EOS

What's the Equation of State?

- We can find a value for a state by using diagram or table → often inconvenient
- Scientists seek an equation that can explain measured variables from experiment

Boyle's law:
P of an ideal gas is inversely proportional to the volume if the temperature is constant.

$$P \propto \frac{1}{V}$$
$$or$$
$$P_1V_1 = P_2V_2$$

Charles's law:
When the P is constant, V of the gas is directly proportional to T

$$V \propto T$$
$$or$$
$$\frac{V_2}{V_1} = \frac{T_2}{T_1}$$

Avogadro's law:
the V and n(moles) of the gas are directly proportional if T, P is constant

$$V \propto n$$
$$or$$
$$\frac{V_1}{n_1} = \frac{V_2}{n_2}$$

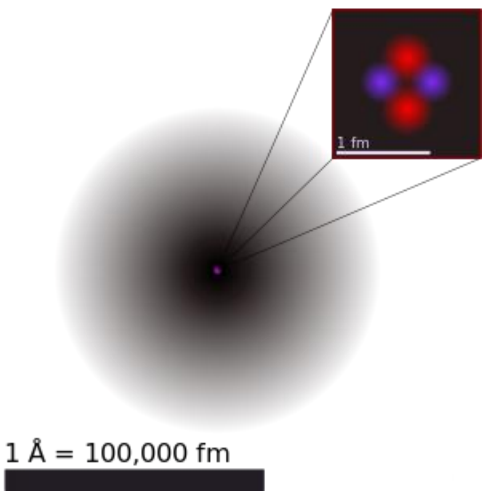
Ideal Gas equation of state $PV = nRT \ (or\ Pv = RT)$

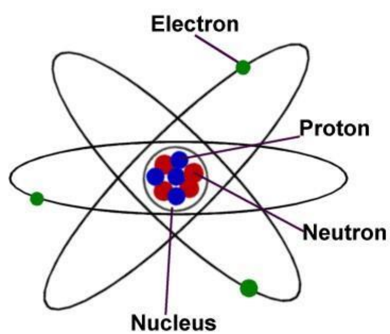
No size(volume)
No intermolecular forces

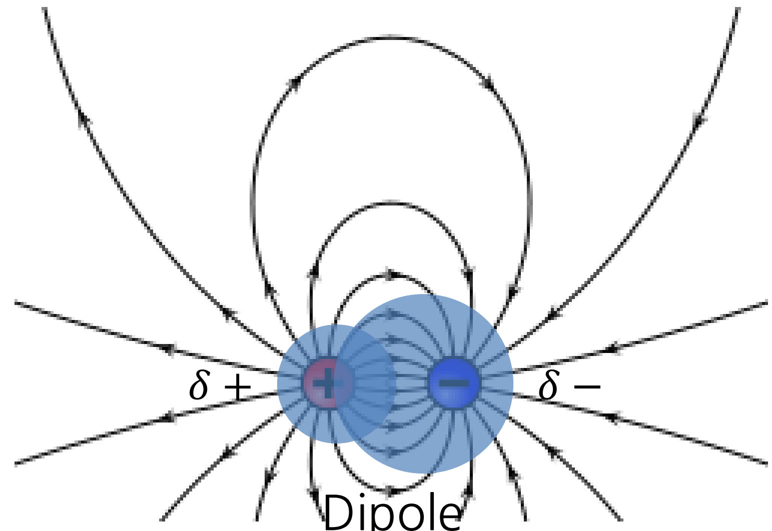
Benoît Paul-Émile Clapeyron
(1799-1864)

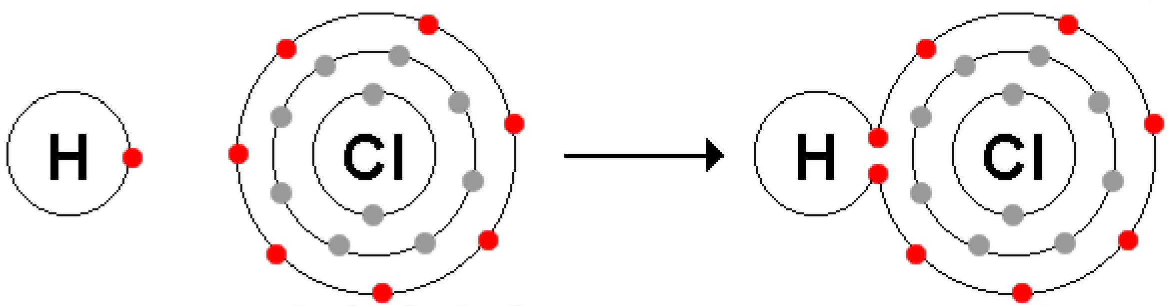
Real molecule

- An atom contains positively charged nucleus(+) surrounded by negatively charged electron cloud.



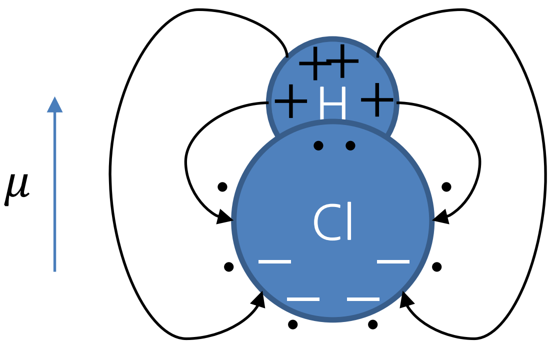


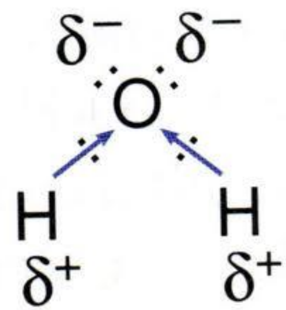


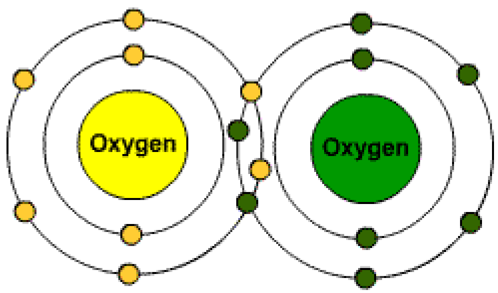


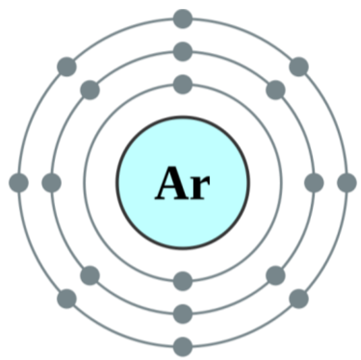
http://www.physchem.co.za/OB11-mat/bonding.htm

