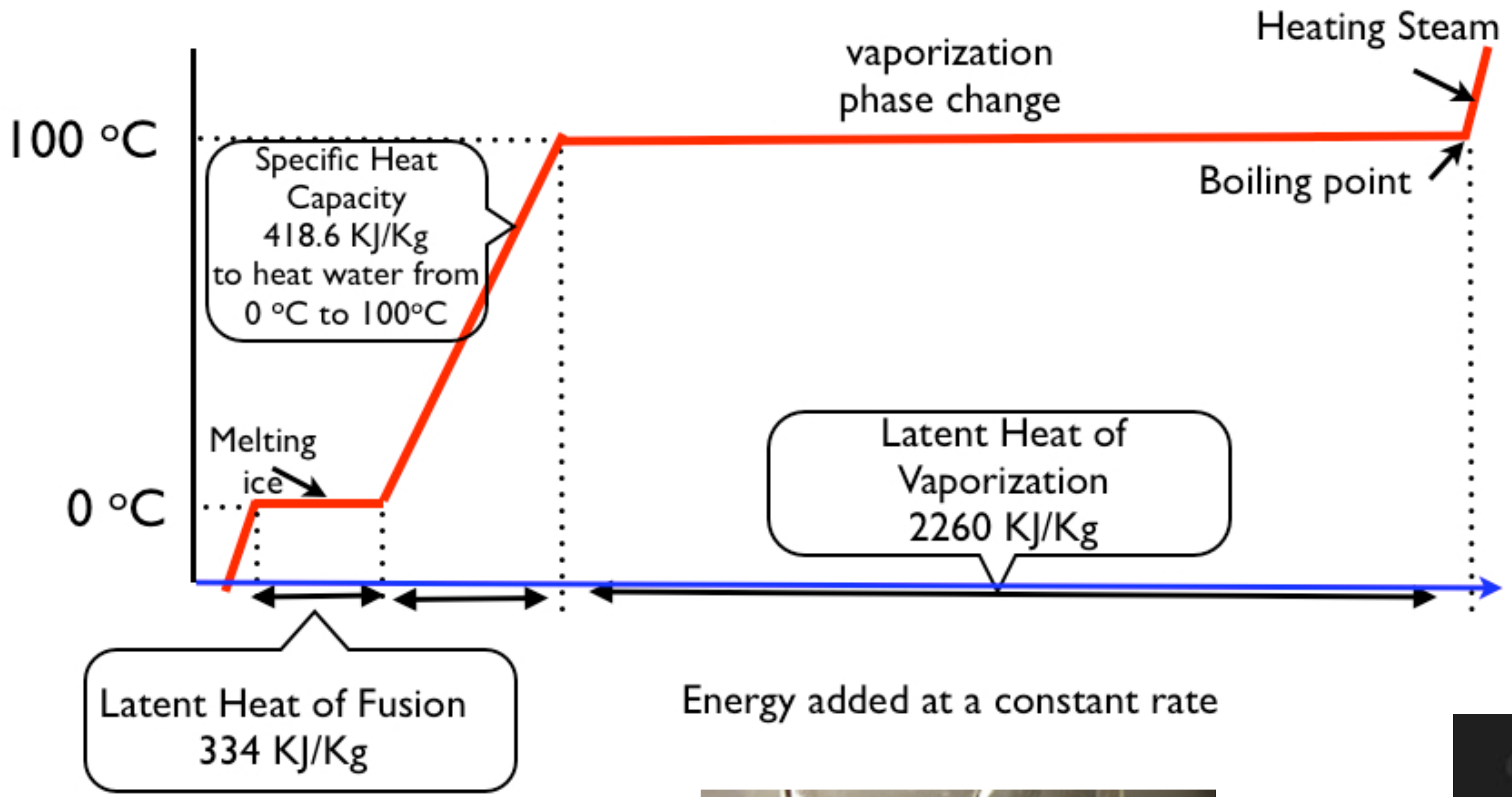
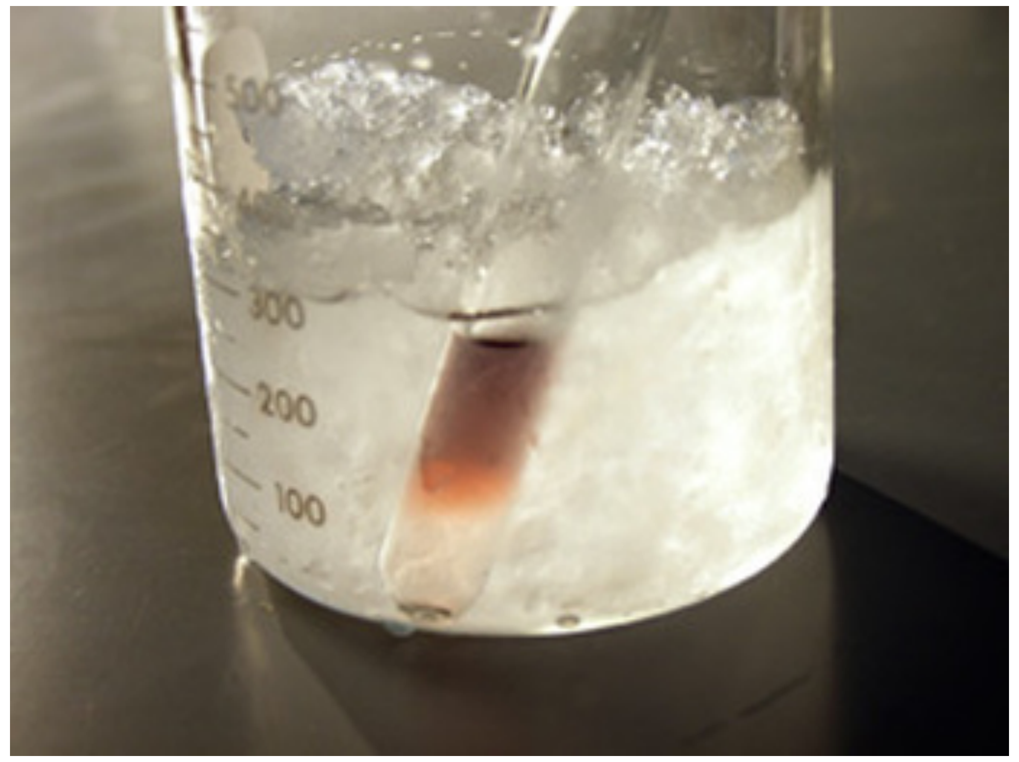
Phase diagrams
1 component

