SIFAT VOLUMETRIK FLUIDA MURNI

Bagian 1

Kaidah Fase Gibbs

Pada kesetimbangan fase dan tidak ada reaksi kimia, berlaku :

$$F = 2 - \pi + N$$

Dengan :

F = derajat kebebasan

π = jumlah fase

N = jumlah komponen

$$F = 2 - \pi + N$$

Contoh:

a. Air (cair) seimbang dengan uapnya

$$F = 2 - 2 + 1 = 1$$

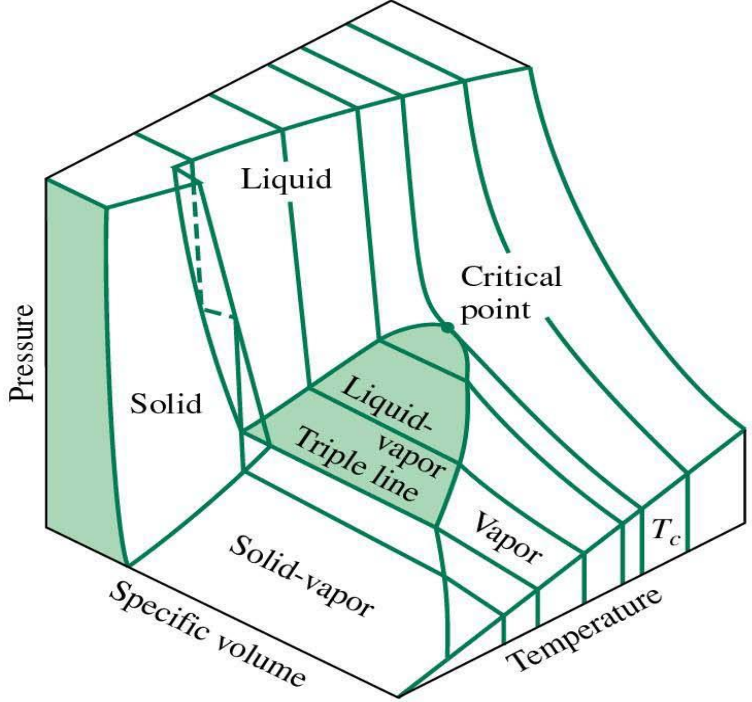
b. Etanol-air (cair) seimbang dengan uapnya

$$F = 2 - 2 + 2 = 2$$

c. Air (cair) seimbang dengan uap air dan gas Nitrogen

$$F = 2 - 2 + 2 = 2$$

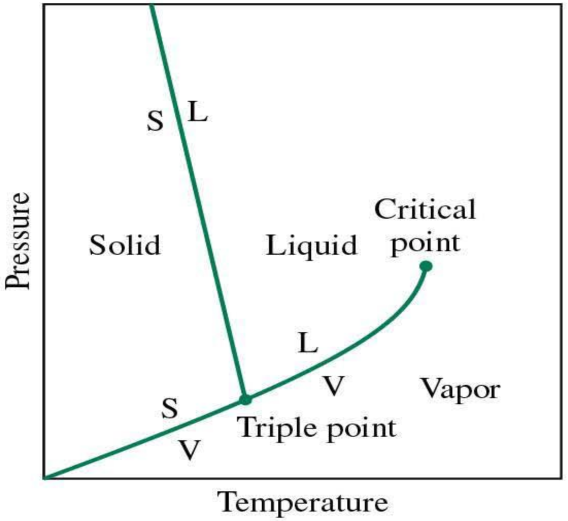
c.



Liquid
Critical point
Pressure
Solid
Liquid-vapor
Triple line
Vapor
T_c
Solid-vapor
Specific volume
Temperature

(a)

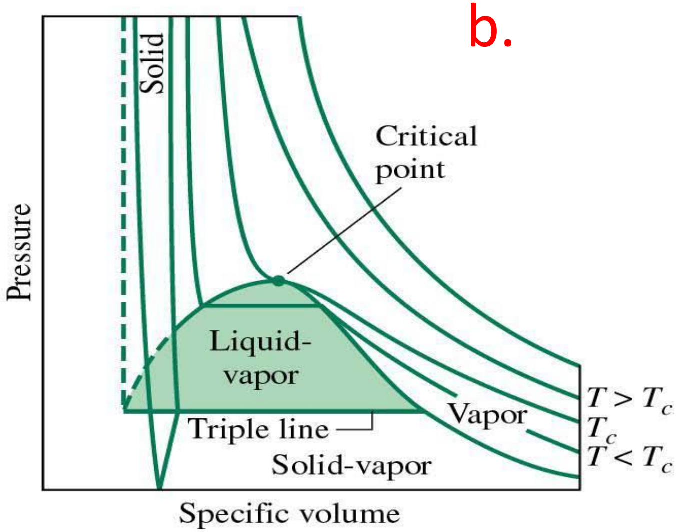
a.