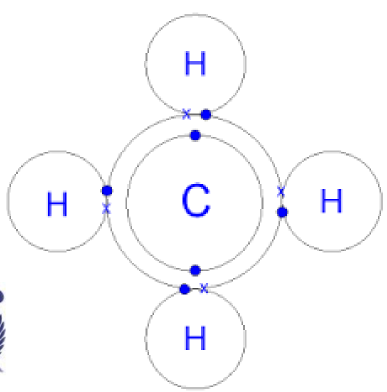
Dipole moment

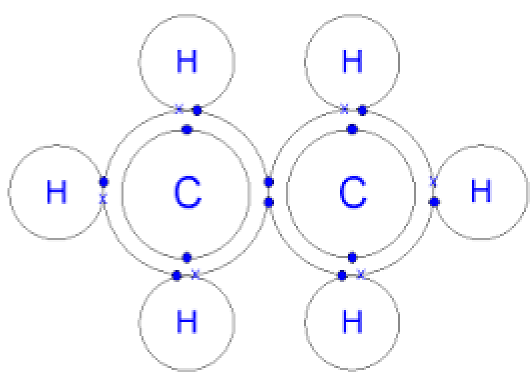










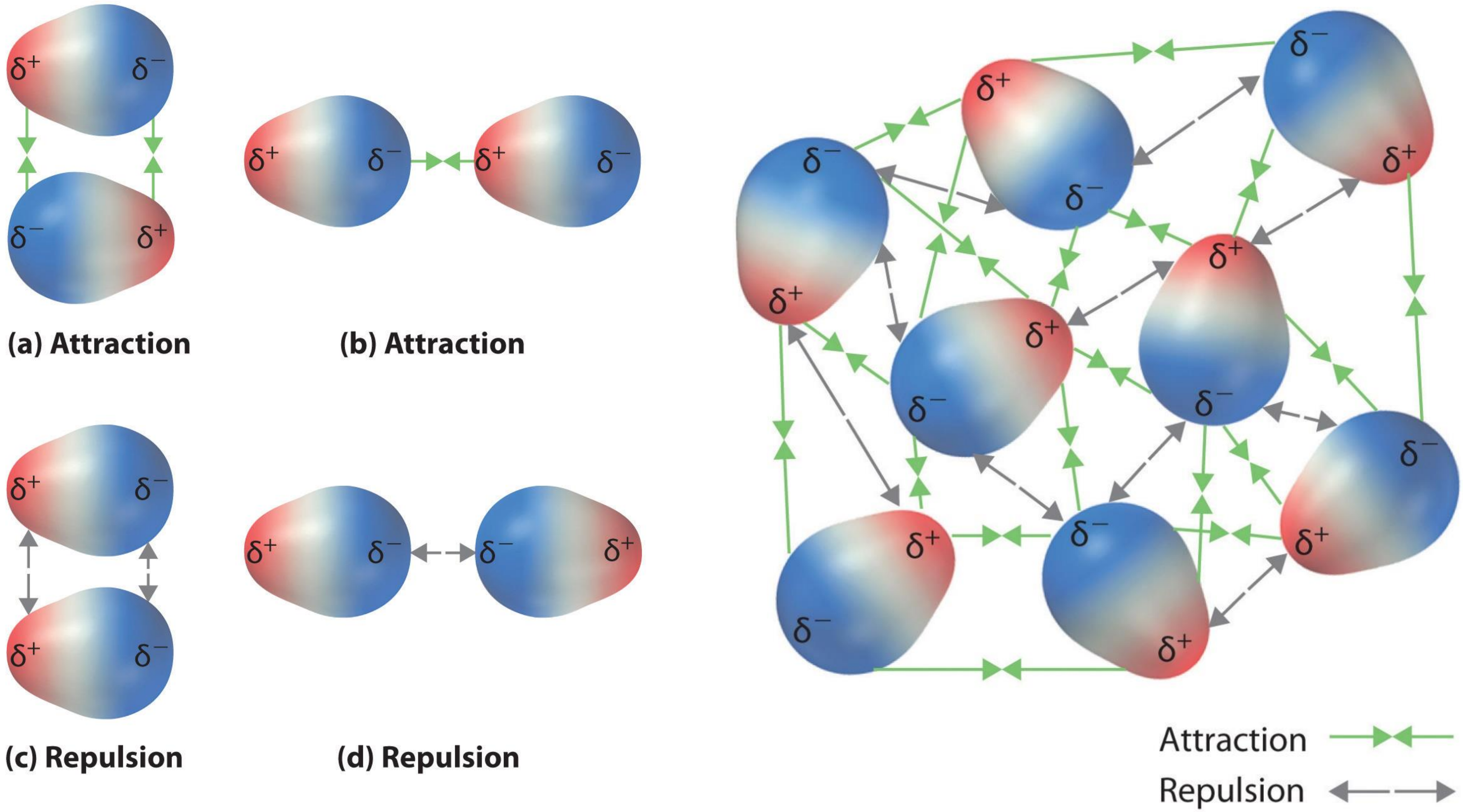


Molecule	μ
HCl	1.08
H_2O	1.85
H_2, N_2, O_2	0
Ne, Ar	0
CH_4, C_2H_6, C_3H_8… (methane, ethane, propane…)	0
CO_2	0

http://www.gcsescience.com/o10.htm

http://www.school-for-champions.com/chemistry/bonding_types.htm#.VRHvsPmUdFo

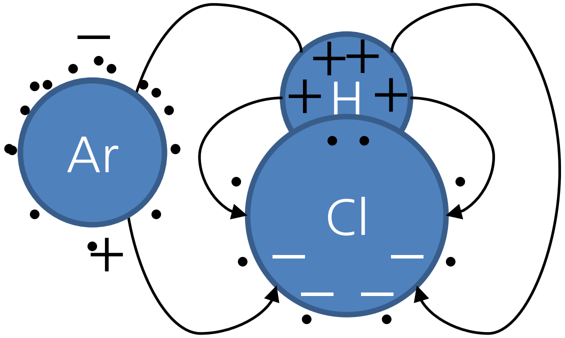
Dipole-dipole force (Keesom force)



http://chemwiki.ucdavis.edu/Wikitexts/UC_Davis/UCD_Chem_2B/UCD_Chem_2B%3A_Larsen/Unit_II%3A_States_of_Matter/Intermolecular_Interactions/11.2%3A_Intermolecular_Forces

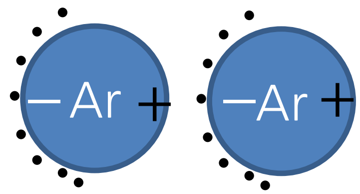
Dipole-induced dipole force (Debye force)

- Dipole-induced dipole force (Debye force)