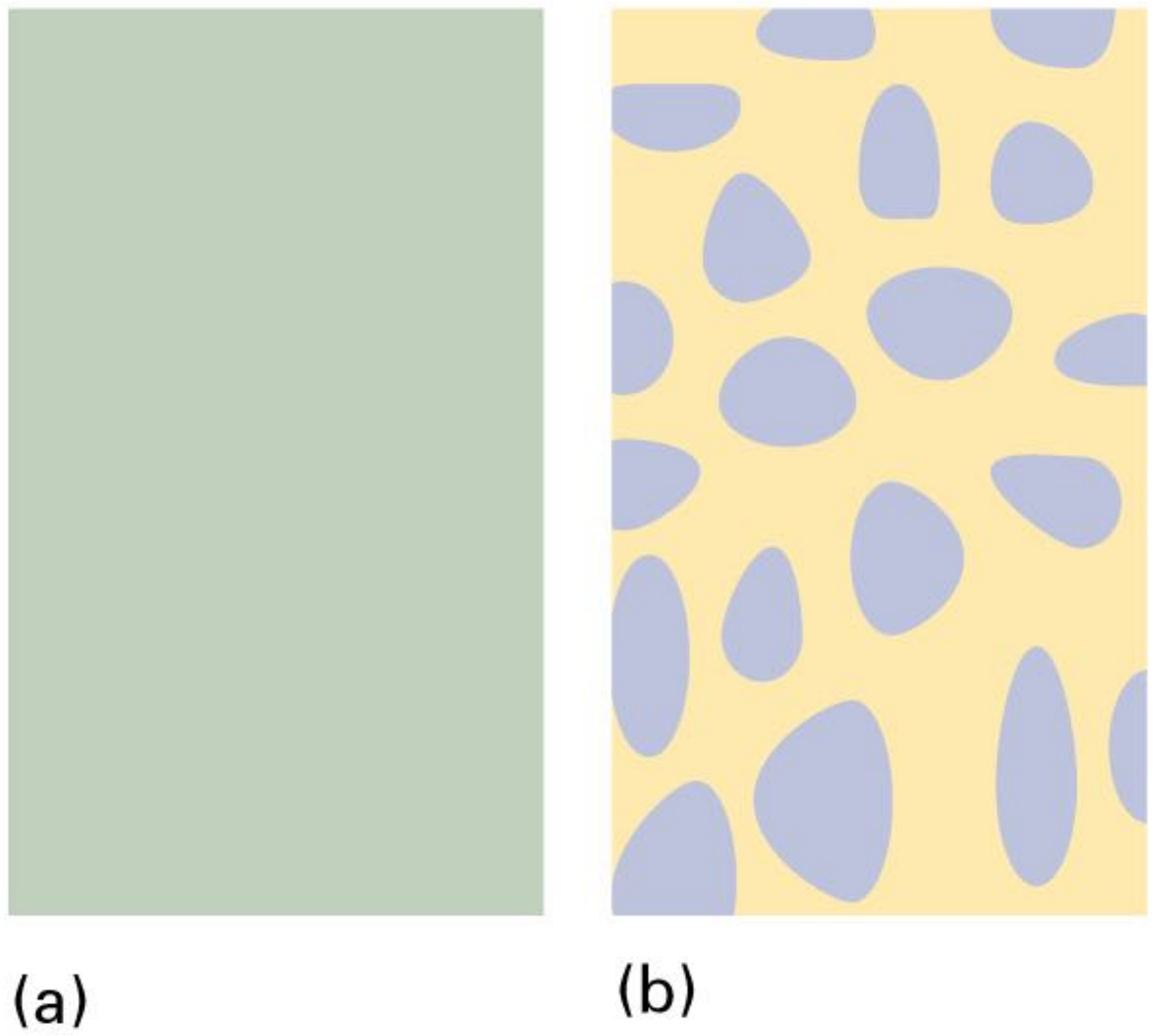
Ice / Water / Steam

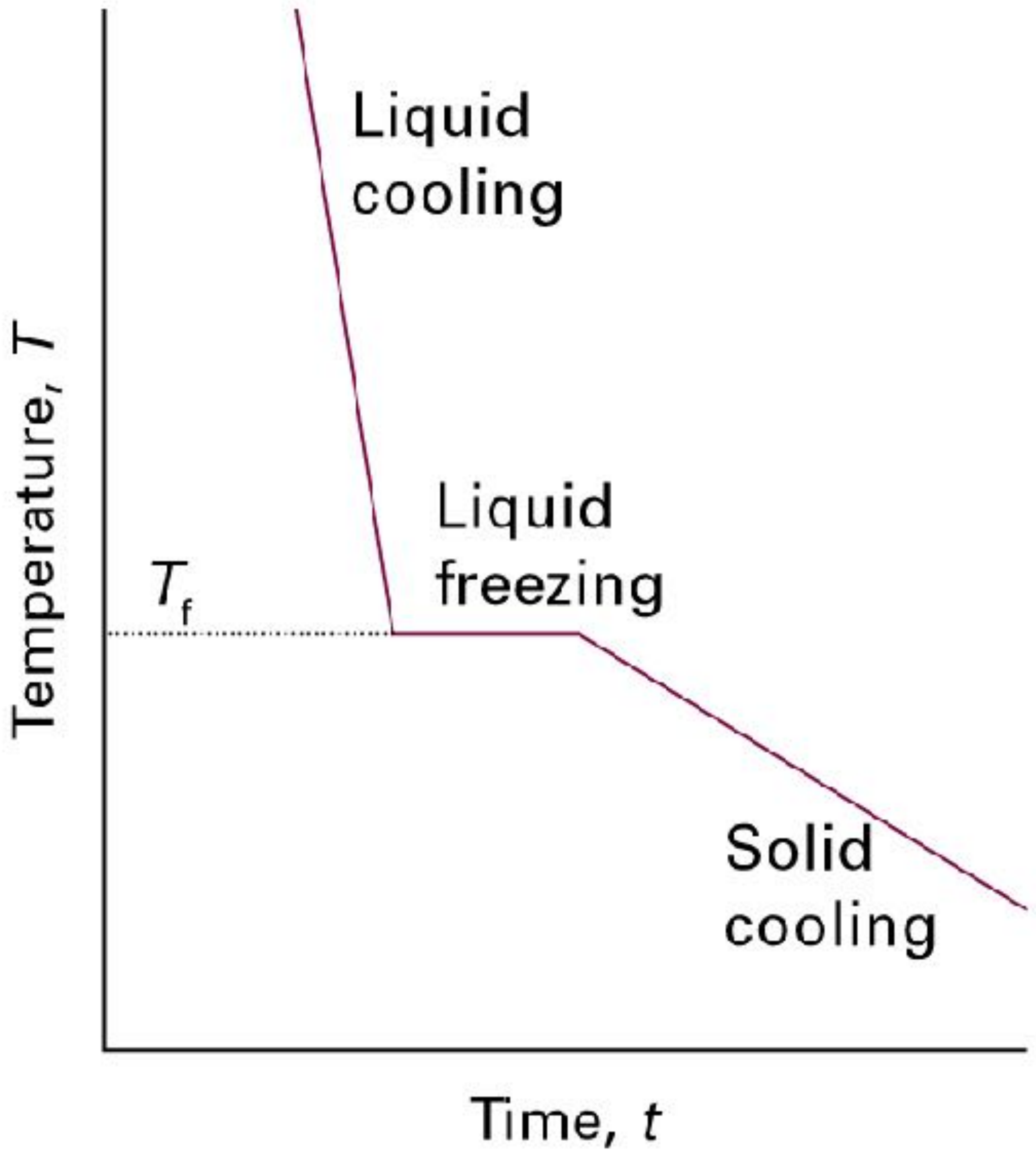




Phase transformation

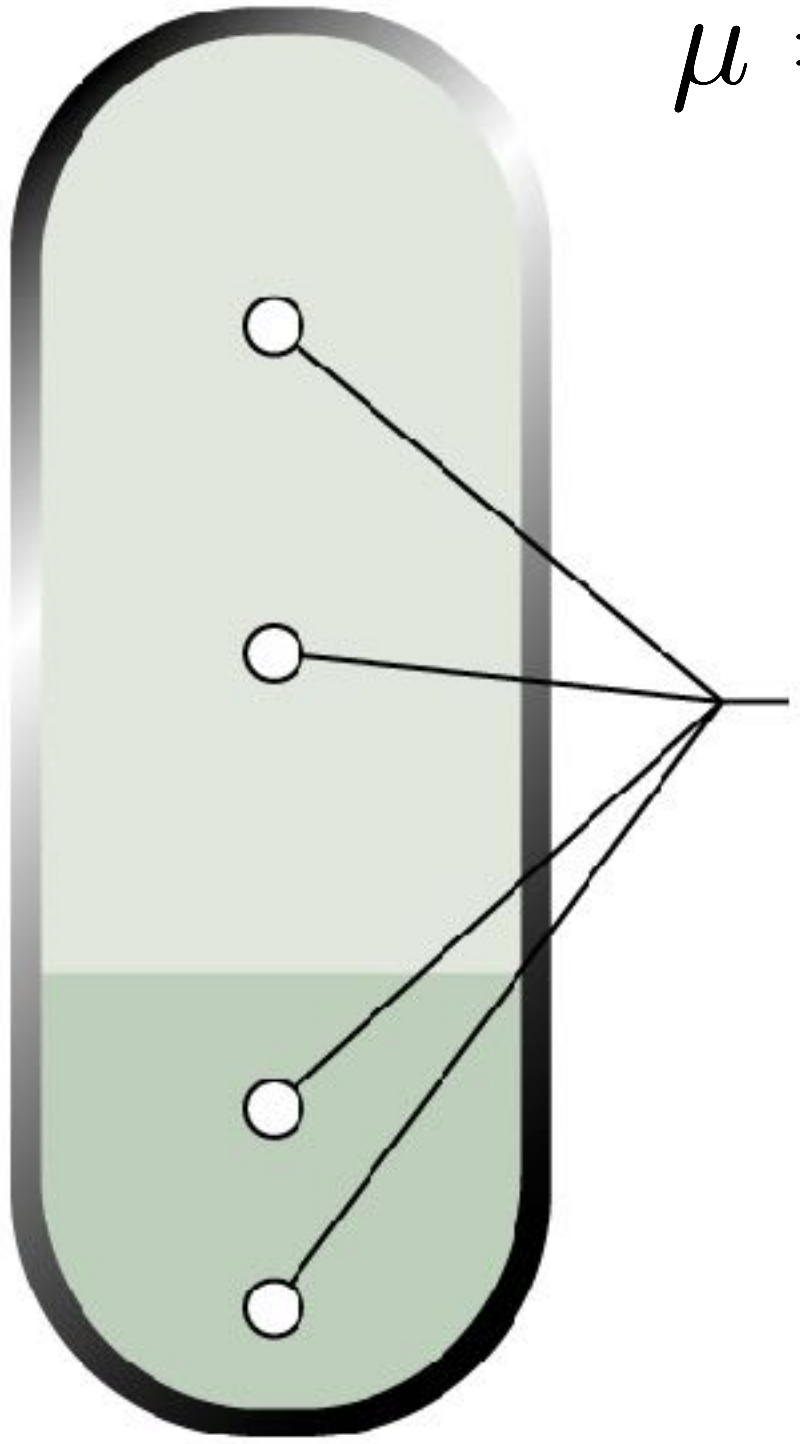
1 phase **2 phases**





Phase equilibrium

same chemical potential everywhere



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

$$G = n_\alpha \mu_\alpha + n_\beta \mu_\beta$$

$$\mathrm{d}G = \mathrm{d}n(\mu_\alpha - \mu_\beta)$$

$$\mathrm{d}n_\alpha = -\mathrm{d}n_\beta = \mathrm{d}n$$

at equilibrium

$$0 = \mathrm{d}n(\mu_\alpha - \mu_\beta)$$

$$\mu_\alpha = \mu_\beta$$

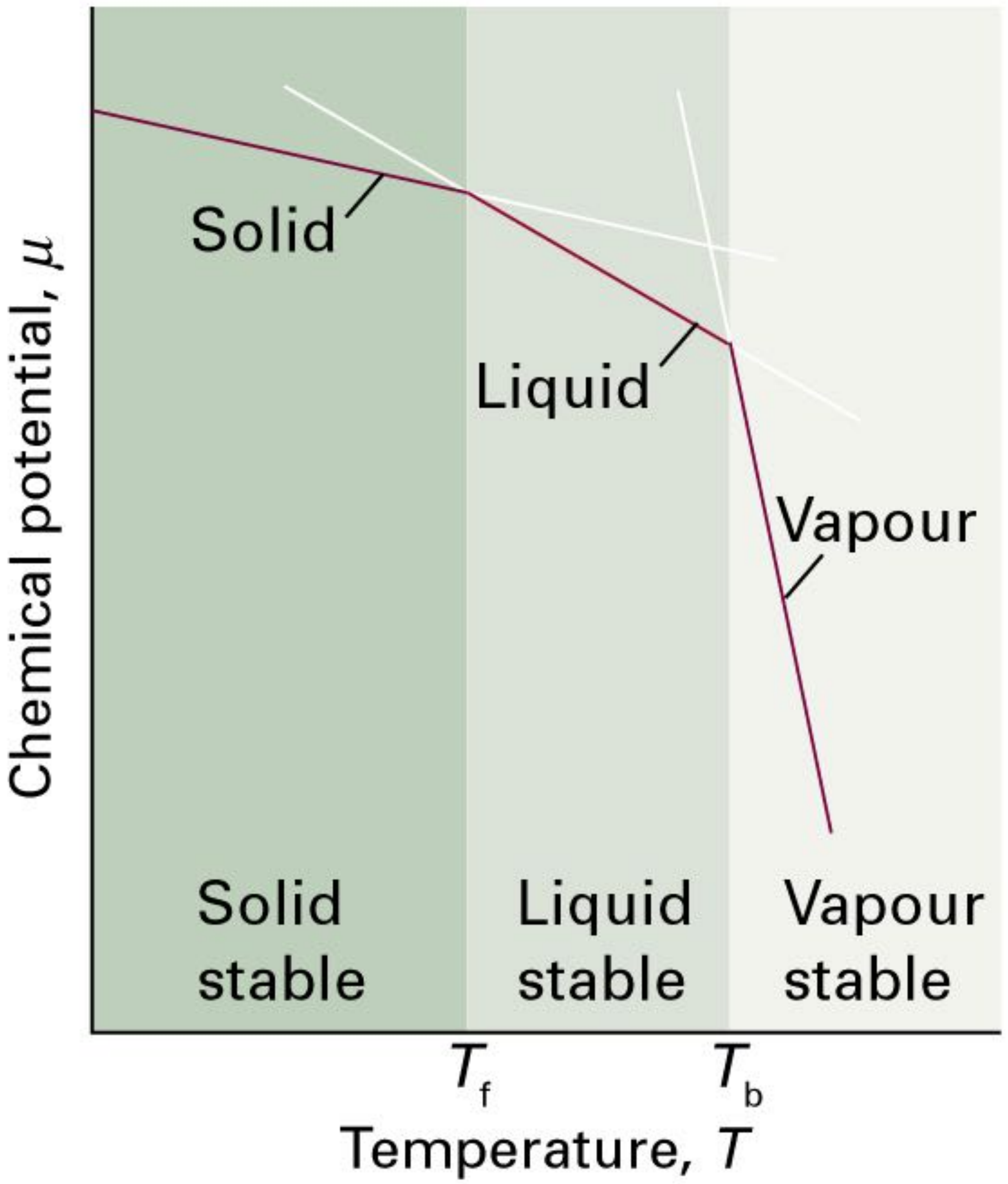
What drives phase transformations

$$\left(\frac{\partial G}{\partial T}\right)_p = -S$$

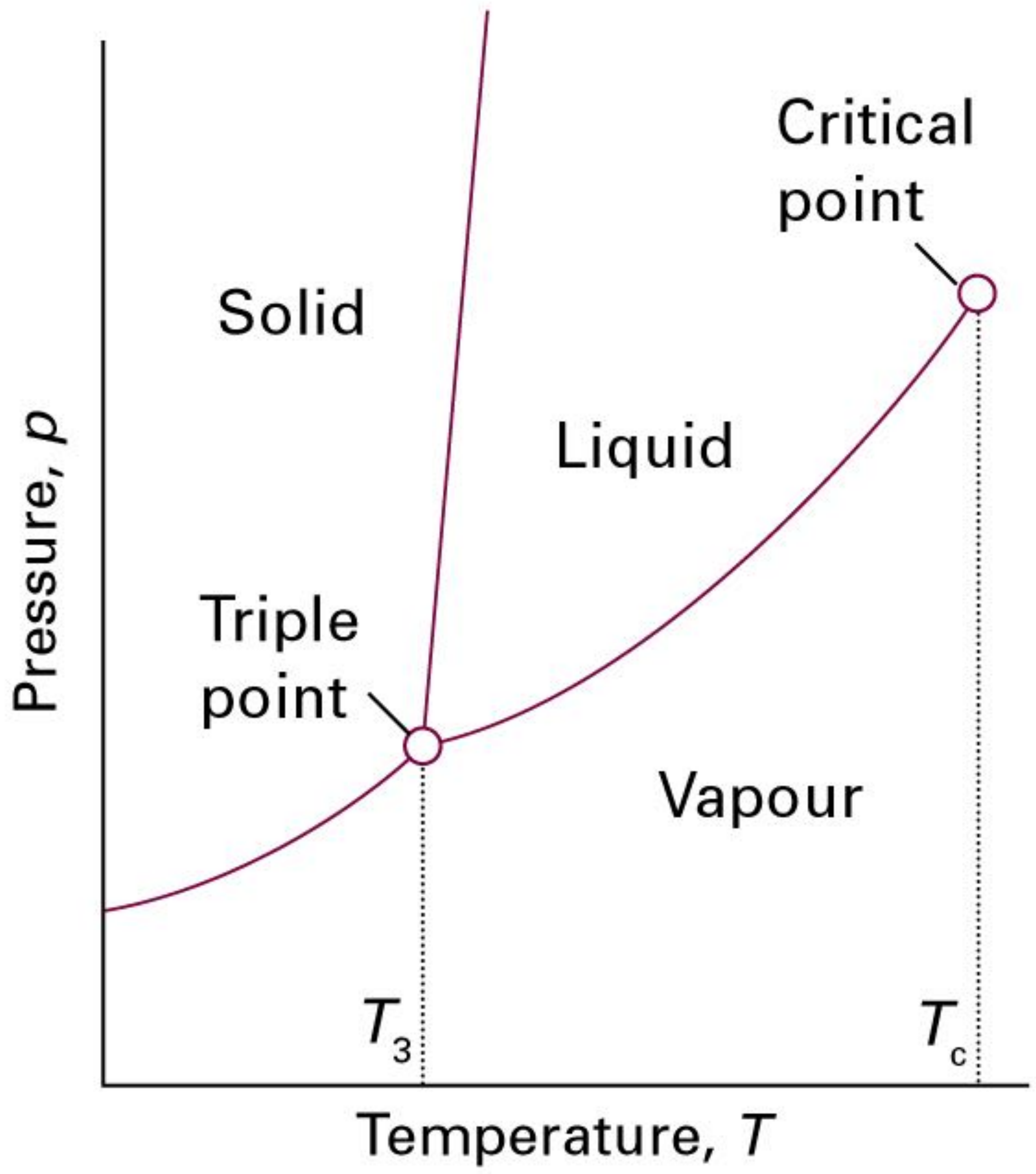
$$\left(\frac{\partial G}{\partial p}\right)_T = V$$