S
L
Pressure
Solid
Liquid
Critical point
L
V
Vapor
S
Triple point
V
Temperature

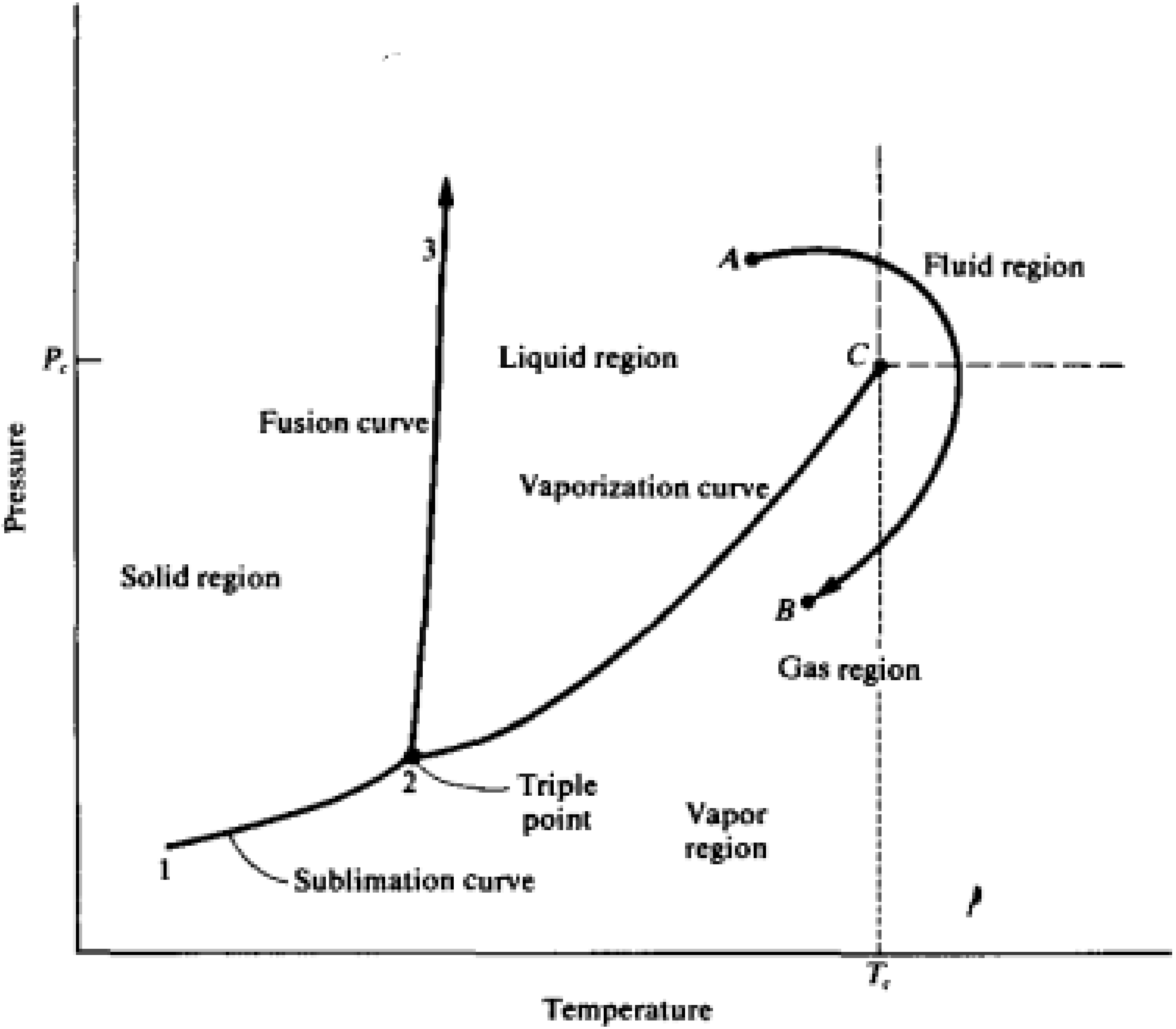
(b)

b.



Solid
Critical point
Pressure
Liquid-vapor
Vapor
Triple line
Solid-vapor
$T > T_c$
T_c
$T < T_c$
Specific volume

(c)


Pressure
P_c
3
Fusion curve
Liquid region
A
Fluid region
C
Vaporization curve
Solid region
B
Gas region
2
Triple point
Vapor region
1
Sublimation curve
T_c
Temperature

Derajat kebebasan pada titik tripel:

$\pi = 3,\ N = 1 \rightarrow \quad F = 2 - 3 + 1 = 0$

Jadi Titik Tripel sudah tertentu.

Pada kurva penguapan :

$\pi = 2,\ N = 1 \rightarrow \quad F = 2 - 2 + 1 = 1$

Jadi pd kurva penguapan kita bisa memilih T tertentu, atau P tertentu. Tapi ingat hanya 1 pilihan T saja atau P saja, yg lain mengikuti saja.

