac{\partial T}{\partial P}\right)_h = \frac{1}{c_p} \left[T \times \frac{R + \frac{a}{vT^2} - \frac{ab}{v^2T^2}}{\left(P - \frac{a}{Tv^2} + \frac{2ab}{Tv^3}\right)} - v \right]$$

(2) Isentropic expansion coefficient $\mu_s = \left(\frac{\partial T}{\partial P}\right)_s$

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

From the above problem (1)

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

Using the first law of thermodynamics and differentiation

$$\left(\frac{\partial s}{\partial T}\right)_P = \frac{1}{T} \left(\frac{\partial h}{\partial T}\right)_P = \frac{c_p}{T}$$

Thus the isentropic expansion coefficient can be expressed as follows.

$$\left(\frac{\partial T}{\partial P}\right)_s = \frac{T}{c_p} \left(\frac{\partial v}{\partial T}\right)_P$$

(Answer)

$$\left(\frac{\partial T}{\partial P}\right)_s = \frac{T(Rv^3T^2 + av^3 - abv)}{c_p(Pv^3T^2 - avT + 2abT)}$$

(3) (Answer)

Isentropic process: **T = 152 K (150 ~ 155 K)**

Isenthalpic process: **T = 285 K (280 ~ 290 K)**

3.

$$Tds = c_p dT - T \left(\frac{\partial v}{\partial T} \right)_p dP$$

Using the first law of thermodynamics

$$Tds = dh - vdP$$

From the derivative of enthalpy

$$Tds = \left[\left(\frac{\partial h}{\partial T} \right)_p dT + \left(\frac{\partial h}{\partial P} \right)_T dP \right] - vdP$$

$$ds = \frac{1}{T} \left(\frac{\partial h}{\partial T} \right)_p dT + \frac{1}{T} \left[\left(\frac{\partial h}{\partial P} \right)_T - v \right] dP$$

From the derivative of entropy

$$ds = \left(\frac{\partial s}{\partial T} \right)_p dT + \left(\frac{\partial s}{\partial P} \right)_T dP$$

Since temperature and pressure are independent

$$\left(\frac{\partial s}{\partial T} \right)_p = \frac{1}{T} \left(\frac{\partial h}{\partial T} \right)_p \quad \& \quad \left(\frac{\partial s}{\partial P} \right)_T = \frac{1}{T} \left[\left(\frac{\partial h}{\partial P} \right)_T - v \right]$$

The differential entropy ds is exact. Therefore

$$\frac{\partial^2 s}{\partial P \partial T} = \frac{\partial^2 s}{\partial T \partial P}$$

$$\left(\frac{\partial h}{\partial P} \right)_T = -T \left(\frac{\partial v}{\partial T} \right)_p + v$$

Substituting all the term

$$\therefore Tds = c_p dT - T \left(\frac{\partial v}{\partial T} \right)_p dP$$

4. (1) Temperature change

The container is adiabatic and no work is done

$$dU = 0 \text{ or } U = \text{Const}$$

Final temperature is

$$T_1 = T_0 + \int_{v_0}^{v_1} \left(\frac{\partial T}{\partial v} \right)_u dv$$

Using cyclical relation

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

Because internal energy of an ideal gas is independent of specific volume

$$\left(\frac{\partial u}{\partial v} \right)_T = 0$$

Substituting the relation

(Answer)

$$\Delta T = T_1 - T_0 = 0$$

(2) Pressure change

Since the air is treated as an ideal gas and temperature is constant regardless of free expansion

$$PV = \text{Const}$$

Volume that air takes increases as twice during expansion. Pressure of air at final state is

$$P_1 = \frac{1}{2} P_0$$

Thus pressure change during expansion is

(Answer)

$$\Delta P = -\frac{1}{2} P_0 = -\frac{(n_{O_2} + n_{N_2})RT_0}{2V_0}$$

In view of the partial pressure of nitrogen and oxygen

Nitrogen: $\Delta P_{N_2} = -0.4 P_0$

Oxygen: $\Delta P_{O_2} = -0.1 P_0$

(3) Specific volume change

Volume that air takes increases as twice

$$V_1 = 2V_0$$

Considering mass conservation, change of specific volume is

(Answer)

$$\Delta v = \frac{2V_0}{n_{O_2} + n_{N_2}} - \frac{V_0}{n_{O_2} + n_{N_2}} = \frac{V_0}{n_{O_2} + n_{N_2}}$$