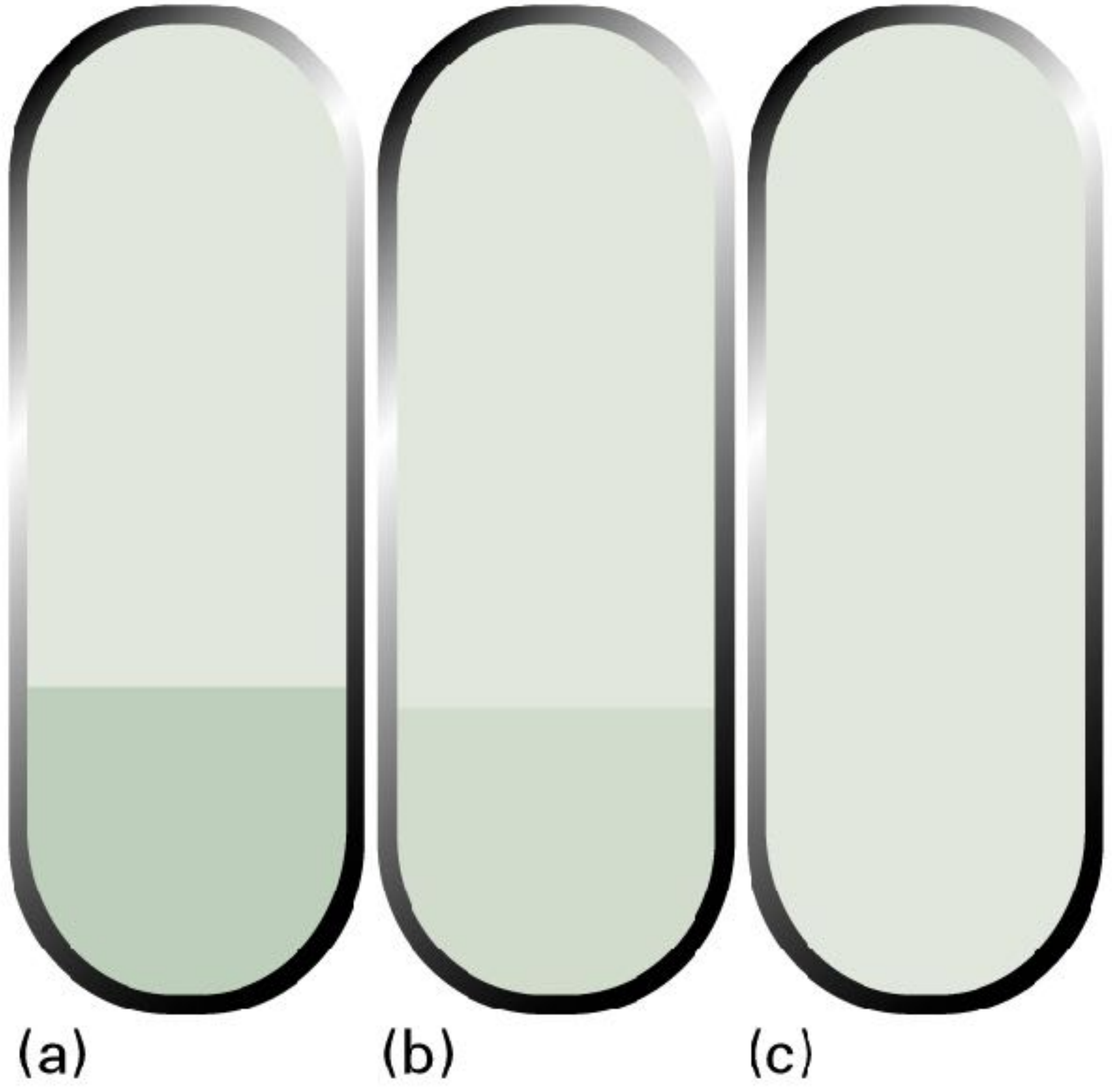
$$\left(\frac{\partial \mu}{\partial T}\right)_p = -S_m$$