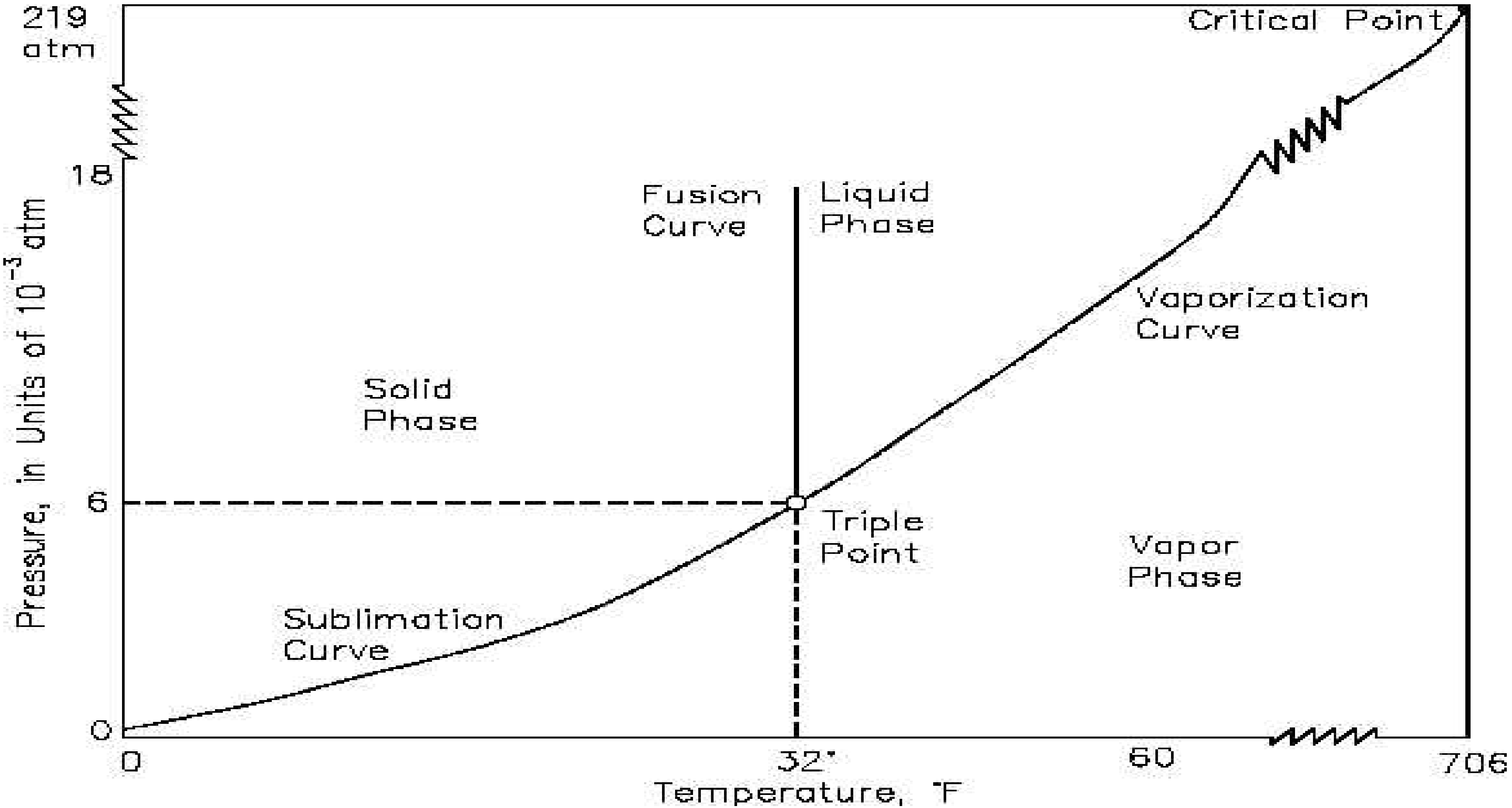
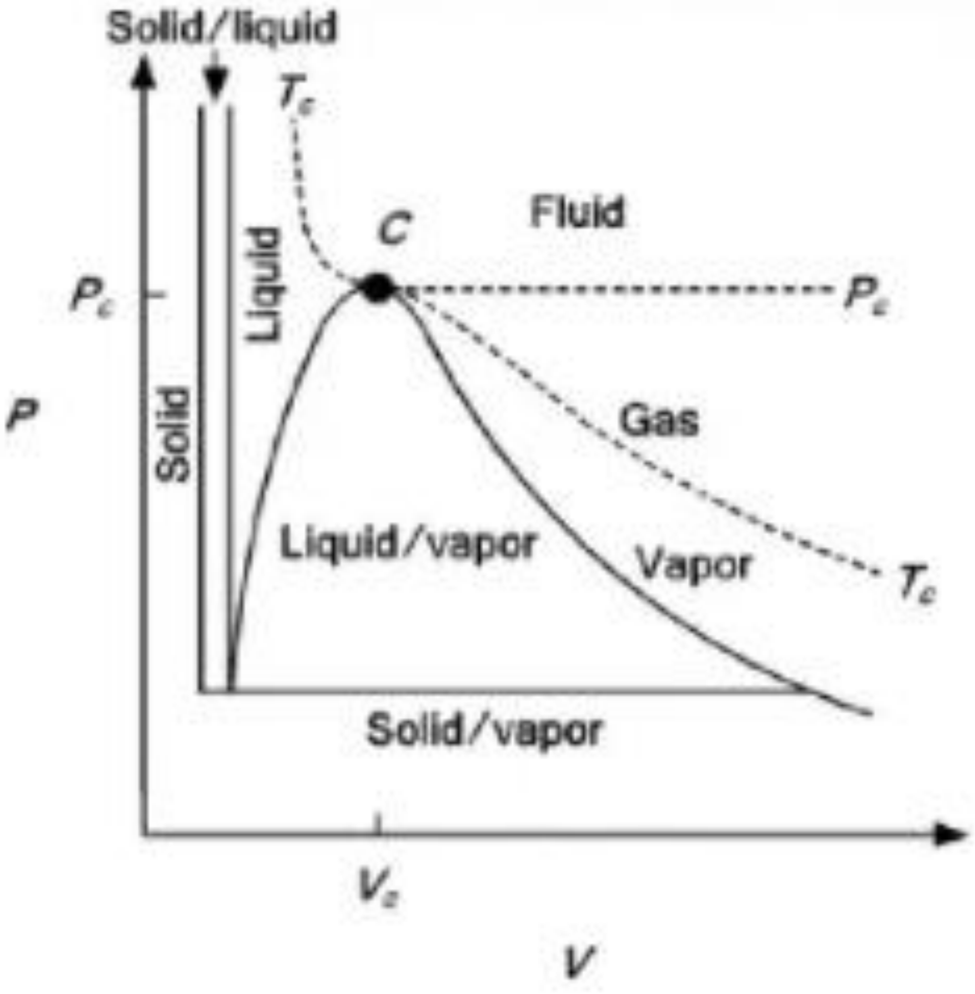
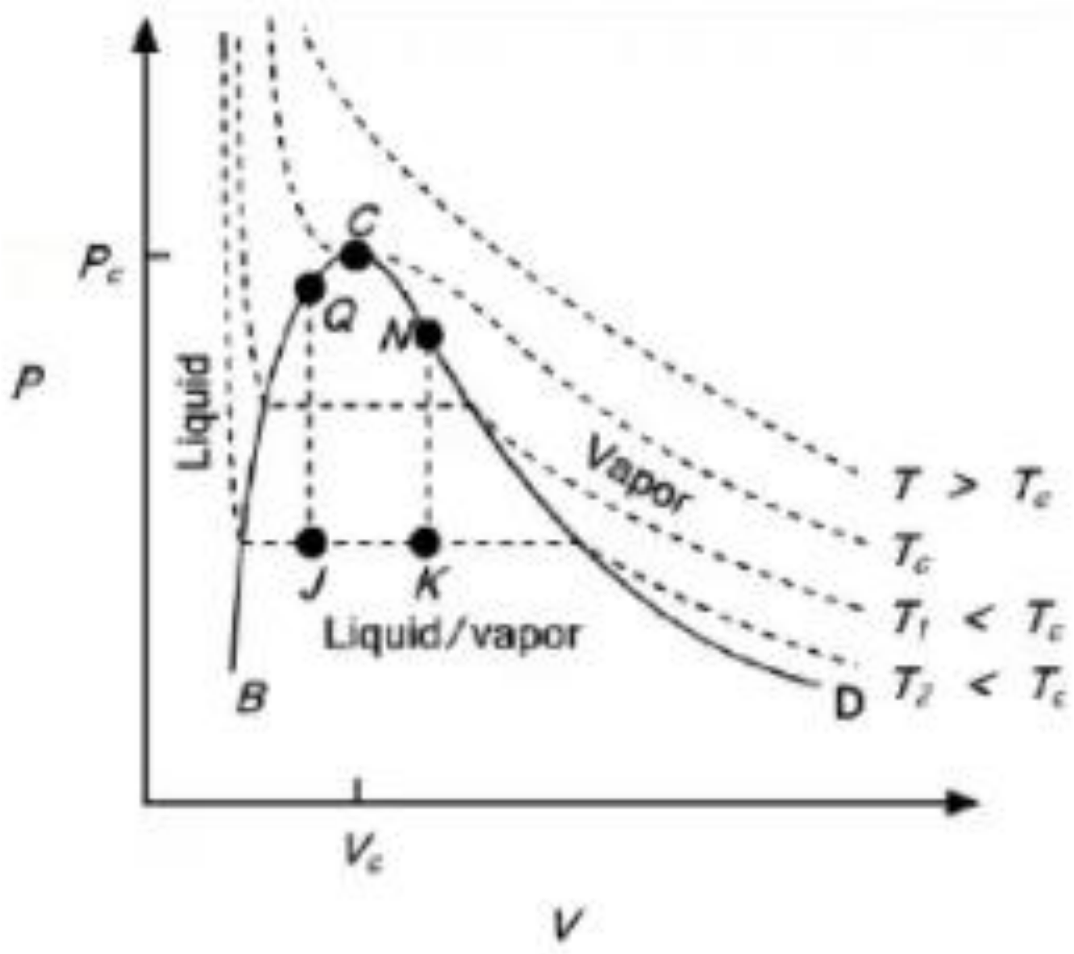