Dispersion Force

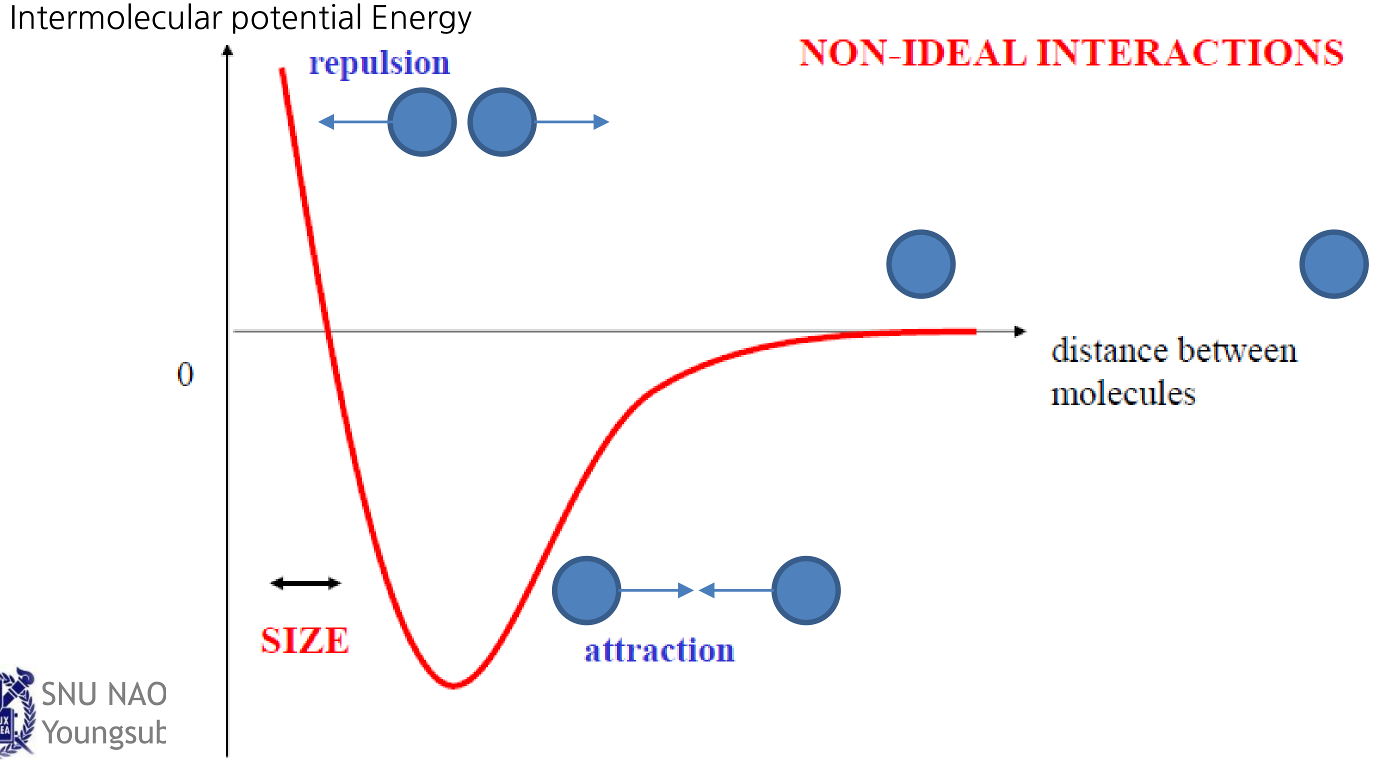
- Instantaneously induced dipole-induced dipole force (London Force)



http://chemwiki.ucdavis.edu/Physical_Chemistry/Quantum_Mechanics/Atomic_Theory/Intermolecular_Forces/London_Dispersion_Interactions

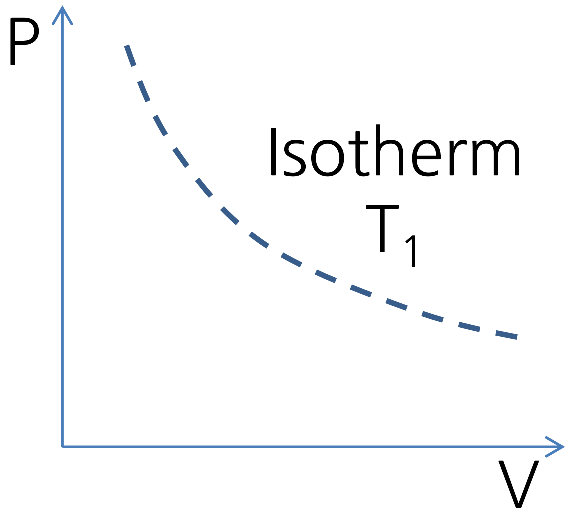
Van der Waals forces

- Collection of
  - dipole-dipole force
  - dipole-induced dipole force
  - induced dipole-induced dipole force (Dispersion force)