$$\left(\frac{\partial \mu}{\partial p}\right)_T = -V_m$$

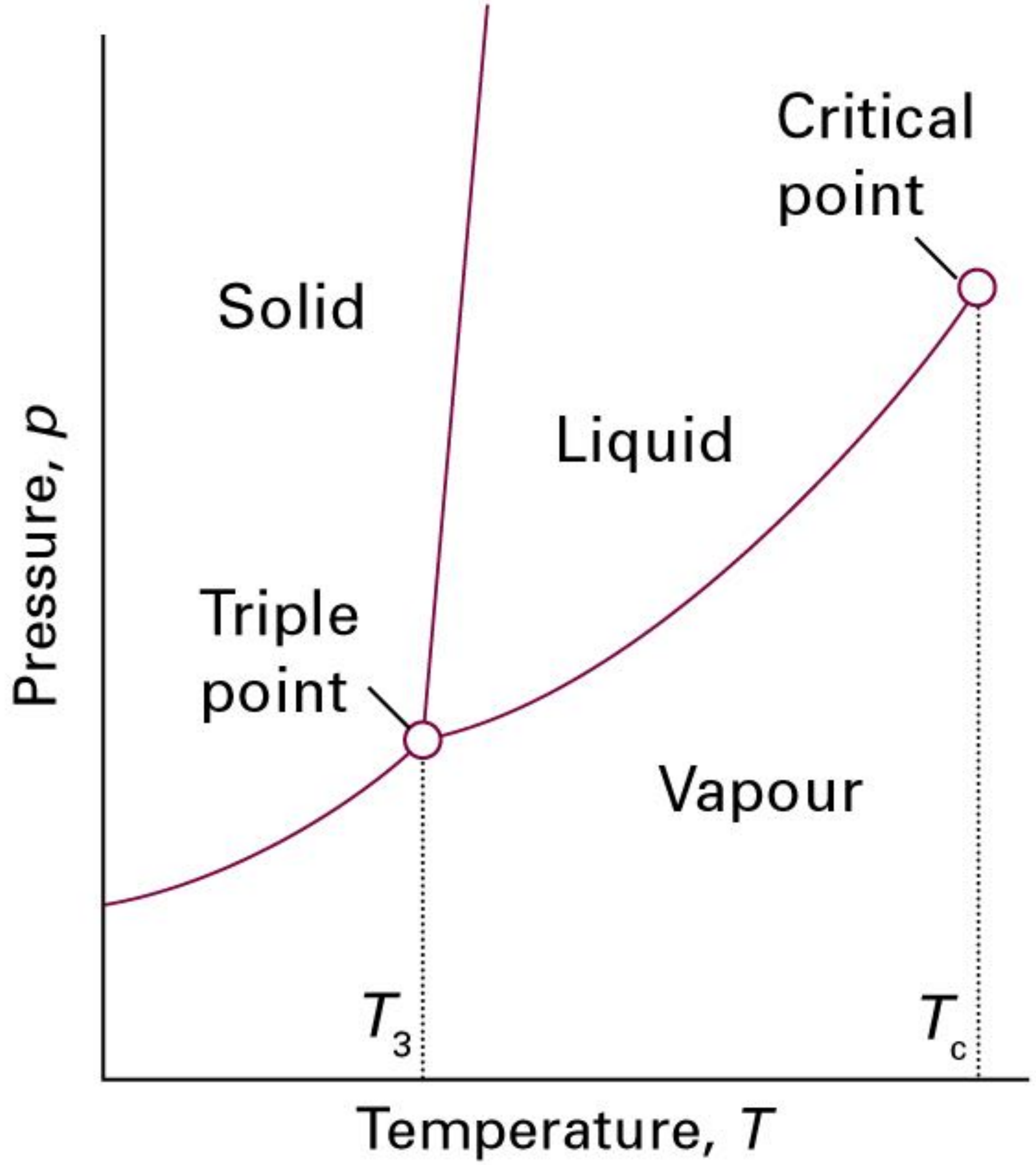


Phase diagram





Coexistence



Standard boiling temperature

$$p^*(T_b) = 1\ bar$$

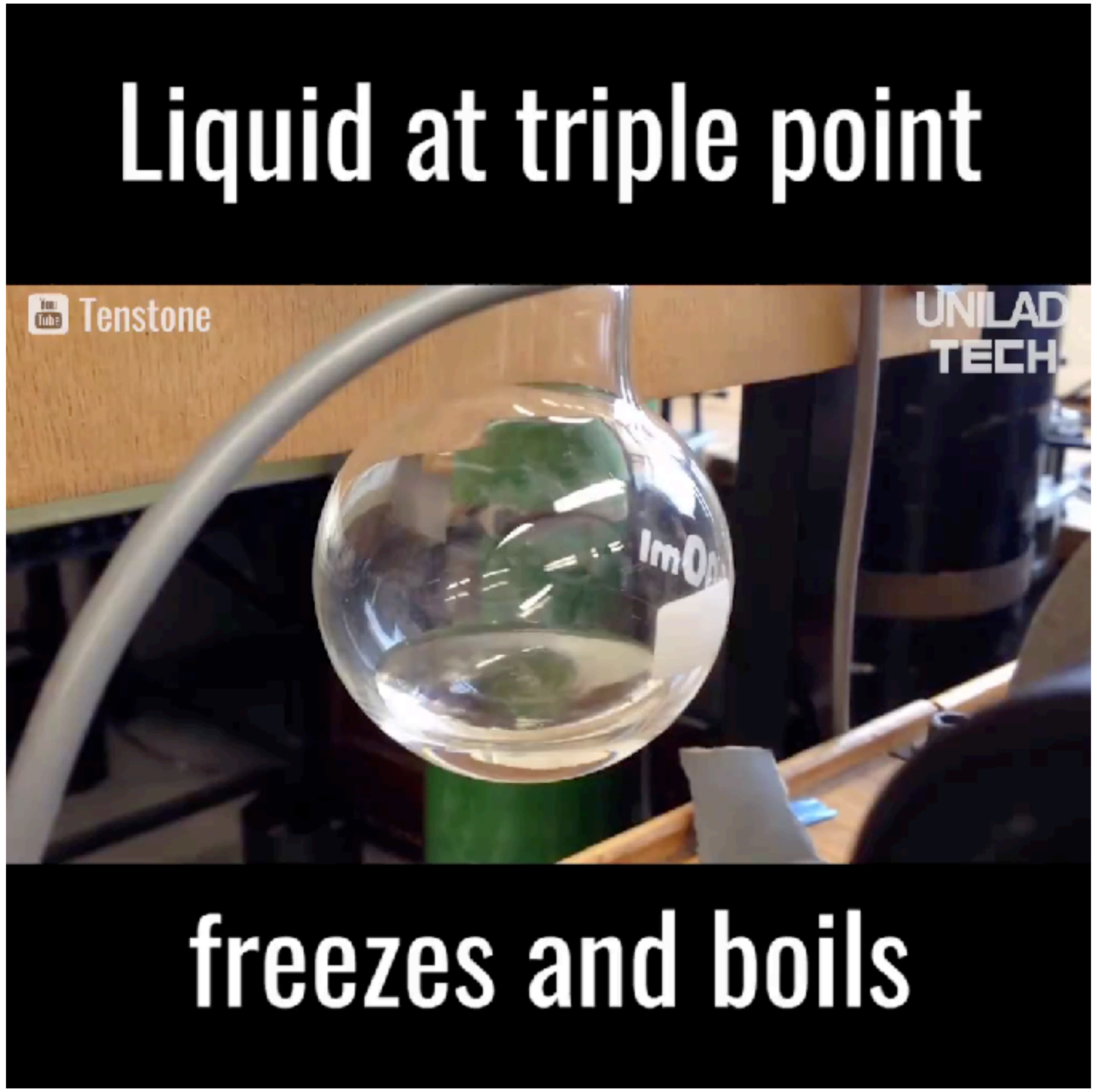
Normal boiling temperature

$$p^*(T_b) = 1\ atm$$

$$1\ atm = 1.01325\ bar$$

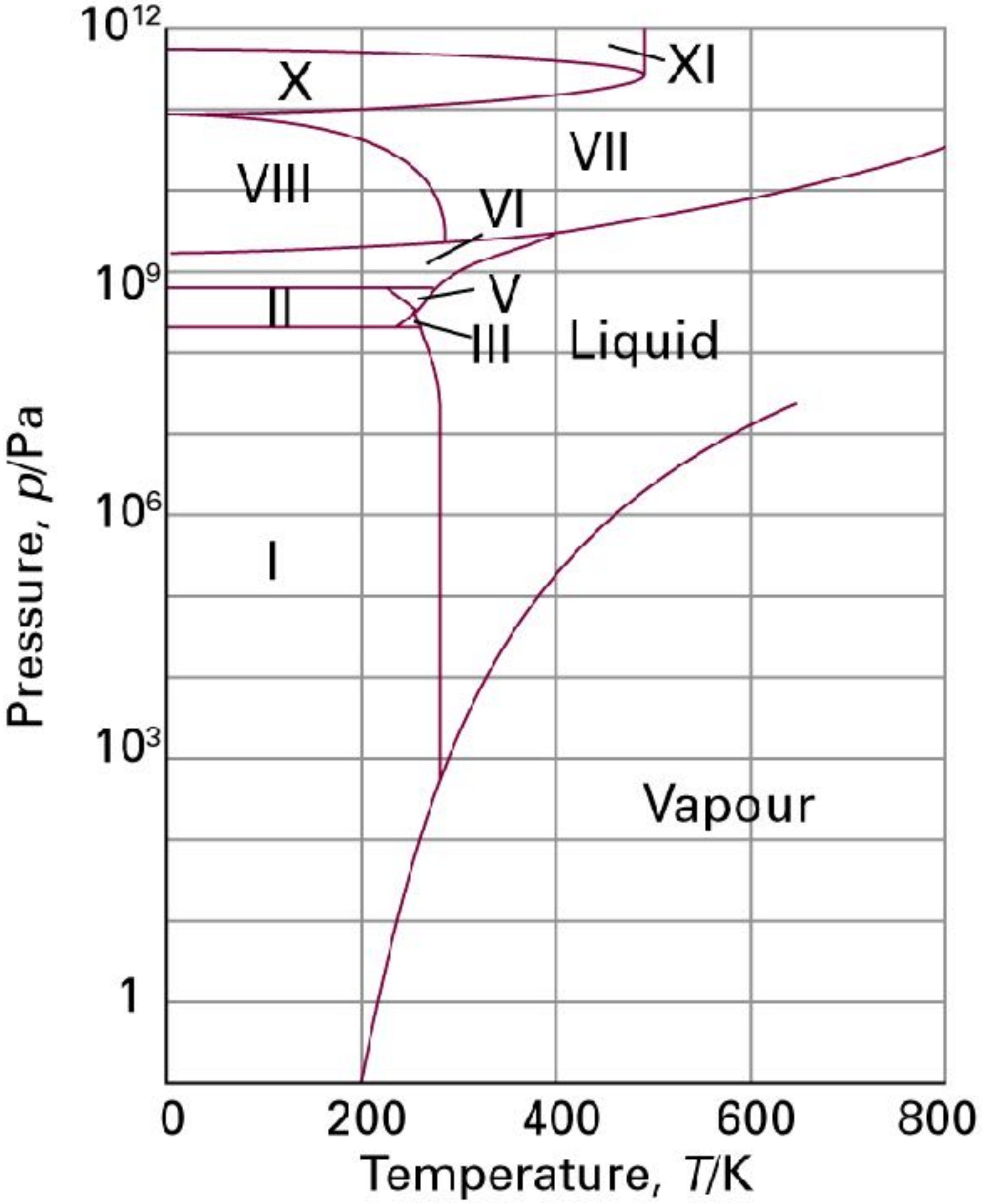
Cyclohexane @ TP

279.48 K (6.33 °C), 5.388 kPa (0.053 atm)



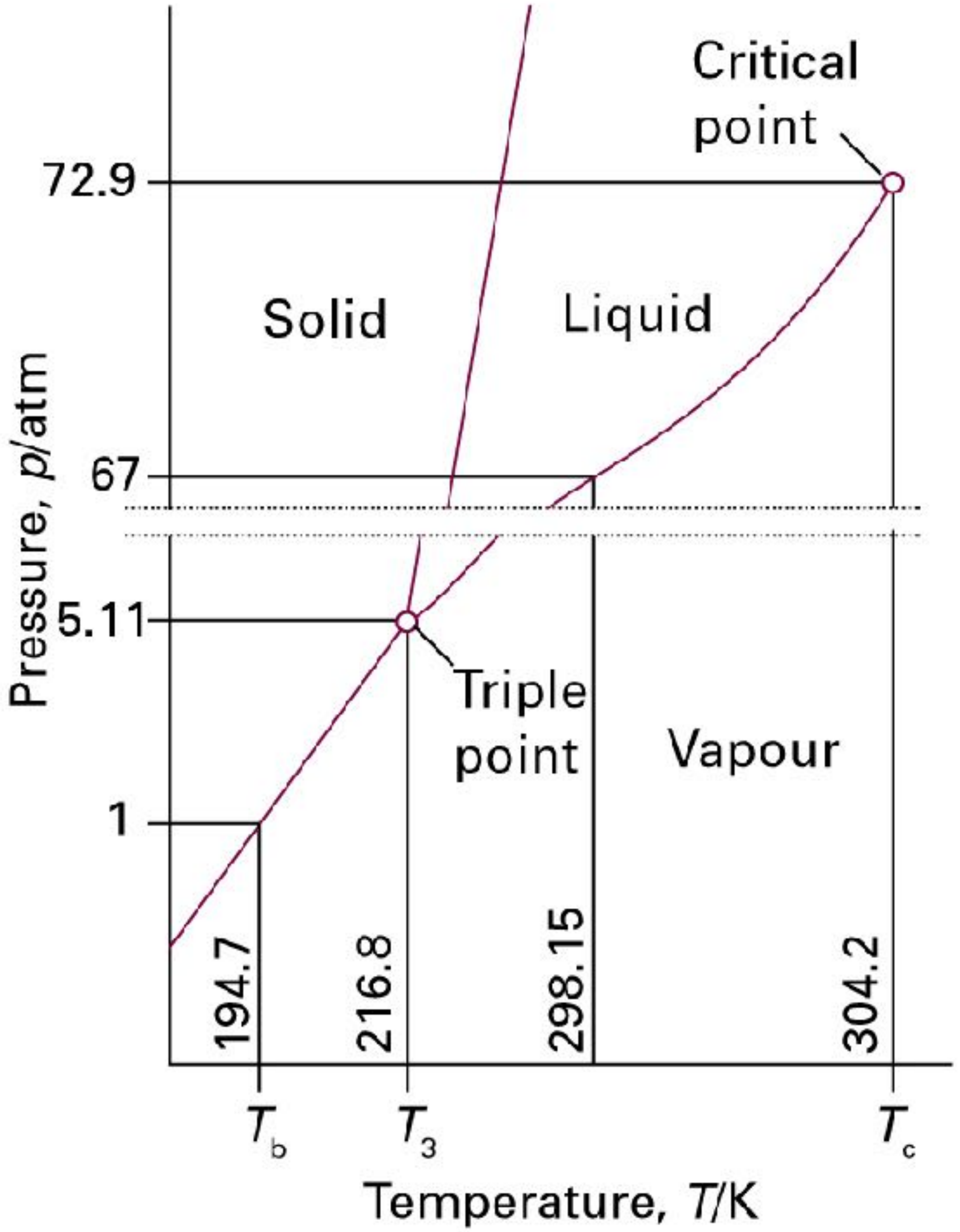
https://www.youtube.com/watch?v=XEbMHmDhq2I

Water



10^12
X
XI
VIII
VII
VI
10^9
II
V
III
Liquid
10^6
I
10^3
Vapour
1
0
200
400
600
800
Temperature, T/K
Pressure, p/Pa