219
atm
18
6
0
Pressure, in Units of 10^{-3} atm
Critical Point
Fusion
Curve
Liquid
Phase
Vaporization
Curve
Solid
Phase
Triple
Point
Vapor
Phase
Sublimation
Curve
0
32°
60
706
Temperature, °F

Diagram PT

a.


Solid/liquid
T_c
C
Fluid
P_c
P_c
Liquid
P
Solid
Gas
Liquid/vapor
Vapor
T_c
Solid/vapor
V_c
V

b.


C
P_c
Q
N
P
Liquid
Vapor
T > T_c
T_c
J
K
T_1 < T_c
Liquid/vapor
B
D
T_2 < T_c
V_c
V

SINGLE PHASE REGION

Persamaan Keadaan (Equation of State = EOS)

adalah :

Persamaan yang menunjukkan hubungan antara P, V dan T suatu zat

atau $f(P, V, T) = 0$

Khas untuk tiap zat.

- An equation of state exists relating pressure, molar or specific volume, and temperature for any pure homogeneous fluid in equilibrium states.
- An equation of state may be solved for any one of the three quantities P, V, or T as a function of the other two.
- Example:

$$\boxed{dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP}$$

Volume expansivity: $\beta \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$

Isothermal compressibility: $\kappa \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$

$$\boxed{\frac{dV}{V} = \beta\ dT - \kappa\ dP}$$

  - For incompressible fluid, both β and κ are zero.
  - For liquids β is almost positive (liquid water between 0°C and 4°C is an exception), and κ is necessarily positive.
  - At conditions not close to the critical point, β and κ can be assumed constant:

$$\boxed{\ln\frac{V_2}{V_1} = \beta(T_2 - T_1) - \kappa(P_2 - P_1)}$$

GAS IDEAL

Gas Ideal

✓EOS berbentuk : $PV = RT$

atau $Z = PV/RT$ dan $Z = 1$

dengan

Z = faktor kompresibilitas

P = pressure, Pa

V = volume molar, m^3/mol

T = temperature absolut, K

R = konstanta gas umum,

$= 8{,}314\ m^3\ Pa\ mol^{-1}\ K^{-1} = 8{,}314\ J\ mol^{-1}\ K^{-1}$

Untuk satuan lain, lihat appendix A SVNA

✓ $U = f(T)$ → Energi dalam hanya fungsi suhu

✓ Berlaku pada tekanan sangat rendah

Hubungan antar Sifat pada Gas Ideal

$$Cv = \left(\frac{\partial U}{\partial T}\right)_V = \frac{dU}{dT} = Cv(T)$$

$$H = U + PV = U(T) + RT = H(T)$$

$$Cp = \left(\frac{\partial H}{\partial T}\right)_P = \frac{dH}{dT} = Cp(T)$$

$$Cp = \frac{dH}{dT} = \frac{dU}{dT} + \frac{d(RT)}{dT} = Cv + R \rightarrow \boxed{Cp = Cv + R}$$

$$dU = Cv\,dT \qquad \Delta U = \int Cv\,dT$$

$$dH = Cp\,dT \qquad \Delta H = \int Cp\,dT$$

Contoh :