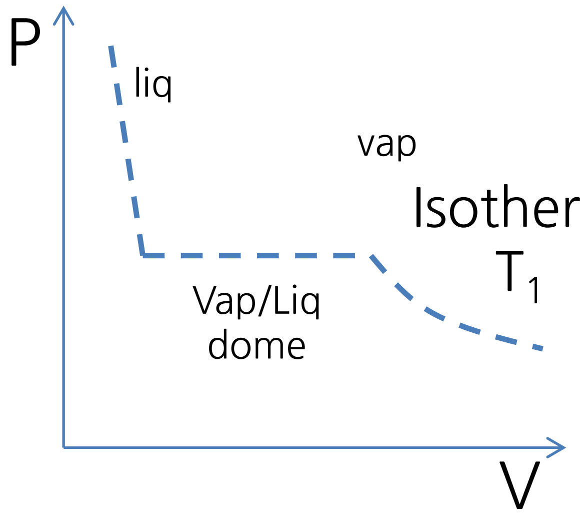


Equation of State

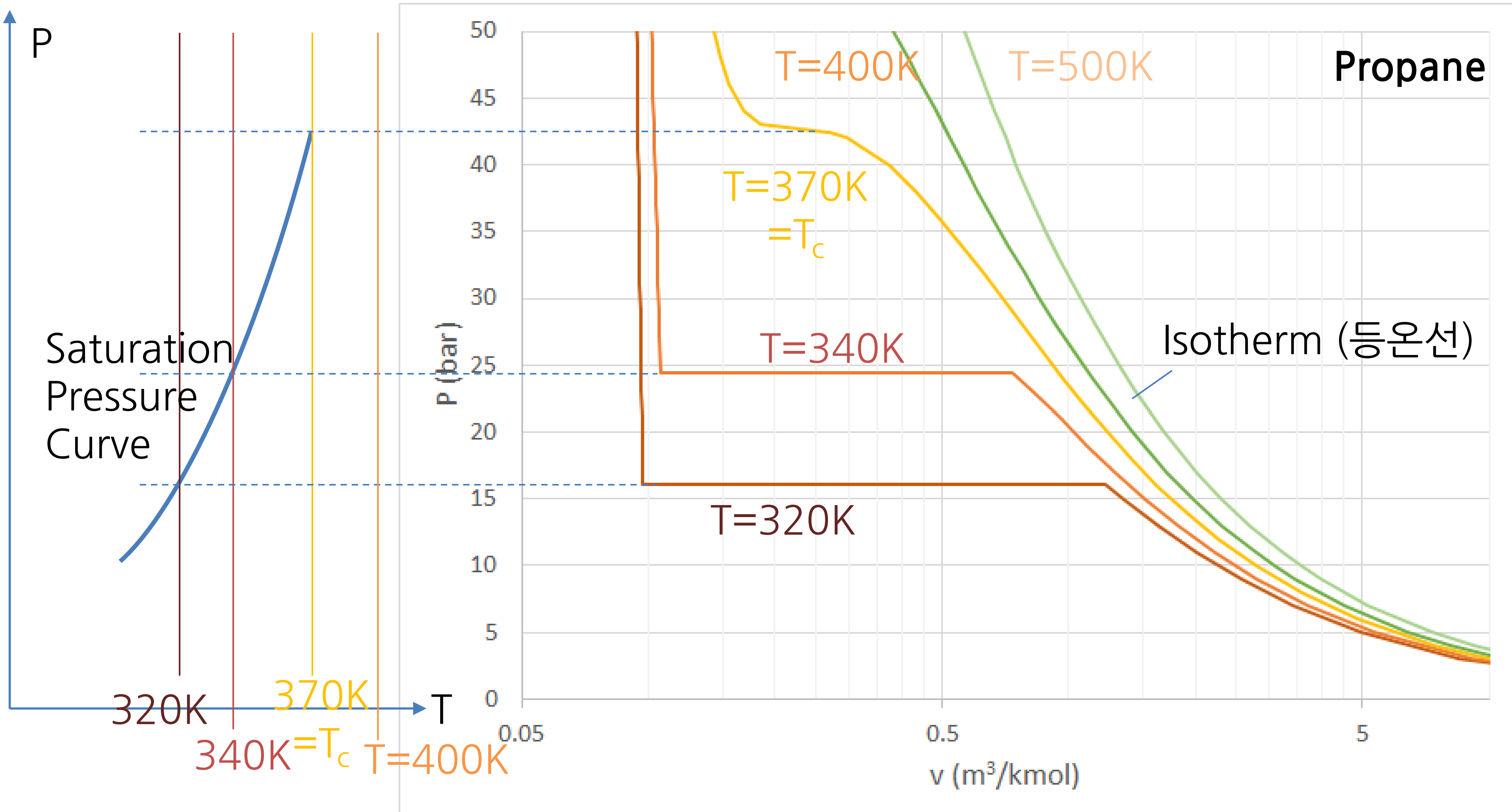
- Ideal gas Pv=RT



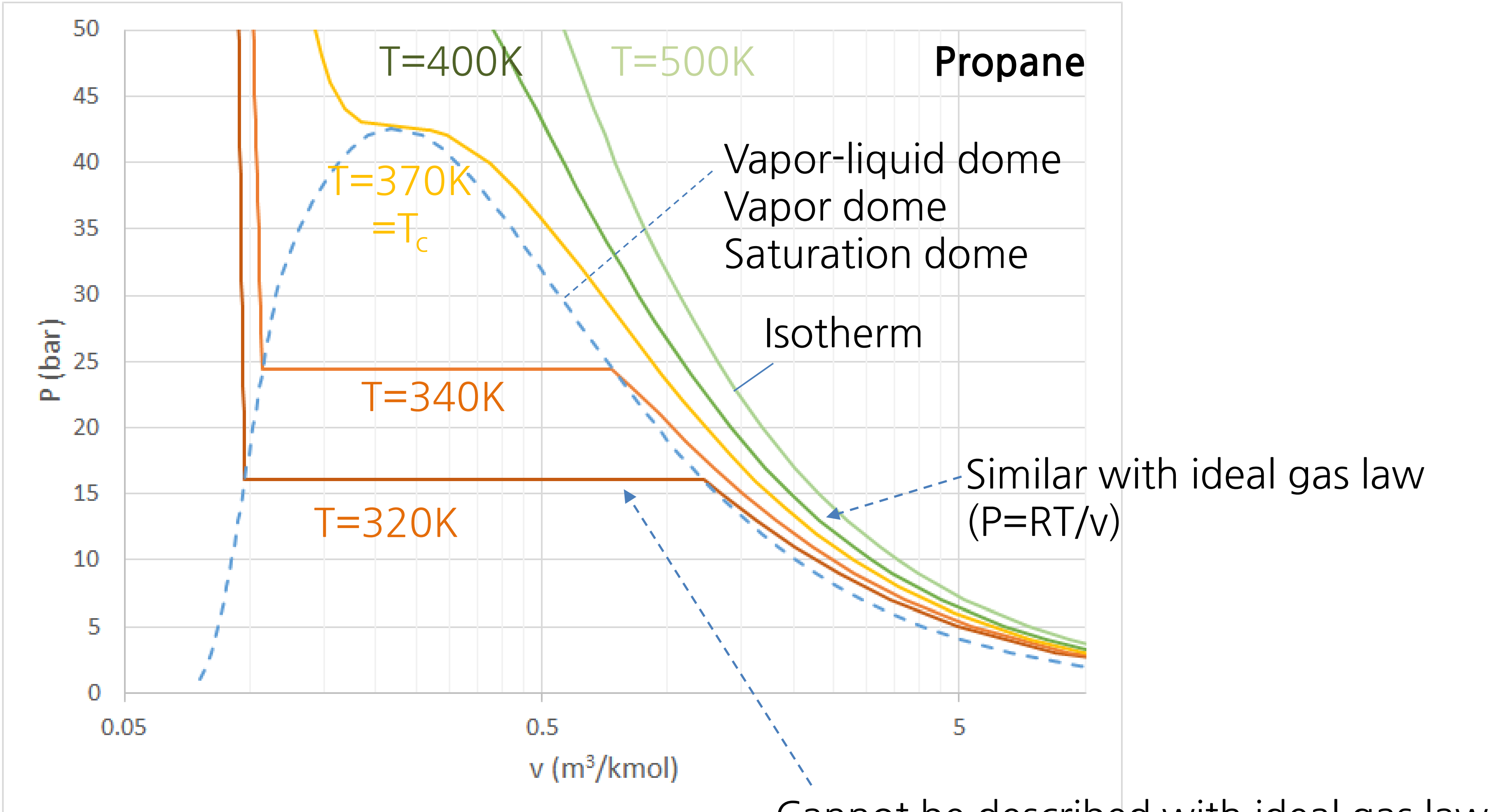
- Real gas



PT diagram and Pv diagram



Pv diagram and isotherm



Cannot be described with ideal gas law

van der Waals Equation

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

Reflect the reducing volume due to the size of molecule.

Reflect the reducing pressure due to the interaction of molecules.