Or $\Delta v = v_0$

(4) Entropy change

From the first law of thermodynamics

$$TdS = dU + PdV$$

Because internal energy is constant and the air is treated as an ideal gas

$$dS = \frac{nR}{V} dV$$

Integrating the equation, entropy change is

(Answer)

$$\Delta S = (n_{O_2} + n_{N_2})R \ln 2$$

(5) Enthalpy change

From the definition of enthalpy

$$H = U + PV$$

Because internal energy and temperature is constant regardless of expansion

(Answer)

$$\Delta H = 0$$

(6) Helmholtz function change

From the definition of Helmholtz function

$$F = U - ST$$

Since internal energy and temperature are constant

(Answer)

$$\Delta F = -T\Delta S = -(n_{O_2} + n_{N_2})RT_0 \ln 2$$

(7) Gibbs function change

From the definition of Gibbs function

$$G = U - ST + PV = F + PV$$

Since PV is constant during free expansion, the Gibbs function change is the same with the change of Helmholtz function

(Answer)

$$\Delta G = -(n_{O_2} + n_{N_2})RT_0 \ln 2$$

5. (1) From mass conservation

$$n_0^v + n_0^l = n_1^v + n_1^l$$
$$n_0^v - n_1^v = -(n_0^l - n_1^l)$$

Gibbs function of each state is

$$G_0 = n_0^v g^v + n_0^l g^l$$
$$G_1 = n_1^v g^v + n_1^l g^l$$

Since the process is reversible

$$G_0 = G_1 \text{ or } (\Delta G)_{T,P} = 0$$
$$g^v(n_0^v - n_1^v) + g^l(n_0^l - n_1^l) = 0$$

From the molecular relation of liquid and vapor state

$$g^v = g^l$$

(2) From the above relation

$$dg^v = dg^l$$

Using a differential expression of Gibbs function

$$-s^l dT + v^l dP = -s^v dT + v^v dP$$
$$\frac{dP}{dT} = \frac{s^v - s^l}{v^v - v^l}$$

From the definition of entropy

$$s^v - s^l = \frac{L}{T}$$

Substituting the equation to entropy term and ignoring specific volume of saturated liquid

$$\frac{dP}{dT} \approx \frac{L}{T v^v}$$

Treating the vapor as an ideal gas

$$\frac{dP}{dT} = \frac{LP}{RT^2}$$

Integrating the equation by considering reference values

$$\ln P - \ln P_0 = \frac{L}{R} \left(\frac{-1}{T} - \frac{-1}{T_0} \right)$$

Saturation pressure as a function of saturation temperature is
(Answer)

$$P = P_0 \exp \left(-\frac{L}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right)$$

6. (1) The equation of state (EOS)

Using a differential expression of Gibbs function

$$dg = -sdT + vdP$$

$$v = \left(\frac{\partial g}{\partial P} \right)_T$$

Differentiating specific Gibbs function with pressure in constant temperature

$$v = \frac{\partial}{\partial P} \left[RT \ln \left(\frac{P}{P_0} \right) - A(T)P \right]_T$$

$$v = \frac{RT}{P} - A(T)$$

(Answer)

$$\therefore P(v + A(T)) = RT$$

(2) The specific entropy

Using the above differential expression of Gibbs function

$$s = - \left(\frac{\partial g}{\partial T} \right)_P$$

Differentiating specific Gibbs function with temperature in constant pressure

$$s = - \frac{\partial}{\partial T} \left[RT \ln \left(\frac{P}{P_0} \right) - A(T)P \right]_P$$

(Answer)

$$s = -R \ln \left(\frac{P}{P_0} \right) + P \left(\frac{\partial A}{\partial T} \right)_P$$

(3) The specific Helmholtz function

From the definition of Helmholtz function

$$f = g - Pv$$

Substituting the above calculated equations

$$f = \left[RT \ln \left(\frac{P}{P_0} \right) - A(T)P \right] - P \left(\frac{RT}{P} - A(T) \right)$$