Hitung densitas gas Nitrogen pada tekanan 1 atm dan suhu 30^{o}C? (Asumsi: Gas ideal)

Jawab:

$R = 82{,}06\ \text{cm}^3\ \text{atm mol}^{-1}\ \text{K}^{-1}$

$V = RT/P = (82{,}06)(30+273{,}15)/(1)$

$= 24\ 876{,}49\ \text{cm}^3/\text{mol}$

Mr N_2 = 28 g/mol

$\rho = (28\ \text{g/mol}) / (24\ 876{,}49\ \text{cm}^3/\text{mol})$

$= 0{,}001144\ \text{g/cm}^3$

Perhitungan Proses dengan Persamaan Gas Ideal

Proses-proses yg akan dibahas (untuk sistem tertutup), a.l. :

1. Proses Isotermal
2. Proses Isobarik
3. Proses Isokhorik
4. Proses Adibatik

Proses Isotermal ($\Delta T = 0$)

$\Delta U = C_v \, \Delta T = 0$ ingat $\left(\frac{\partial U}{\partial T}\right)_V = Cv$

$\Delta H = C_p \, \Delta T = 0$ ingat $\left(\frac{\partial H}{\partial T}\right)_P = Cp$

$$\Delta U = Q + W = 0$$

$$Q = -W = \int_{V_1}^{V_2} P\, dV \qquad \text{(ingat} \quad P = \frac{RT}{V}\text{)}$$

$$Q = -W = \int_{V_1}^{V_2} \frac{RT}{V}\, dV = RT \ln \frac{V_2}{V_1}$$

$$\text{(ingat } \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \text{ dan } T_2 = T_1 \text{ sehingga } \frac{V_2}{V_1} = \frac{P_1}{P_2}\text{)}$$

$$Q = -W = RT \ln \frac{P_1}{P_2} = -RT \ln \frac{P_2}{P_1} = RT \ln \frac{V_2}{V_1} \qquad \text{(T tetap)}$$

Proses Isobarik

$\Delta U = \int Cv\, dT$ dan $\Delta H = \int Cp\, dT$

$Q = \Delta H = \int Cp\, dT$ (P tetap)

$$W = -\int P\, dV = -P\int dV = -\int R\, dT = -R\int dT$$
$$= -R\,(T_2 - T_1) = -P\,(V_2 - V_1)$$

Cek dgn Hk I : $\Delta U = Q + W$

$$Cv\, dT = Cp\, dT - R\, dT$$

$$Cv = Cp - R \rightarrow Cp = Cv + R$$

Proses Isokhorik ($\Delta V=0$)

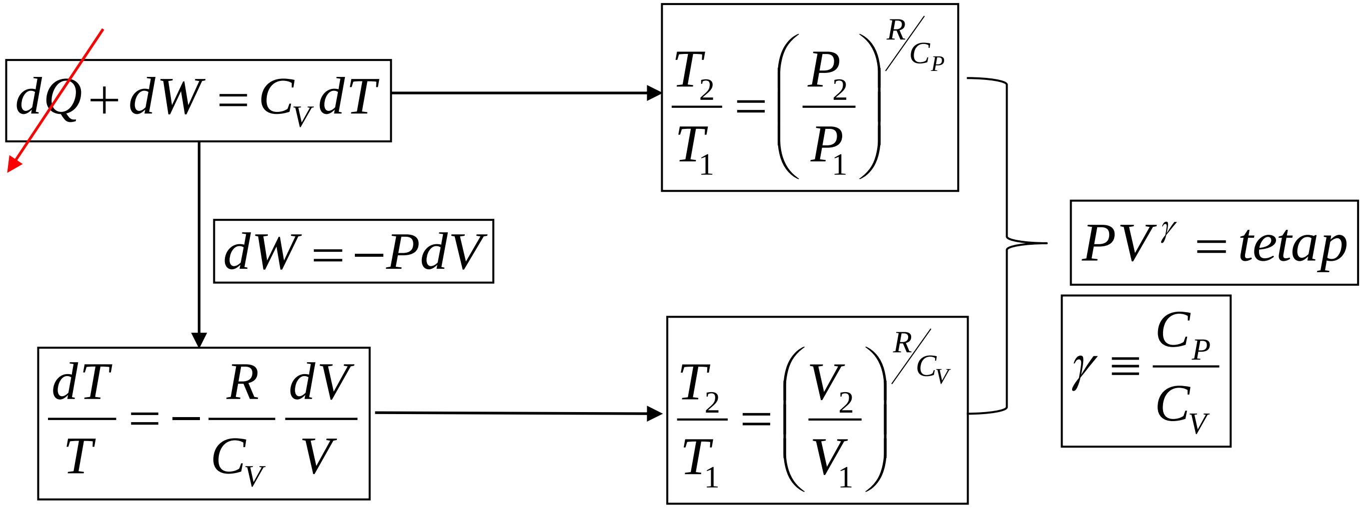
$\Delta U = \int Cv\, dT$ dan $\Delta H = \int Cp\, dT$

$Q = \Delta U = \int Cv\, dT$ (V tetap)

$W = -\int P\, \overset{=0}{\cancel{dV}} = 0 \rightarrow W = 0$

Cek dgn Hk I : $\Delta U = Q + \cancel{W} \rightarrow \Delta U = Q$

Proses Adiabatik (Q=0)



$$d\cancel{Q} + dW = C_V\, dT$$

$$dW = -P\,dV$$

$$\frac{dT}{T} = -\frac{R}{C_V}\frac{dV}{V}$$

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{R/C_P}$$

$$\frac{T_2}{T_1} = \left(\frac{V_2}{V_1}\right)^{R/C_V}$$

$$PV^{\gamma} = tetap$$

$$\gamma \equiv \frac{C_P}{C_V}$$

$$\boxed{\begin{aligned} &T\,V^{\gamma-1} = tetap \rightarrow T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1} \\ &T\,P^{(1-\gamma)/\gamma} = tetap \\ &P\,V^{\gamma} = tetap \end{aligned}}$$