Number of molecules per unit volume: $N \propto$

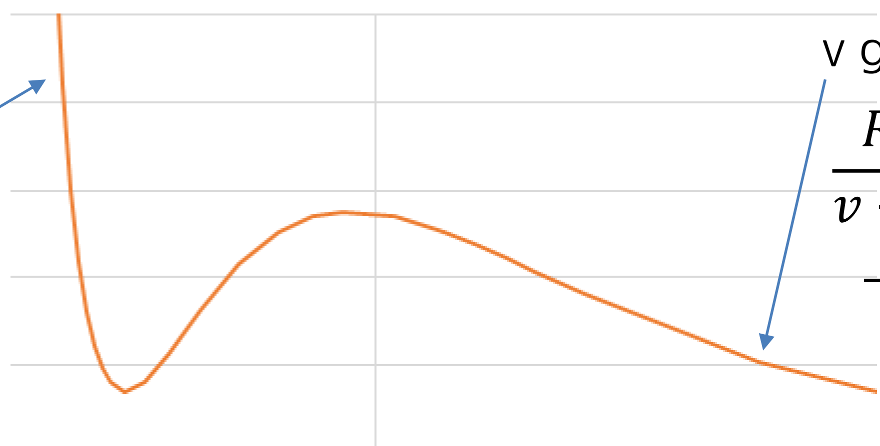
Number of combination:

$${}_N C_2 = \frac{N(N-1)}{2} \propto N^2 \propto \left(\frac{n}{V}\right)^2 = \frac{1}{v^2}$$

Then, if you adjust a and b,
You can make a shape that is similar to the isotherm!

v near b

$$\frac{RT}{v-b} \approx \infty$$



v goes to very large

$$\frac{RT}{v-b} \approx \frac{RT}{v}$$

$$-\frac{a}{v^2} \approx 0$$

$$\Longrightarrow P = \frac{RT}{v}$$

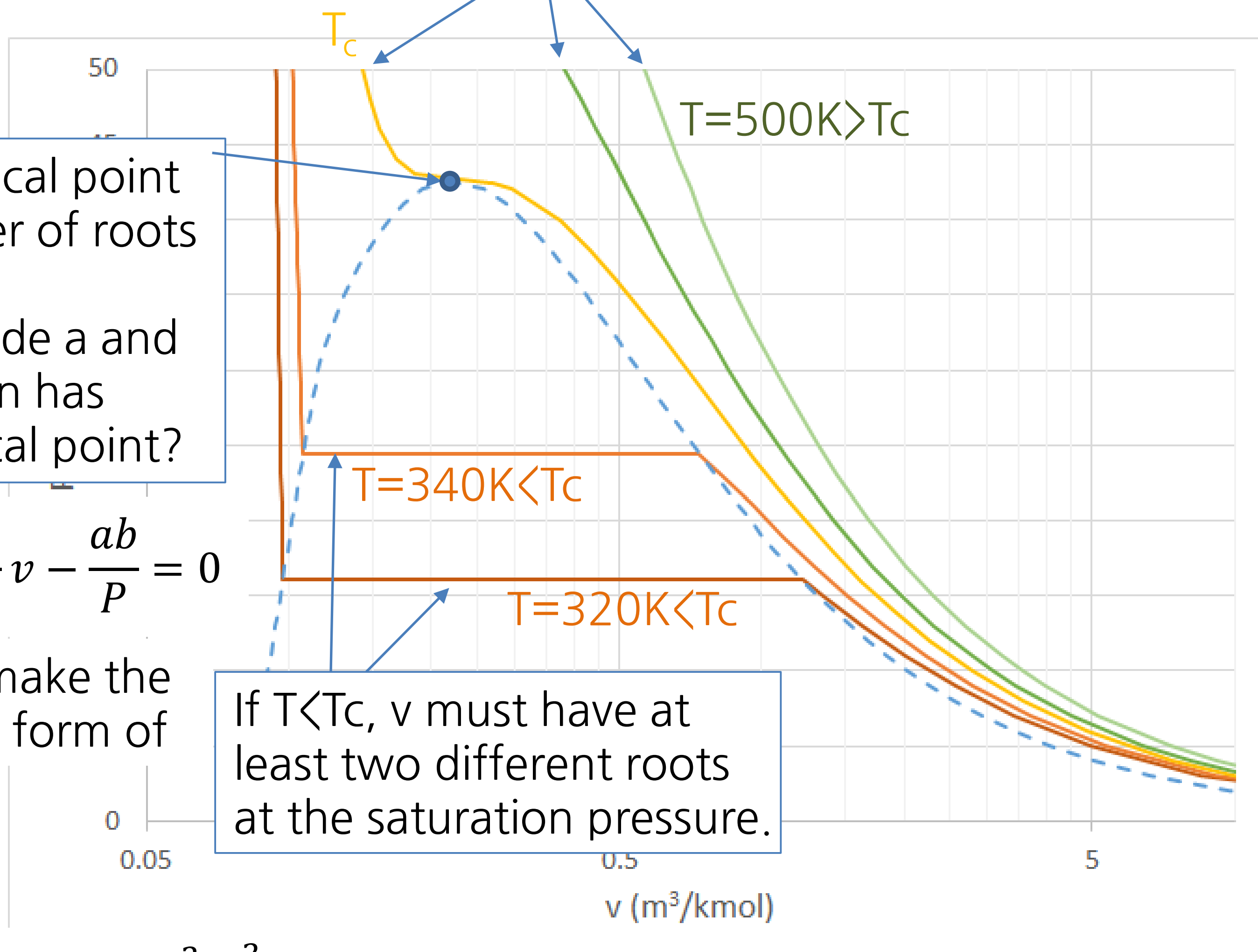
Cubic EOS

- 2 parameters (a: attraction, b: size)
  - Van der Waals
    - $P = \frac{RT}{v-b} - \frac{a}{v^2}$ or $(Pv^3 - (RT + Pb)v^2 + av - ab = 0)$
    - $a = \frac{27}{64}\frac{(RT_c)^2}{P_c} = \frac{0.42188R^2{T_c}^2}{P_c}$, $b = \frac{(RT_c)}{8P_c} = 0.125RT_c/P_c$

$$P = \frac{RT}{v-b} - \frac{a}{v^2} \quad \Rightarrow \quad v^3 - \left(\frac{RT}{P} + b\right)v^2 + \frac{a}{P}v - \frac{ab}{P} = 0$$

  - Redlich-Kwong
    - $P = \frac{RT}{v-b} - \frac{a}{\sqrt{T}v(v+b)}$
    - $a = 0.42748R^2{T_c}^{2.5}/P_c, b = 0.08664RT_c/P_c$

If T>=Tc, only one v for all P



In this graph, the critical point means that the number of roots change.

Then how about decide a and b to make the equation has triple roots at the critical point?

If T<Tc, v must have at least two different roots at the saturation pressure.

$$v^3 - \left(\frac{RT}{P} + b\right)v^2 + \frac{a}{P}v - \frac{ab}{P} = 0$$

Let's set a and b to make the equation becomes a form of

$$(v - v_c)^3 = 0$$

$$a = \frac{27}{64}\frac{(RT_c)^2}{P_c} = \frac{0.42188R^2{T_c}^2}{P_c}$$

$$b = \frac{(RT_c)}{8P_c} = 0.125RT_c/P_c$$

Analytic solution of cubic equation

$$Ax^3 + Bx^2 + Cx + D = 0$$

$\Downarrow$ $x = t - \frac{B}{3A}$

$$t^3 + Pt + Q = 0 \qquad P = \left(\frac{-B^2 + 3AC}{3A^2}\right) \qquad Q = \frac{2B^3 - 9ABC + 27A^2D}{27A^3}$$

$\Downarrow$ $u + v = t$

$$z^2 + Qz - \frac{P^3}{27} = 0 \qquad z_1 = u^3 = -\frac{Q}{2} + \sqrt{\frac{Q^2}{4} + \frac{P^3}{27}} \qquad z_2 = v^3 = -\frac{Q}{2} - \sqrt{\frac{Q^2}{4} + \frac{P^3}{27}}$$