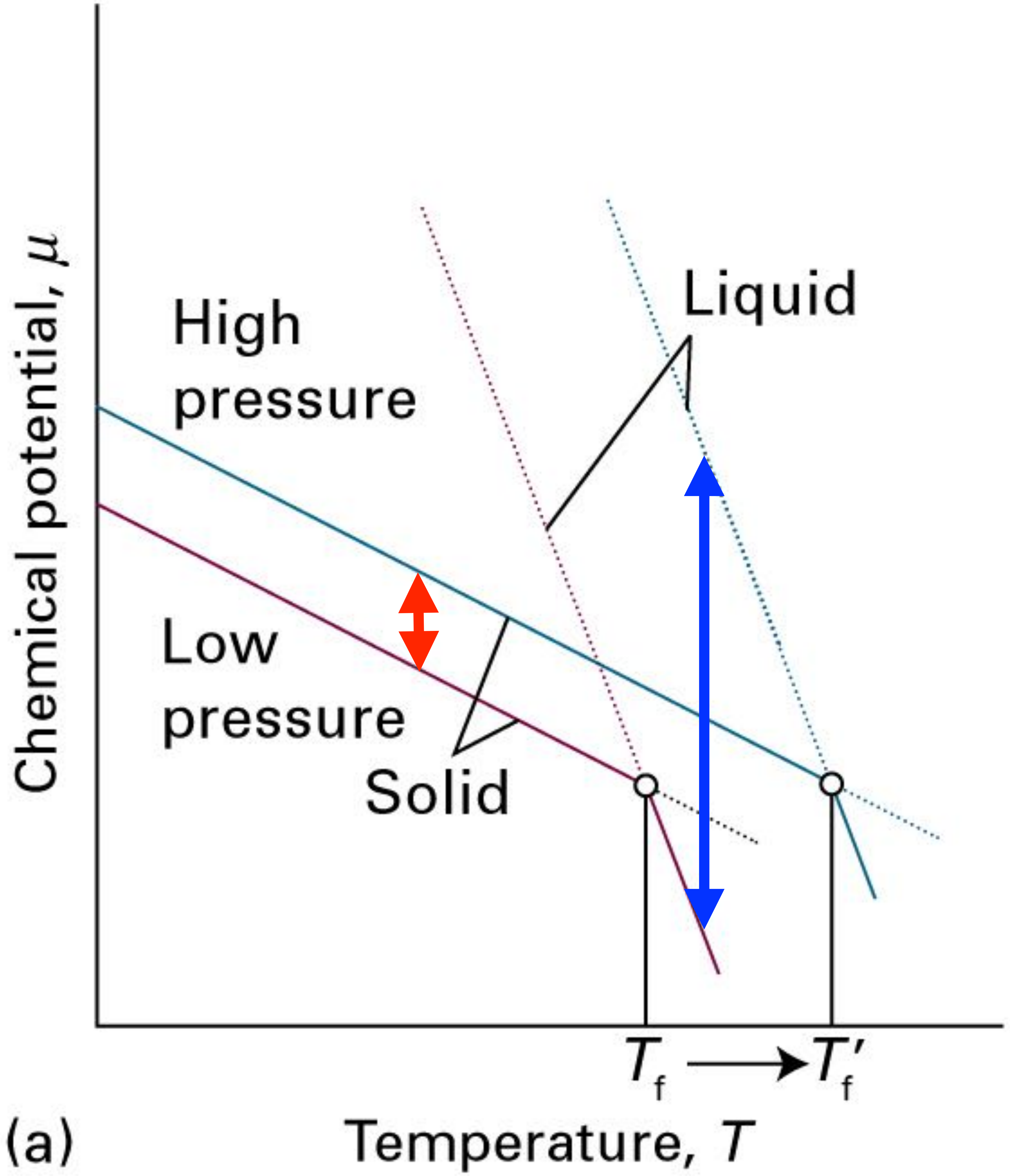
CO_2

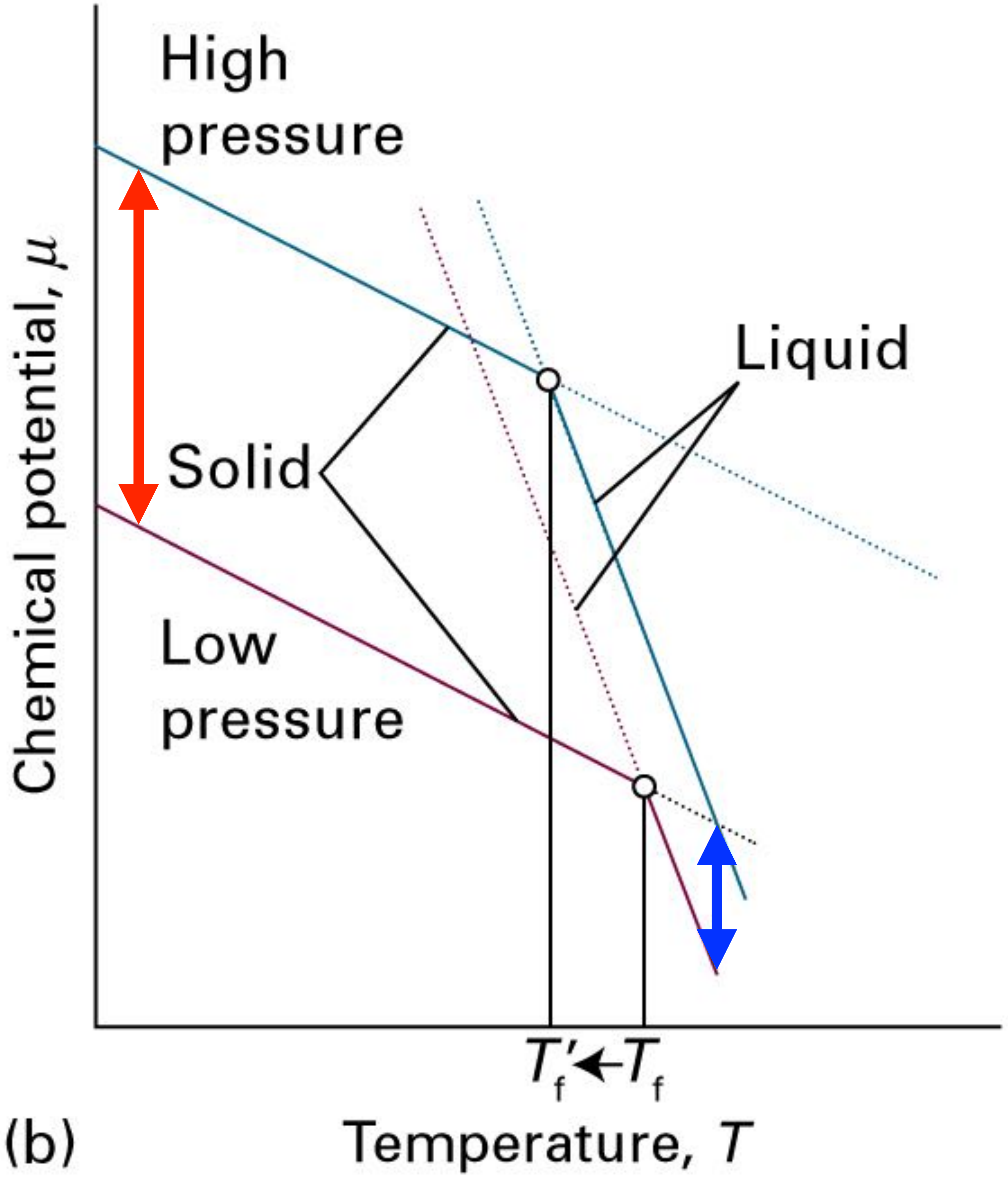


Critical point
72.9
Solid
Liquid
67
Pressure, p/atm
5.11
Triple point
Vapour
1
194.7
216.8
298.15
304.2
T_b
T_3
T_c
Temperature, T/K

Pressure dependence

$$\left(\frac{\partial \mu}{\partial p}\right)_T = V_m$$





Location of the phase boundaries

equilibrium between two phases

$$\mathrm{d}G = V\mathrm{d}p - S\mathrm{d}T \qquad \mathrm{d}\mu = V_m\mathrm{d}p - S_m\mathrm{d}T$$

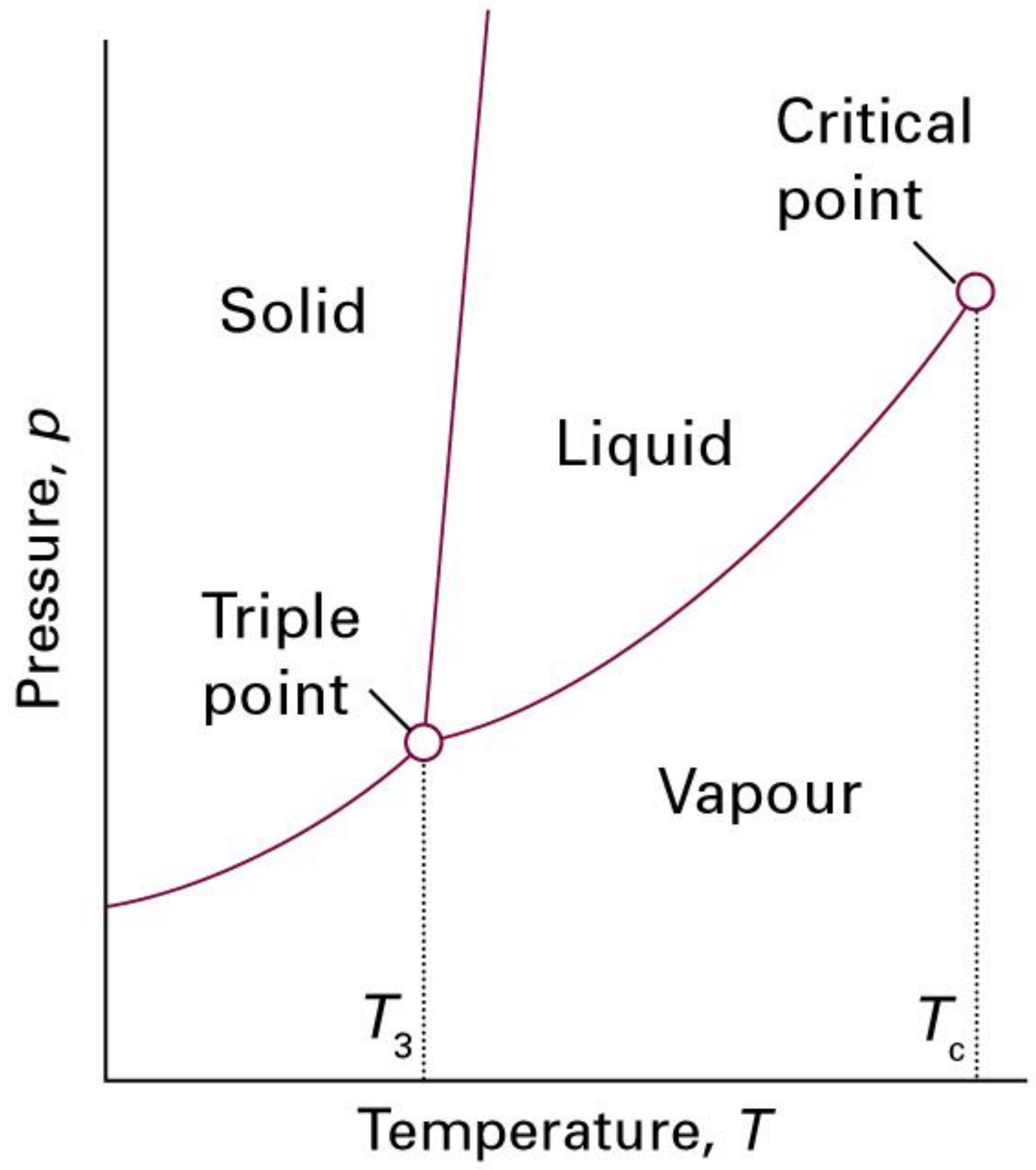
$$\mu(\alpha; p, T) = \mu(\beta; p, T)$$

$$V_m(\alpha)\mathrm{d}p - S_m(\alpha)\mathrm{d}T = V_m(\beta)\mathrm{d}p - S_m(\beta)\mathrm{d}T$$

$$\Delta S_m \mathrm{d}T = \Delta V_m \mathrm{d}p$$

Clapeyron Equation

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta S_m}{\Delta V_m} = \frac{\Delta H_m}{T\Delta V_m}$$



How to use it

solid/liquid transformation

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta_f H_m}{T \Delta_f V_m}$$

$$\mathrm{d}p = \frac{\Delta_f H_m}{\Delta_f V_m} \frac{\mathrm{d}T}{T}$$

$$\int_{p_0}^{p_1} \mathrm{d}p = \int_{T_0}^{T_1} \frac{\Delta_f H_m}{\Delta_f V_m} \frac{\mathrm{d}T}{T}$$

$$\int_{p_0}^{p_1} \mathrm{d}p = \frac{\Delta_f H_m}{\Delta_f V_m} \int_{T_0}^{T_1} \frac{\mathrm{d}T}{T}$$

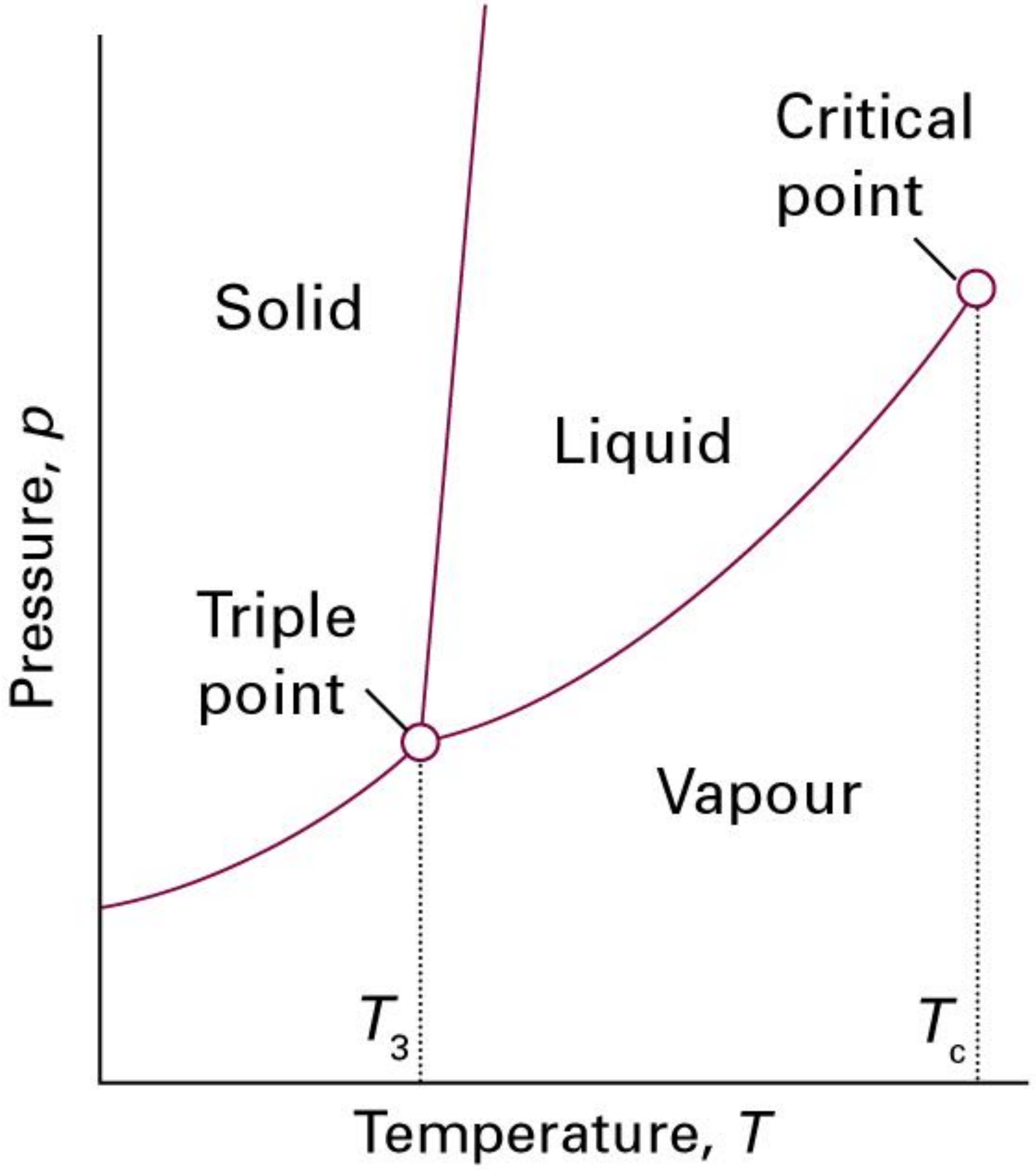
$$\boxed{p_1 - p_0 = \frac{\Delta_f H_m}{\Delta_f V_m} \ln\left(\frac{T_1}{T_0}\right)}$$

$$\boxed{T_1 = T_0 \exp\left(\frac{\Delta p \Delta_f V_m}{\Delta_f H_m}\right)}$$