γ = 1,67 pada gas monoatomik (He, Ne, Ar dsb)

γ = 1,4 pada gas diatomik (H_2, N_2, O_2)

γ = 1,3 pada gas poli atomik sederhana (CO_2, SO_2, NH_3, CH_4)

Proses Adiabatik (lanjutan)

dari Hk I: $\Delta U = Q + W \rightarrow W = \Delta U$

$$W = \int Cv\, dT = Cv\, \Delta T \qquad (Cv = \frac{R}{\gamma - 1})$$

$$= \frac{R}{\gamma - 1} \Delta T = \frac{RT_2 - RT_1}{\gamma - 1} = \frac{P_2V_2 - P_1V_1}{\gamma - 1}$$

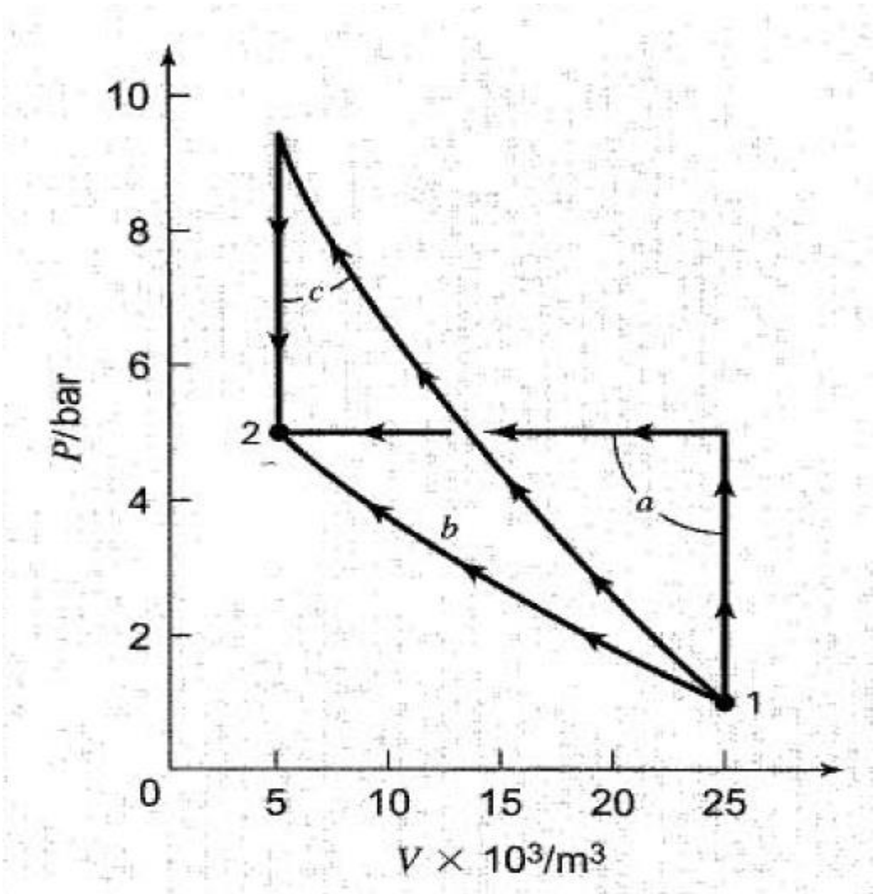
$$W = \frac{P_1V_1}{\gamma - 1}\left[\left(\frac{P_2}{P_1}\right)^{\frac{\gamma - 1}{\gamma}} - 1\right] = \frac{RT_1}{\gamma - 1}\left[\left(\frac{P_2}{P_1}\right)^{\frac{\gamma - 1}{\gamma}} - 1\right]$$

Irreversible Process

- The work of an irreversible process is calculated:
  - First, the work is determined for a mechanically reversible process.
  - Second, the result is multiple or divided by an efficiency to give the actual work.

Ex. 1

Air is compressed from an initial condition of 1 bar and 25°C to a final state of 5 bar and 25 °C by three different mechanically reversible processes in a closed system. (1) heating at constant volume followed by cooling at constant pressure; (2) isothermal compression; (3) adiabatic compression followed by cooling at constant volume. Assume air to be an ideal gas with the constant heat capacities, $C_V = (5/2)R$ and $C_P = (7/2)R$. Calculate the work required, heat transferred, and the changes in internal energy and enthalpy of the air in each process.



Choose the system as 1 mol of air, contained in an imaginary frictionless piston /cylinder arrangement.

For R = 8.314 J/mol.K, $C_V = 20.785$, $C_P = 29.099$ J/mol.K

The initial and final molar volumes are: $V_1 = 0.02479$ m^3 and $V_2 = 0.004958$ m^3

The initial and final temperatures are identical: $\Delta U = \Delta H = 0$

(1) $Q = C_V\Delta T + C_P\Delta T = -9915$ J; $W = \Delta U - Q = 9915$ J

(2) $Q = -W = RT\ln\left(\frac{P_1}{P_2}\right) = -3990$ J

(3) adiabatic compression: $\boxed{T_2 = T_1\left(\frac{V_1}{V_2}\right)^{\gamma-1} = 567.57\ K}$ $\boxed{P_2 = P_1\left(\frac{V_1}{V_2}\right)^{\gamma} = 9.52\ bar}$

$$\boxed{W = C_V\Delta T = 5600\ J}$$

cooling at constant V, W = 0.

overall, W = 5600 J, $Q = \Delta U - W = -5600$ J.