Case 1, D: $\frac{Q^2}{4} + \frac{P^3}{27} \geq 0$ →One real root for x

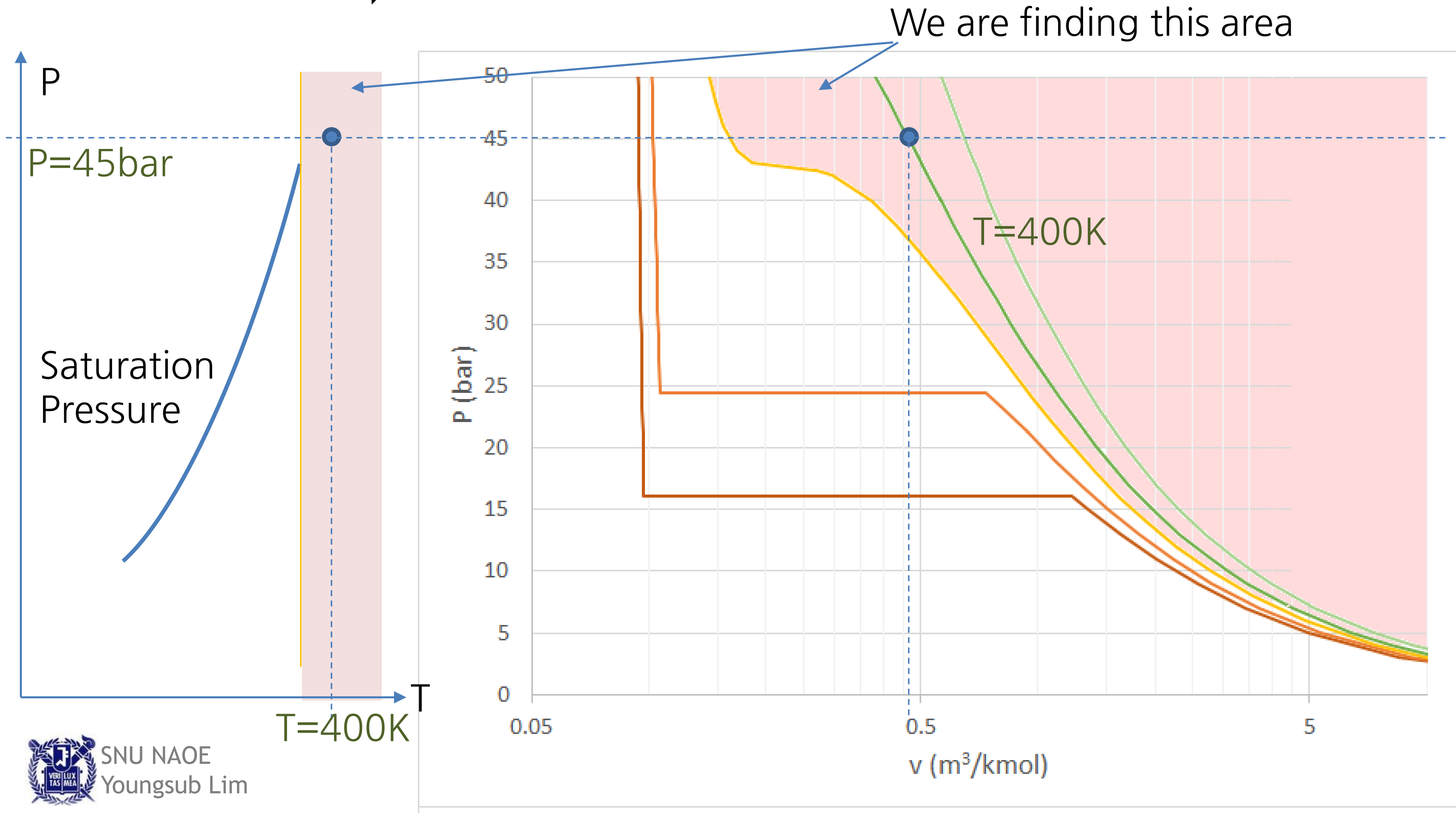
$$x = t - \frac{B}{3A} = u + v - \frac{B}{3A} = \sqrt[3]{-\frac{Q}{2} + \sqrt{\frac{Q^2}{4} + \frac{P^3}{27}}} + \sqrt[3]{-\frac{Q}{2} - \sqrt{\frac{Q^2}{4} + \frac{P^3}{27}}} - \frac{B}{3A}$$

Case 2, D: $\frac{Q^2}{4} + \frac{P^3}{27} < 0$ →Three real roots for x

$$x_k = t_k - \frac{B}{3A} = 2\sqrt{-\frac{P}{3}}\cos\left(\frac{1}{3}\arccos\left(\frac{3Q}{2P}\sqrt{-\frac{3}{P}}\right) + \frac{2}{3}k\pi\right) - \frac{B}{3A}, \qquad k = 0,1,2$$