Location of the phase boundaries

liquid-vapour

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta S_m}{\Delta V_m} = \frac{\Delta H_m}{T\Delta V_m}$$



$$\Delta_v V_m \approx V_m(g) = \frac{RT}{p}$$

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta_v H_m}{T\Delta_v V_m} \approx \frac{p\Delta_v H_m}{RT^2}$$

$$\frac{\mathrm{d}\ln p}{\mathrm{d}T} \approx \frac{\Delta_v H_m}{RT^2}$$

Clausius-Clapeyron Equation

How to use it

$$\frac{\mathrm{d}\ln p}{\mathrm{d}T} = \frac{\Delta_v H_m}{RT^2}$$

$$\mathrm{d}\ln p = \frac{\Delta_v H_m}{R}\frac{\mathrm{d}T}{T^2}$$

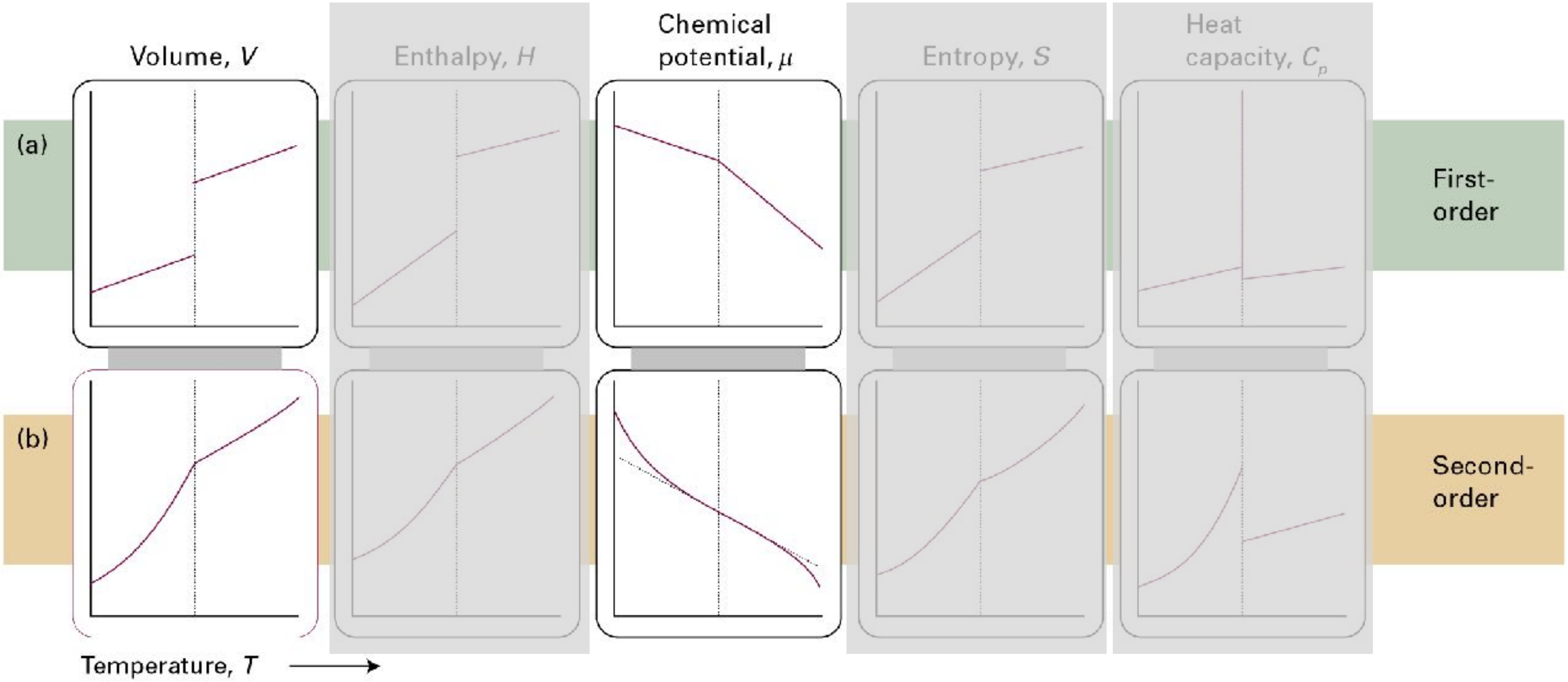
$$\int_{p_0}^{p_1} \mathrm{d}\ln p = \frac{\Delta_v H_m}{R}\int_{T_0}^{T_1}\frac{\mathrm{d}T}{T^2}$$

$$\boxed{\ln\left(\frac{p_1}{p_0}\right) = -\frac{\Delta_v H_m}{R}\left(\frac{1}{T_1} - \frac{1}{T_0}\right)}$$

Ehrenfest classification

of phase transitions

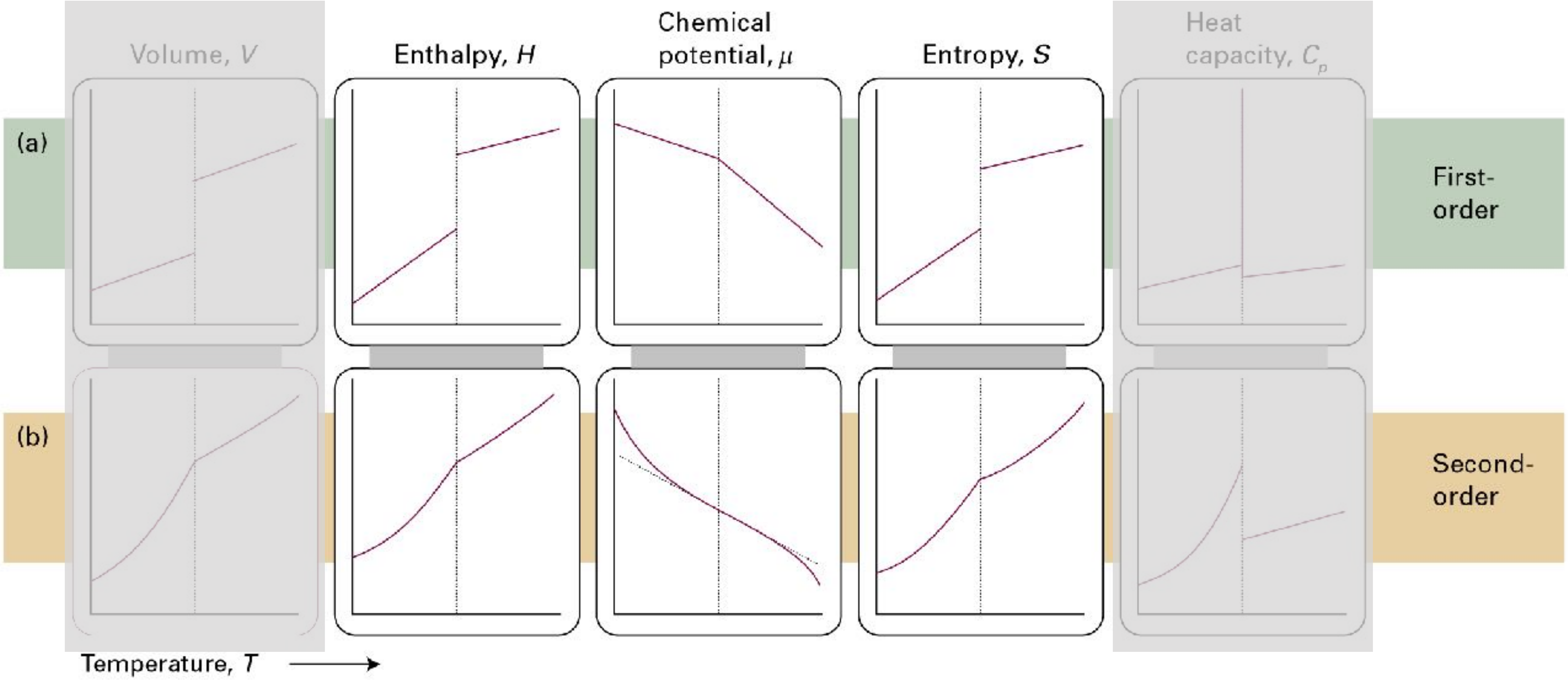
$$\left[\frac{\partial\mu(\beta)}{\partial p}\right]_T - \left[\frac{\partial\mu(\alpha)}{\partial p}\right]_T = V_m(\beta) - V_m(\alpha) = \Delta_{trs}V$$



Ehrenfest classification

of phase transitions

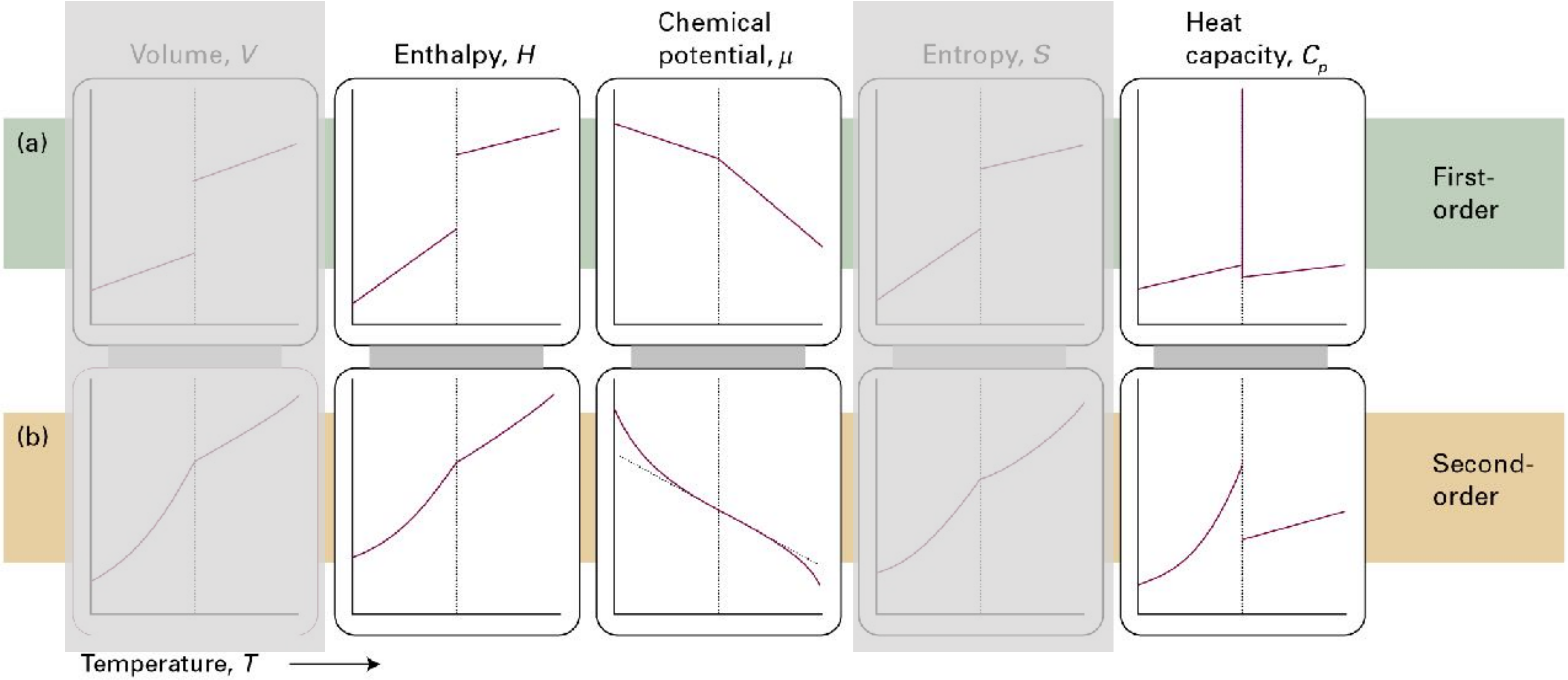
$$\left[\frac{\partial\mu(\beta)}{\partial T}\right]_p - \left[\frac{\partial\mu(\alpha)}{\partial T}\right]_p = -S_m(\beta) - S_m(\alpha) = -\Delta_{trs}S = -\frac{\Delta_{trs}H}{T}$$