Ex. 2

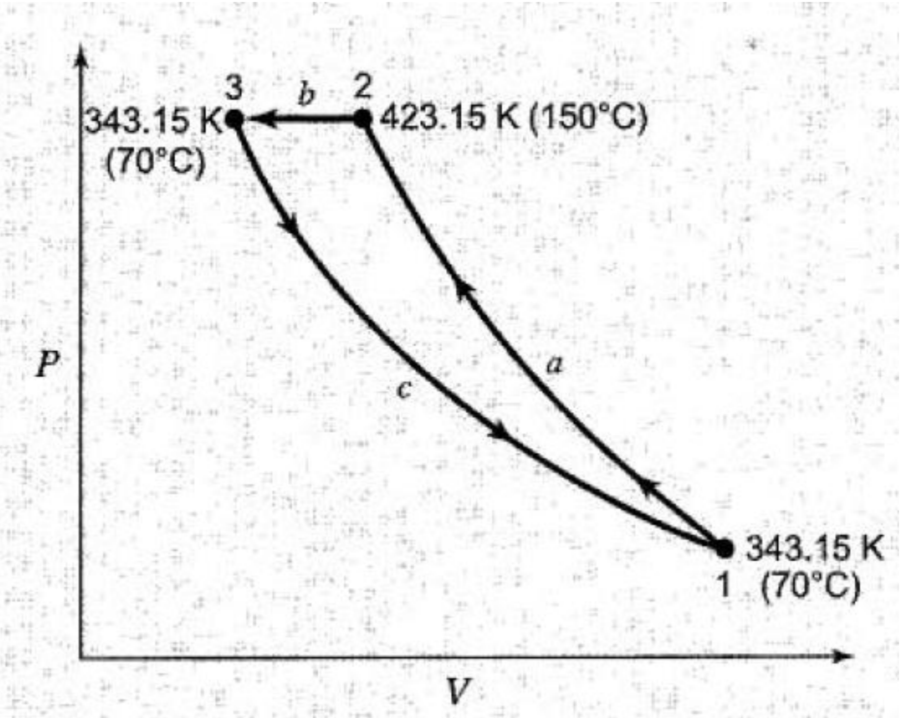
An ideal gas undergoes the following sequence of mechanically reversible processes in a closed system:

(1) From an initial state of 70°C and 1 bar, it is compressed adiabatically to 150 °C.

(2) It is then cooled from 150 to 70 °C at constant pressure.

(3) Finally, it is expanded isothermally to its original state.

Calculate W, Q, ΔU, and ΔH for each of the three processes and for the entire cycle. Take $C_V = (3/2)R$ and $C_P = (5/2)R$. If these processes are carried out irreversibly but so as to accomplish exactly the same changes of state (i.e. the same changes in P, T, U, and H), then different values of Q and W result. Calculate Q and W if each step is carried out with an efficiency of 80%.



Choose the system as 1 mol of air, contained in an imaginary frictionless piston /cylinder arrangement. For R = 8.314 J/mol.K, C_V = 12.471, C_P = 20.785 J/mol.K

(1) For an ideal gas undergoing adiabatic compression, Q = 0

$\Delta U = W = C_V \Delta T = 12.471(150 - 70) = 998$ J

$\Delta H = C_P \Delta T = 20.785(150 - 70) = 1663$ J

$$\boxed{P_2 = P_1 \left(\frac{T_2}{T_1} \right)^{\gamma/(\gamma-1)} = 1.689\ bar}$$

(2) For the constant-pressure process:

$Q = \Delta H = C_P \Delta T = 20.785(70 - 150) = -1663$ J

$\Delta U = C_V \Delta T = 12.471(70 - 150) = -998$ J

$W = \Delta U - Q = 665$ J

(3) Isotherm process, ΔU and ΔH are zero:

$$\boxed{Q = -W = RT \ln\left(\frac{P_3}{P_1} \right) = 1495\ J}$$

(4) Overall: $Q = 0 - 1663 + 1495 = -168$ J

$W = 998 + 665 - 1495 = 168$ J

$\Delta U = 0$

$\Delta H = 0$

Irreversible processes:

(1) For 80% efficiency:

W(irreversible) = W(reversible) / 0.8 = 1248 J

ΔU(irreversible) = ΔU(reversible) = 998 J

Q(irreversible) = ΔU – W = -250 J

(2) For 80% efficiency:

W(irreversible) = W(reversible) / 0.8 = 831 J

$\Delta U = C_V \Delta T = 12.471(70 - 150) = -998$ J

$Q = \Delta U - W = -998 - 831 = -1829$ J

(3) Isotherm process, ΔU and ΔH are zero:

W(irreversible) = W(reversible) x 0.8 = -1196 J

$Q = \Delta U - W = 1196$ J

(4) Overall: $Q = -250 - 1829 + 1196 = -883$ J

$W = 1248 + 831 - 1196 = 883$ J

$\Delta U = 0$

$\Delta H = 0$

The total work required when the cycle consists of three irreversible steps is more than 5 times the total work required when the steps are mechanically reversible, even though each irreversible step is assumed 80% efficient.

Ex. 3

A 400g mass of nitrogen at 27 °C is held in a vertical cylinder by a frictionless piston. The weight of the piston makes the pressure of the nitrogen 0.35 bar higher than that of the surrounding atmosphere, which is at 1 bar and 27°C. Take $C_V = (5/2)R$ and $C_P = (7/2)R$. Consider the following sequence of processes:

(1) Immersed in an ice/water bath and comes to equilibrium

(2) Compressed reversibly at the constant temperature of 0°C until the gas volume reaches one-half the value at the end of step (1) and fixed the piston by latches

(3) Removed from the ice/water bath and comes to equilibrium to thermal equilibrium with the surrounding atmosphere

(4) Remove the latches and the apparatus return to complete equilibrium with its surroundings.