Example with real Pv diagram

- When T>=Tc



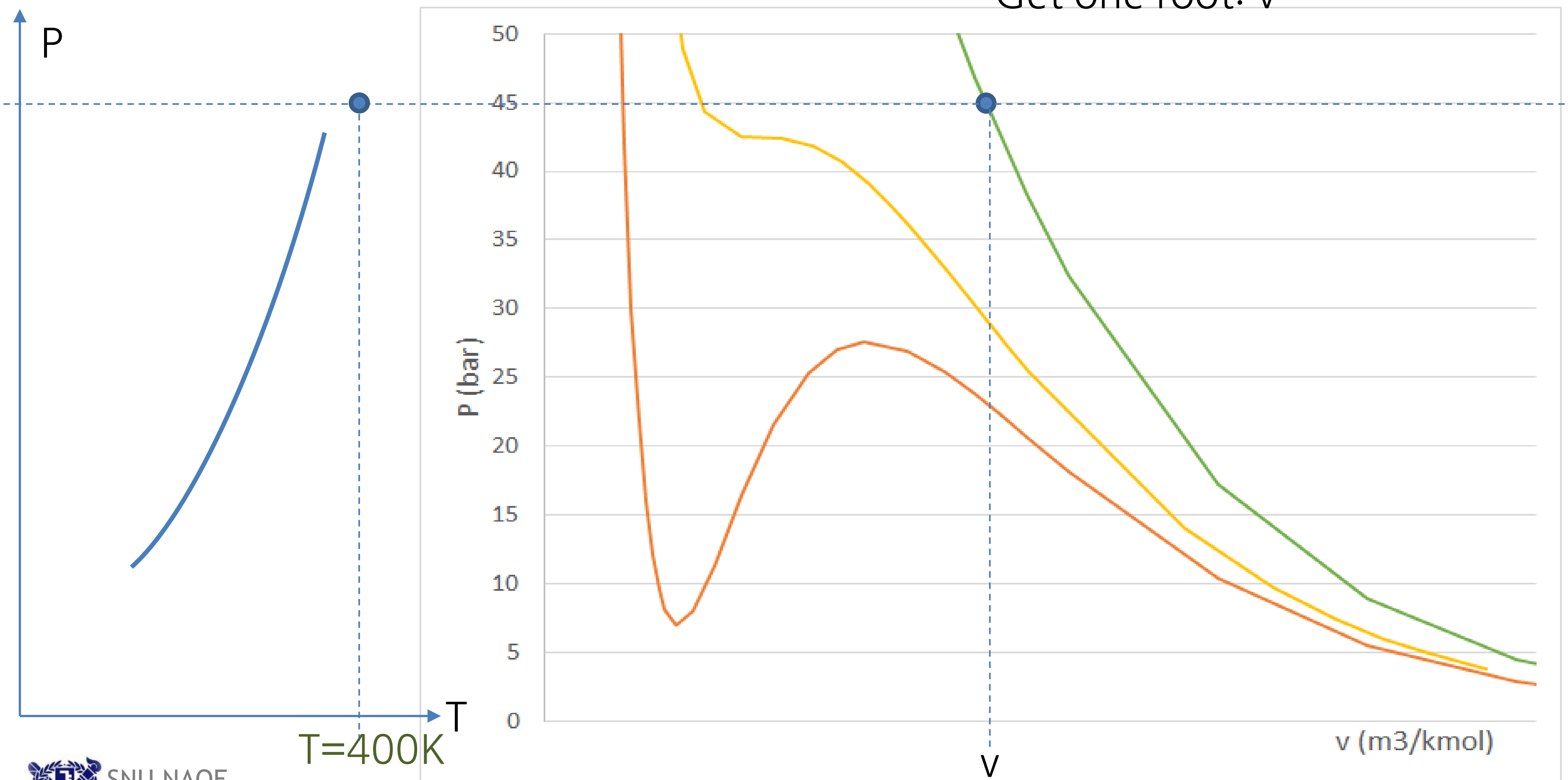
Example with EOS
T>Tc

(1) T>Tc, EOS has only one root when you solve it.
→use it as v

Solve EOS

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

Get one root: v



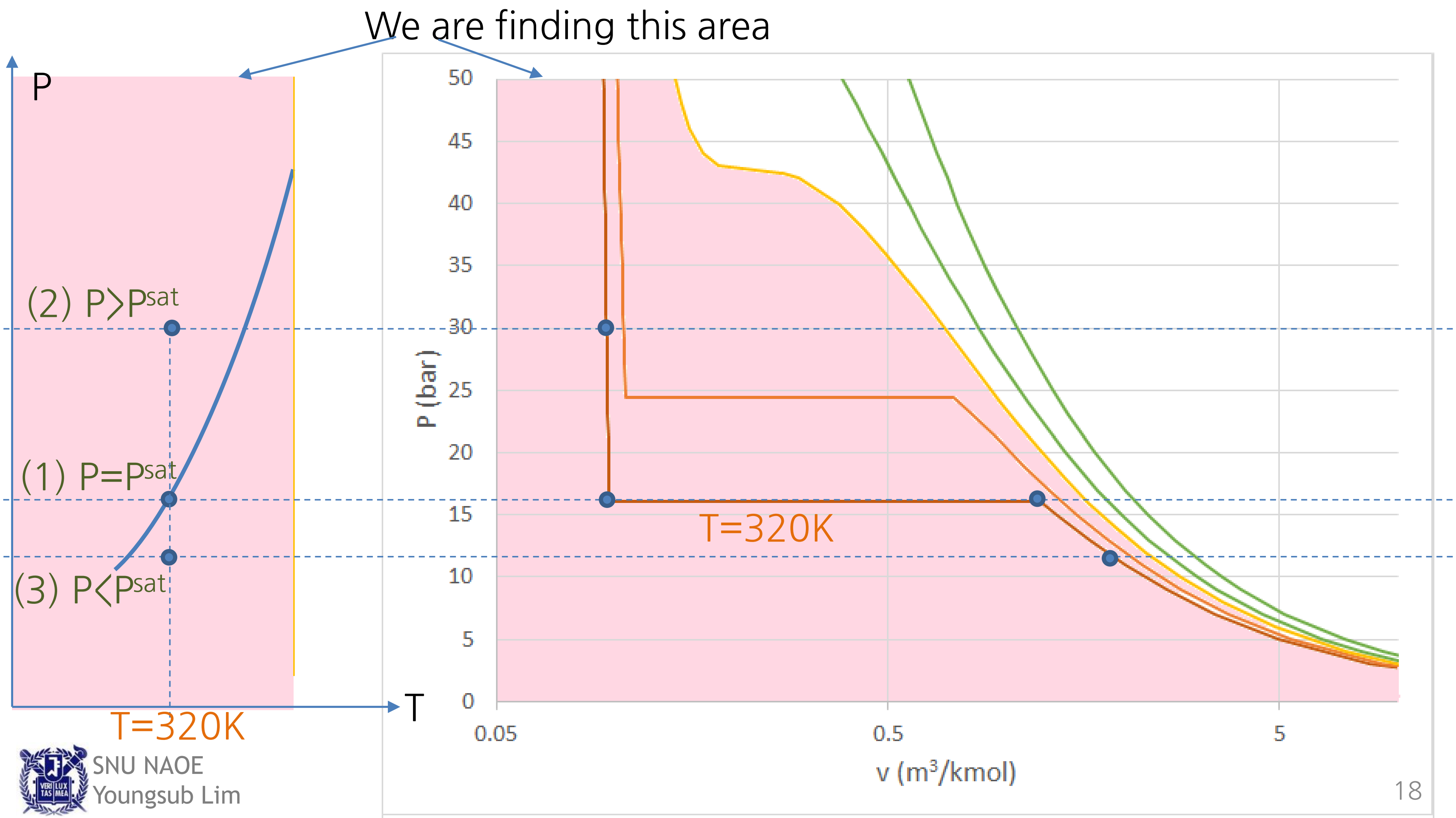
Example with real Pv

T<Tc with real isothermal line

(1) T<Tc, P=P^{sat}
→smallest one for v_l^{sat}, largest one for v_v^{sat}

(2) T<Tc, P>P^{sat}, one v for liquid

(3) T<Tc, P<P^{sat}, one v for vapor



SNU NAOE
Youngsub Lim

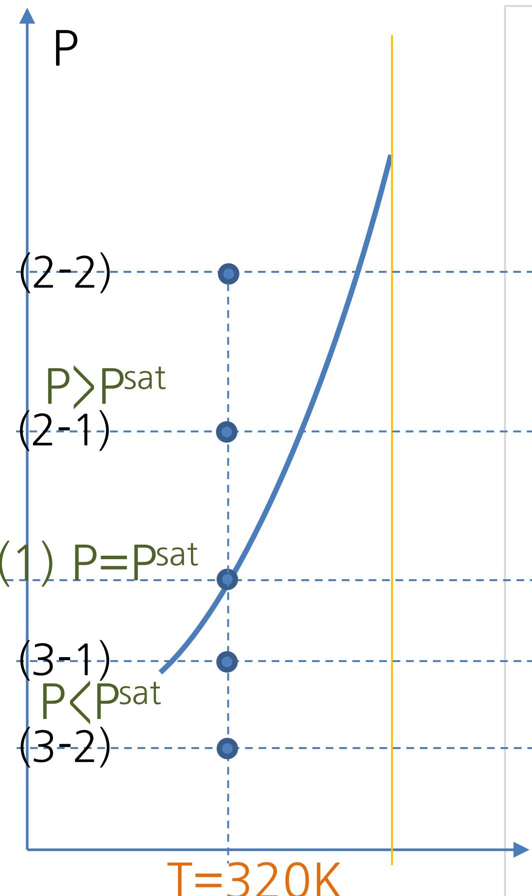
Example with EOS

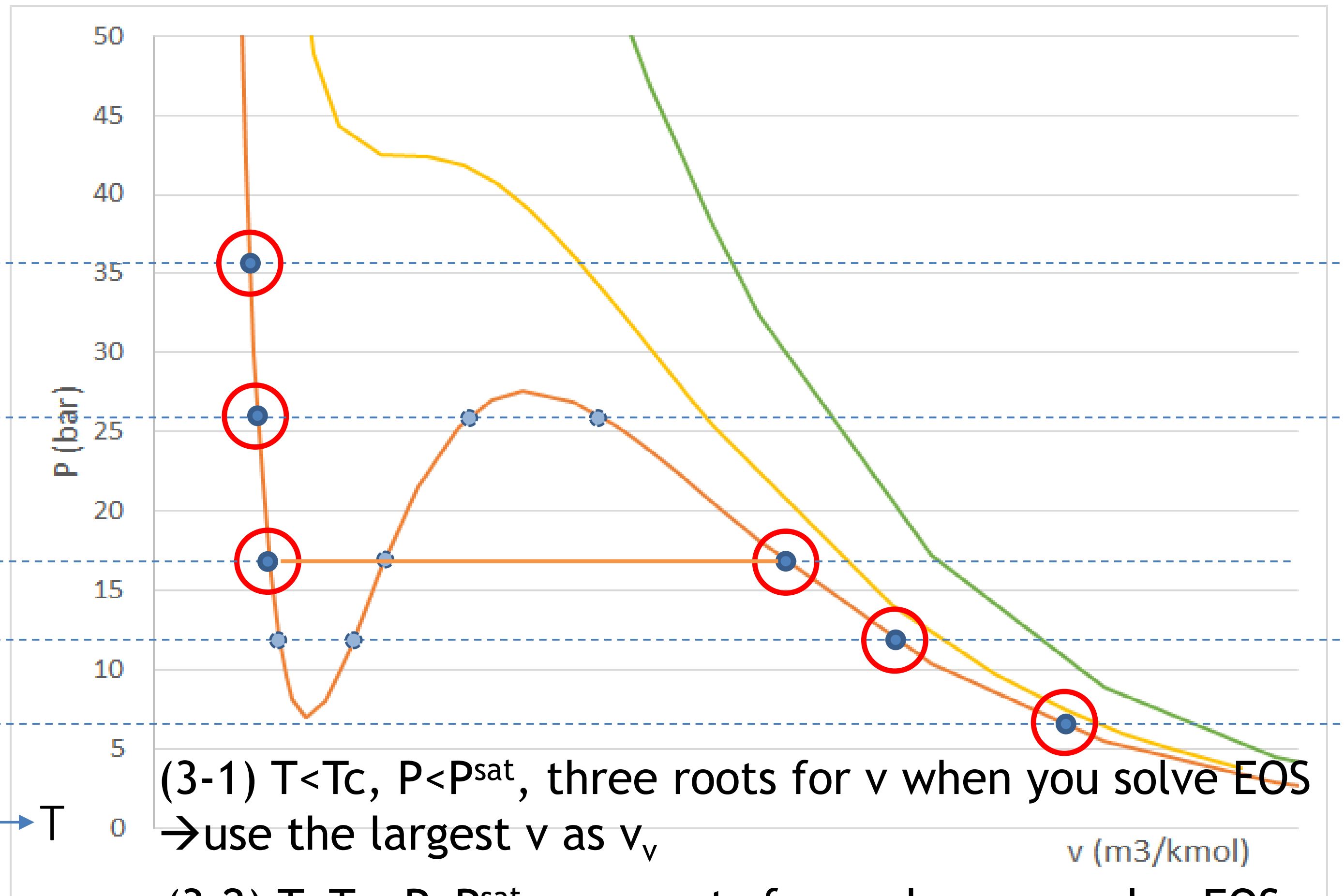
T<Tc

(1) T<Tc, $P=P^{sat}$, three roots for v when you solve EOS
→use the smallest v as v_l^{sat}, and the largest v as v_v^{sat}

(2-1) T<Tc, $P>P^{sat}$, three roots for v when you solve EOS
→use the smallest v as v_l

(2-2) T<Tc, $P>P^{sat}$, one root for v when you solve EOS
→use the v as v_l





(3-1) T<Tc, $P<P^{sat}$, three roots for v when you solve EOS
→use the largest v as v_v

(3-2) T<Tc, $P<P^{sat}$, one roots for v when you solve EOS
→use the v for v_v

Flowchart for solving vdW EOS for pure substance

with given T, P

Start with T, P

↓