Ehrenfest classification

of phase transitions

$$C_p = \left(\frac{\mathrm{d}H}{\mathrm{d}T}\right)_p$$



Phase diagrams
2 components

Vapour pressure of a mixture

ideal case

It was experimentally found that for an ideal solution

$$p_A = x_A p_A^*$$

which is now called "**Raoult's law**",
after the scientist who discovered it

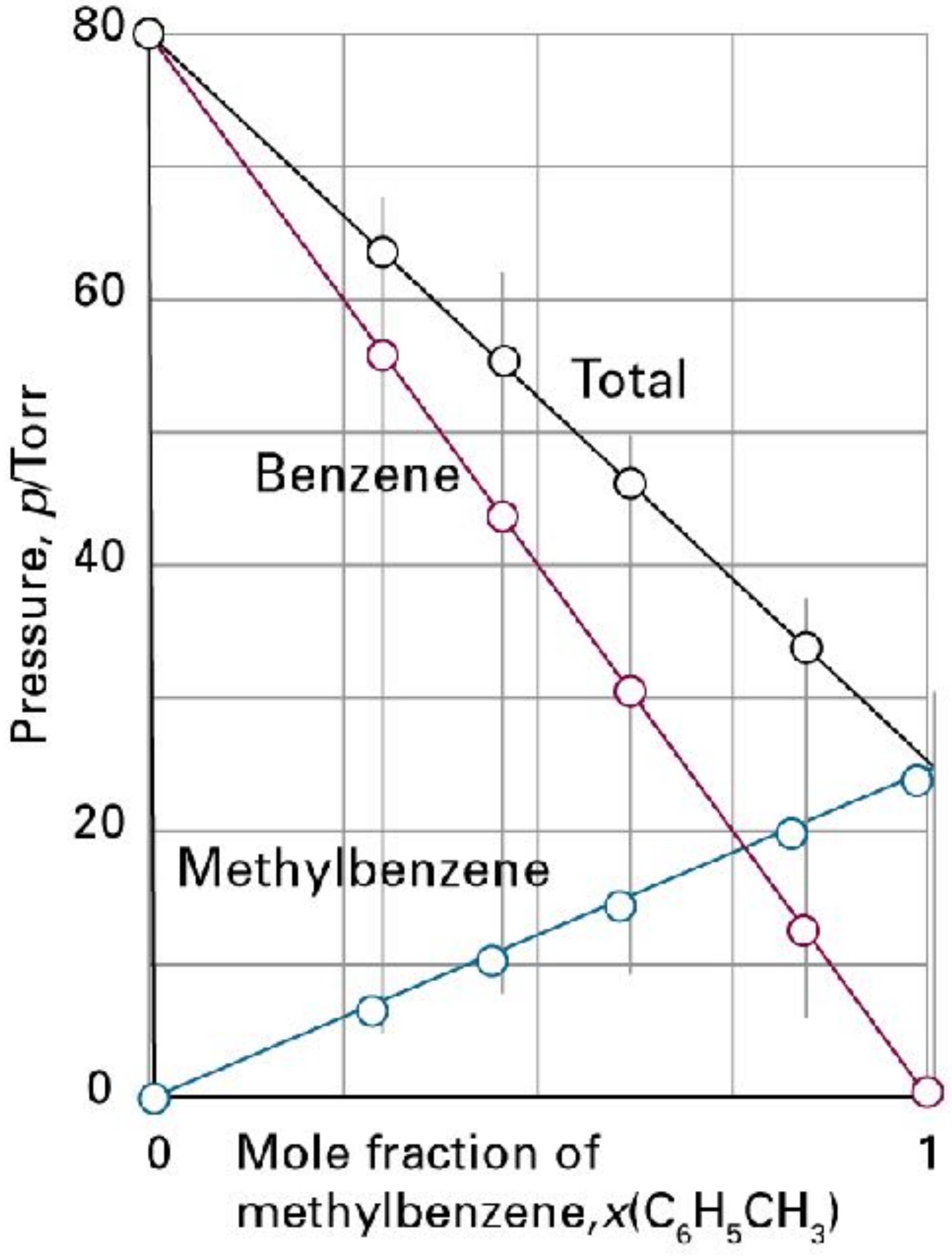
$$p = p_A + p_B$$

$$p = x_A p_A^* + x_B p_B^*$$

$$p = x_A p_A^* \boxed{- x_A p_B^* + x_A p_B^*} + x_B p_B^*$$

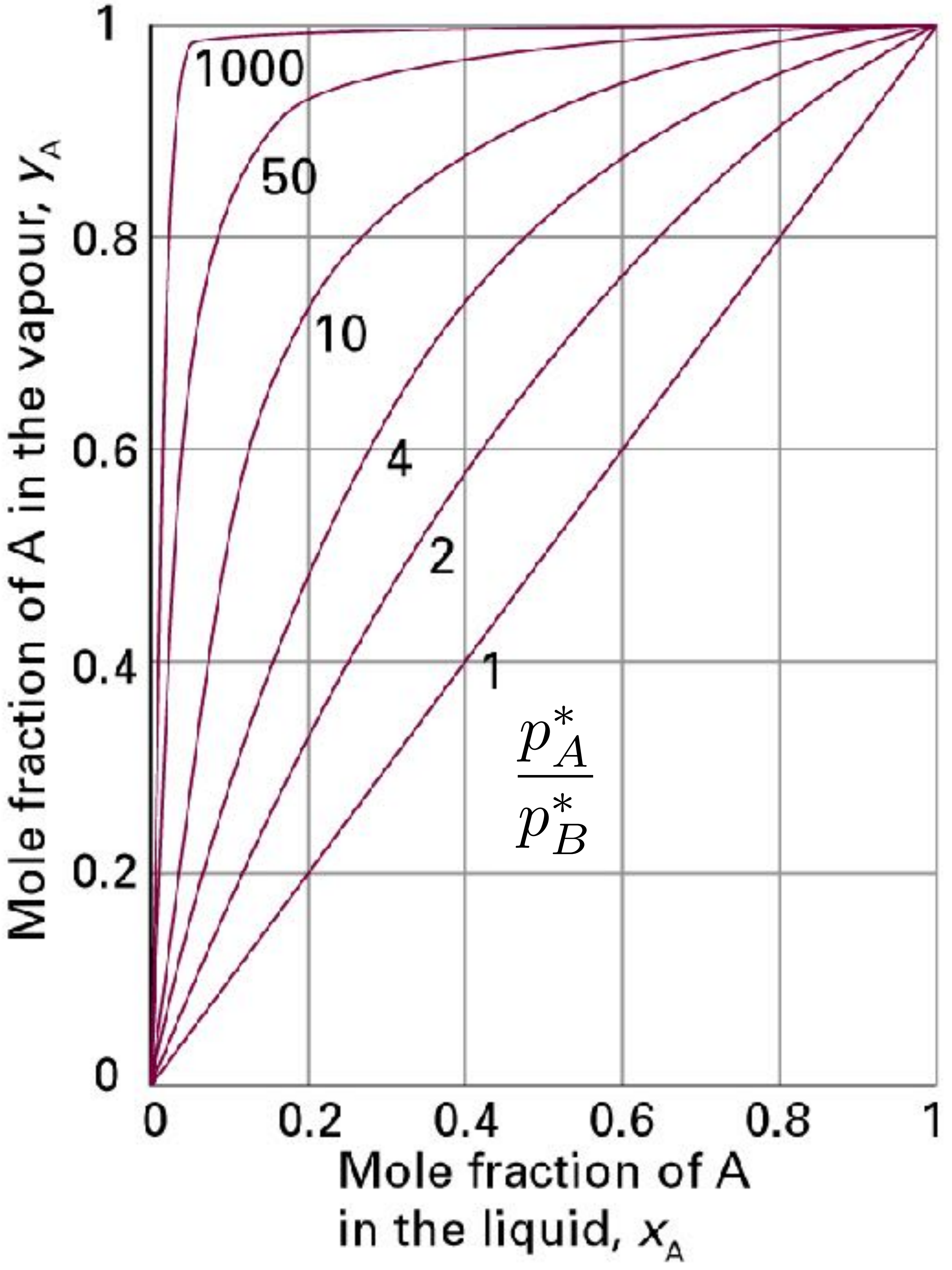
$$p = (p_A^* - p_B^*) x_A + (x_A + x_B) p_B^*$$