Nitrogen may be considered an ideal gas. Calculate W, Q, ΔU, and ΔH for each step of the cycle.

The steps:

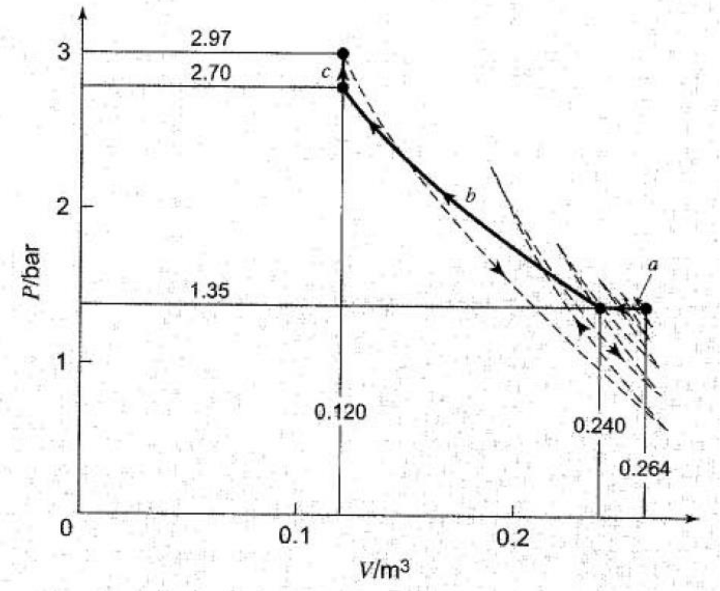
$$n = \frac{m}{M} = 14.286\ mol$$

(1) $27^\circ C, 1.35 bar \xrightarrow{const\ P} 0^\circ C, 1.35 bar$

(2) $0^\circ C, V_2 \xrightarrow{const\ T} 0^\circ C, V_3 = \frac{1}{2} V_2$

(3) $0^\circ C, V_3 \xrightarrow{const\ V} 27^\circ C, V_4 = V_3$

(4) $27^\circ C, P_4 \xrightarrow{T_4 = T_1} 27^\circ C, 1.35 bar$



(1) $\boxed{W_1 = -n\int PdV = -nP\Delta V = -nR\Delta T = 3207\ J}$ $\boxed{Q_1 = n\Delta H_1 = nC_P\Delta T = 11224\ J}$

$\boxed{n\Delta U_1 = Q_1 + W_1 = -11224 + 3207 = -8017\ J}$

(2) $\boxed{\Delta U_2 = \Delta H_2 = 0}$ $\boxed{Q_2 = -W_2 = nRT\ln\frac{V_3}{V_2} = -22487\ J}$

(3) $\boxed{W_3 = 0}$ $\boxed{Q_3 = n\Delta U_3 = nC_V\Delta T = 8017\ J}$ $\boxed{n\Delta H_3 = nC_P\Delta T = 11224\ J}$

(4) the oscillation of the piston → irreversible process with $T_4 = T_1$

$\boxed{\Delta U_4 = \Delta H_4 = 0}$ $\boxed{Q_4 = -W_4}$

Ex. 4

Air flows at a steady rate through a horizontal insulated pipe which contains a partly closed valve. The conditions of the air upstream from the valve are 20°C and 6 bar, and the downstream pressure is 3 bar. The line leaving the valve is enough larger than the entrance line so that the kinetic-energy change as it flows through the valve is negligible. If air is regarded as an ideal gas, what is the temperature of the air some distance downstream from the valve?

Flow through a partly closed valve is known as a throttling process.
For steady flow system:

$$\begin{tikzcd} \cancel{\frac{d(mU)_{cv}}{dt}} + \Delta\left[\left(H + \cancel{\frac{1}{2}u^2} + \cancel{zg}\right)\dot{m}\right]_{fs} = \cancel{\dot{Q}} + \cancel{\dot{W}} \arrow[r] & \boxed{\Delta H = 0} \arrow[d] \\ \text{Ideal gas:} \quad \Delta H = \int C_P \, dT \arrow[r] & \boxed{T_2 = T_1} \end{tikzcd}$$

The result that ΔH = 0 is general for a throttling process.

If the flow rate of the air is 1 mol/s and if the pipe has an inner diameter of 5 cm, both upstream and downstream from the valve, what is the kinetic-energy change of the air and what is its temperature change? For air, $C_P = (7/2)R$ and the molar mass is $M = 29$ g/mol.

Upstream molar volume:

$$\boxed{V_1 = \frac{RT_1}{P_1} = \frac{83.14\times 293.15}{6}\times 10^{-6} = 4.062\times 10^{-3}\ m^2/mol} \quad \boxed{u_1 = n\frac{1}{A\rho} = n\frac{V}{A} = 2.069\ m/s}$$

Downstream molar volume:

$$\boxed{V_2 = 2V_1} \quad \boxed{u_2 = 2u_1 = 4.138\ m/s}$$

The rate of the change in kinetic energy:

$$\boxed{\dot{m}\Delta\left(\frac{1}{2}u^2\right) = \dot{n}M\left(\frac{1}{2}u^2\right) = (1\times 29\times 10^{-3})\frac{(4.138^2 - 2.069^2)}{2} = 0.186\ J/s}$$

$$\cancel{\frac{d(mU)_{cv}}{dt}} + \Delta\left[\left(H + \frac{1}{2}u^2 + \cancel{zg}\right)\dot{m}\right]_{fs} = \cancel{\dot{Q}} + \cancel{\dot{W}} \longrightarrow \boxed{\dot{m}\left(\frac{C_P}{M}\Delta T + \Delta\left(\frac{1}{2}u^2\right)\right) = 0}$$

$$\downarrow$$

$$\boxed{\Delta T = -0.0064\ K}$$