(Answer)

$$f = RT \left(\ln \left(\frac{P}{P_0} \right) - 1 \right)$$

7. Chemical potential can be expressed by Gibbs function and molecules.

$$\mu = \frac{G}{n}$$

From the definition of Gibbs function

$$G = U - TS + PV = H - TS$$

When we treat entropy as a function of temperature and volume

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

$$dS = \frac{nc_v}{T} dT + \frac{nR}{V} dV$$

Substituting entropy by taking reference value into account

$$S = nc_v \ln T + nR \ln V + S_0$$

Differential expression of enthalpy is

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

When considering only temperature and volume

$$H = nc_p T + H_0$$

Substituting enthalpy and entropy into the Gibbs function equation

$$G = nc_p T + H_0 - T(nc_v \ln T + nR \ln V + S_0)$$

From the above relation

$$\therefore \mu = c_p T - c_v T \ln T - R T \ln V - s_0 T + h_0$$

where s_0 , h_0 are reference values

8. (1) Molecular flux, Φ (Number of collisions per unit time and unit length)
Local curve of velocity circle of which radii is v

$$\frac{dL}{L} = \frac{vd\theta}{2\pi v}$$

The number of molecules in the space is

$$d^2n_{\theta v}dA = dn_v \times \frac{vd\theta}{2\pi v} \times (vdt\sin\theta dl)$$

Where dn_v means density in the range of v to $v+dv$.

The number of collisions per unit length and time

$$d\Phi = \frac{d^2n_{\theta v}dA}{dldt} = \frac{1}{2\pi} vdn_v \sin\theta d\theta$$

Integrating the equation in the given range

$$\int \frac{d^2n_{\theta v}dA}{dldt} = \frac{1}{2\pi} \int_0^\infty vdn_v \int_0^\pi \sin\theta d\theta$$

Since $\bar{v} = \frac{1}{n} \int_0^\infty vdn_v$

(Answer)

$$\Phi = \frac{n\bar{v}}{\pi}$$

- (2) Pressure of the gas, P

Momentum change of one molecule

$$mv\sin\theta - (-mv\sin\theta) = 2mv\sin\theta$$

Change in momentum due to collisions

$$dp = \iint 2mv\sin\theta \times \frac{1}{2\pi} vdn_v \sin\theta d\theta$$

Integrating in the given range

$$dp = \frac{m}{\pi} \int_0^\infty v^2 dn_v \int_0^\pi \sin^2 \theta d\theta dldt$$

Since $\overline{v^2} = \frac{1}{n} \int_0^\infty v^2 dn_v$

$$dp = \frac{1}{2} mn\overline{v^2} dldt$$

From the definition of force

$$dF = \frac{dp}{dt}$$

Pressure acting on the given unit length

(Answer)

$$dP = \frac{dF}{dl} = \frac{1}{2} mn\overline{v^2}$$

9. Fraction of the total molecules lying in the range

$$\frac{dN_v}{N} = f(v)dv$$

Number of molecules lies in the range of v to $v + dv$

$$dN_v = Nf(v)dv$$

Density of the molecules

$$\rho = \frac{dN_v}{dv} = Nf(v)$$

Because of the homogeneous distribution and elastic collisions, the form of $f(v)$ is

$$f(v) = \alpha e^{-\beta v^2}$$

Where α, β are constants

Number of molecules in one dimension is

$$dN_v = N\alpha e^{-\beta v^2} dv$$

Considering two constraints, total number of molecules and its energy

Total number of molecules is

$$N = \int_0^{\infty} dN_v = N\alpha \int_0^{\infty} e^{-\beta v^2} dv$$

Because $\int_0^{\infty} e^{-ax^2} dx = \frac{1}{2} \sqrt{\frac{\pi}{a}}$

$$1 = \frac{\alpha}{2} \sqrt{\frac{\pi}{\beta}}$$

Total energy of the molecules in one dimensional system is

$$\frac{1}{2} NkT = \frac{1}{2} m \int_0^{\infty} v^2 dN_v = \frac{1}{2} m \times N\alpha \int_0^{\infty} v^2 e^{-\beta v^2} dv$$

Because $\int_0^{\infty} x^2 e^{-ax^2} dx = \frac{1}{4} \sqrt{\frac{\pi}{a^3}}$

$$kT = \frac{m\alpha}{4} \sqrt{\frac{\pi}{\beta^3}}$$

Solving the simultaneous equations, two constants are

$$\beta = \frac{m}{2kT}$$

$$\alpha = \sqrt{\frac{2m}{\pi kT}}$$

Substituting two constants into density function

(Answer)

$$\rho = \frac{dN_v}{dv} = N \sqrt{\frac{2m}{\pi kT}} e^{-\frac{m}{2kT} v^2}$$