Read database for given substance ← $T_c, P_c, (A, B, C)_{for\ Antoine\ eq.}$

↓

Calculate EOS coefficients

$$a = \frac{27}{64}\frac{R^2 T_c^{2.5}}{P_c}, \qquad b = \frac{RT_c}{8P_c}$$

↓

Calculate cubic eq. coefficients of EOS

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

$$Pv^3 - (Pb + RT)v^2 + av - ab = 0$$

$$\hat{A} = P$$

$$\hat{B} = -(Pb + RT)$$

$$\hat{C} = a$$

$$\hat{D} = -ab$$

$$p = \frac{3\hat{A}\hat{C} - \hat{B}^2}{3\hat{A}^2} \qquad q = \frac{2\hat{B}^3 - 9\hat{A}\hat{B}\hat{C} + 27\hat{A}^2\hat{D}}{27\hat{A}^3}$$

$$D = \frac{q^2}{4} + \frac{p^3}{27}$$

→

Solve cubic eq. and calculate v

① if D>=0,

$$v = \sqrt[3]{-\frac{q}{2} + \sqrt{D}} + \sqrt[3]{-\frac{q}{2} - \sqrt{D}} - \frac{\hat{B}}{3\hat{A}}$$

② if D<0,

$$v_k = 2\sqrt{-\frac{p}{3}}\cos\left(\frac{1}{3}\arccos\left(\frac{3q}{2p}\sqrt{-\frac{3}{p}}\right) + \frac{2}{3}k\pi\right) - \frac{\hat{B}}{3\hat{A}}$$

$$(k = 0,1,2)$$

Calculate P^{sat} at given T from Antoine eq.

$$P^{sat} = 10^5 \exp\left(A - \frac{B}{T + C}\right)$$

if $P < P^{sat}$, return $\mathrm{Max}[v_k]$ as vapor volume
if $P > P^{sat}$, return $\mathrm{Min}[v_k]$ as liquid volume
if $P = P^{sat}$, return $\mathrm{Max}[v_k]$ as sat. vapor volume
and $\mathrm{Min}[v_k]$ as sat. liquid volume