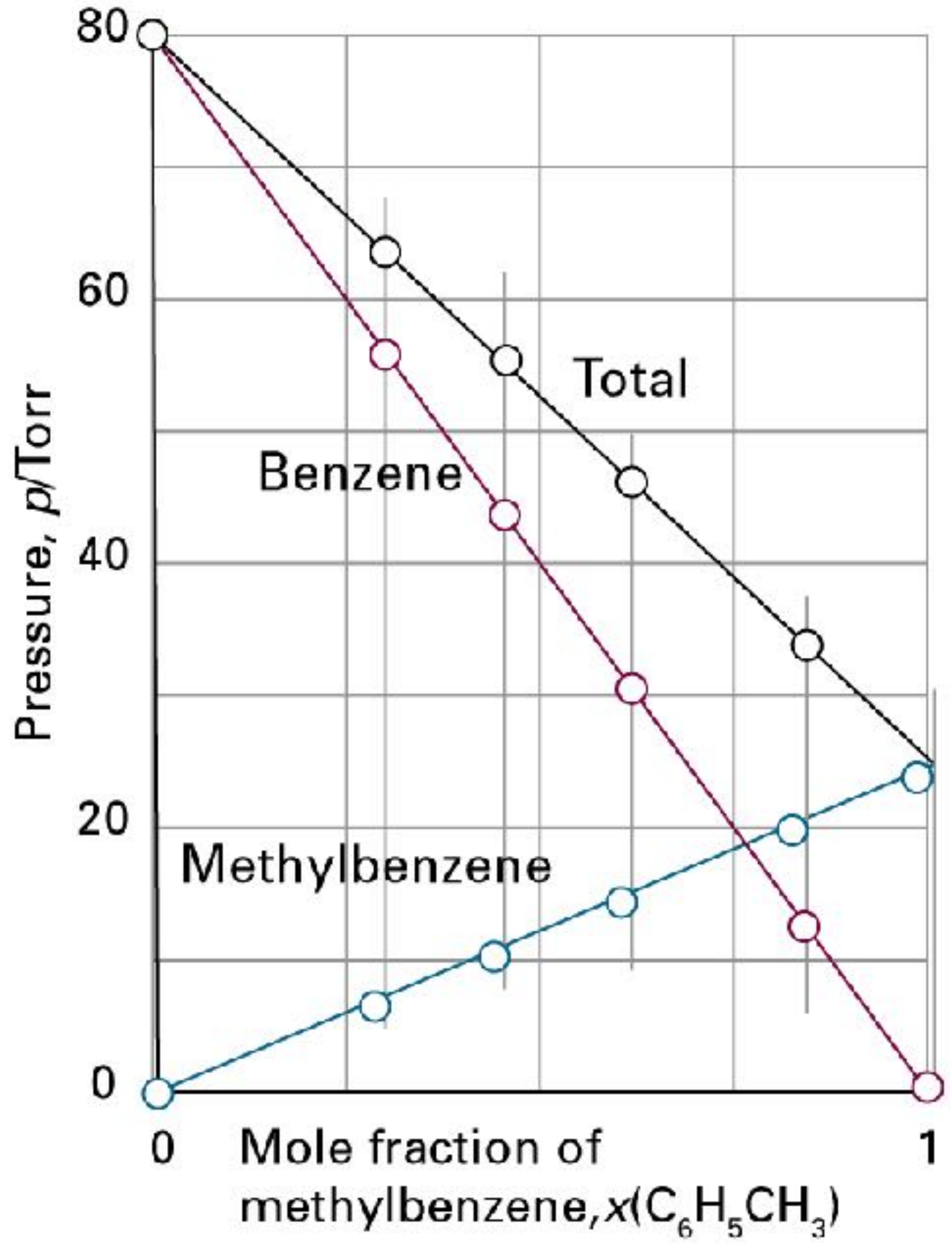
$$p = (p_A^* - p_B^*) x_A + p_B^*$$



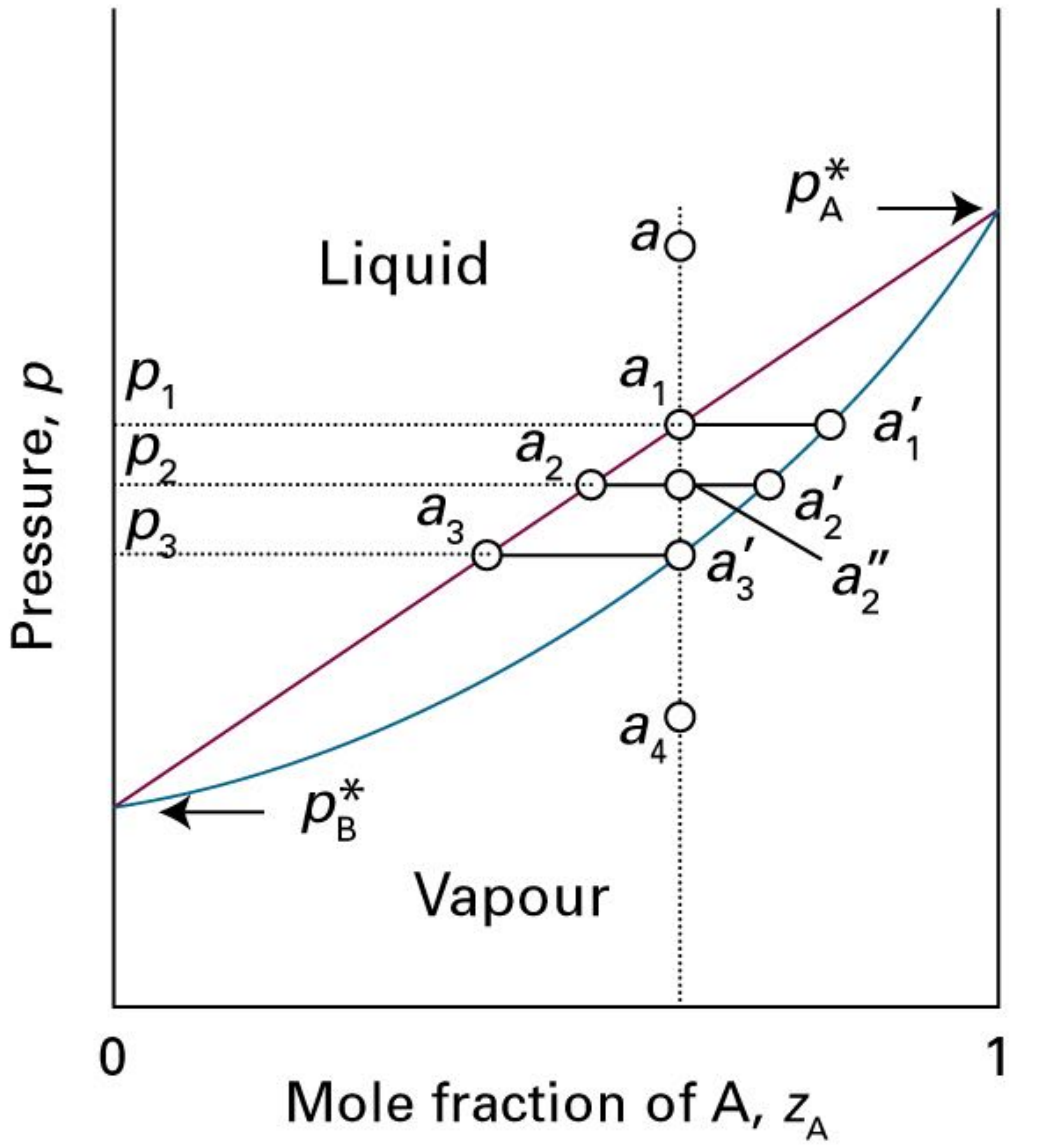
Composition of the vapour

$$y_A = \frac{p_A}{p} = \frac{x_A p_A^*}{(p_A^* - p_B^*)x_A + p_B^*}$$

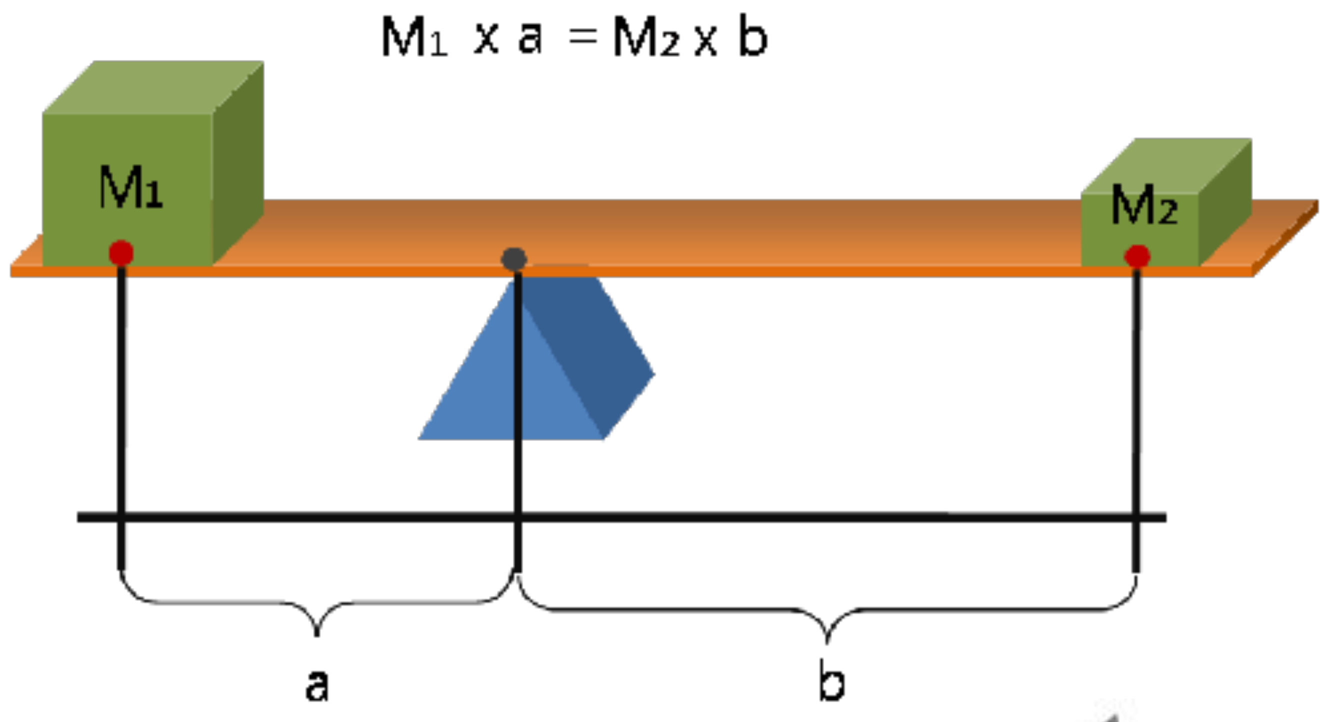




Binary mixture phase diagram

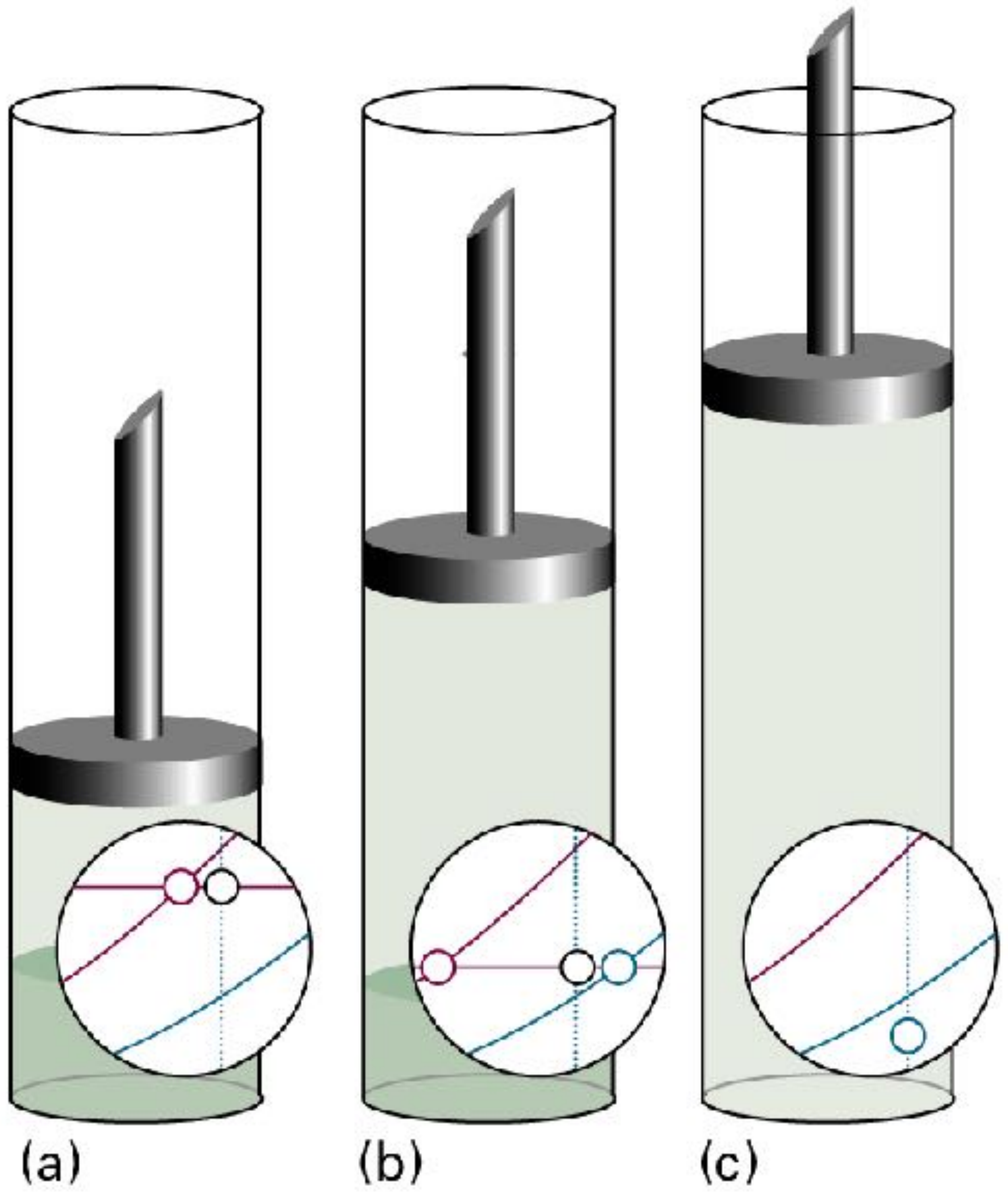


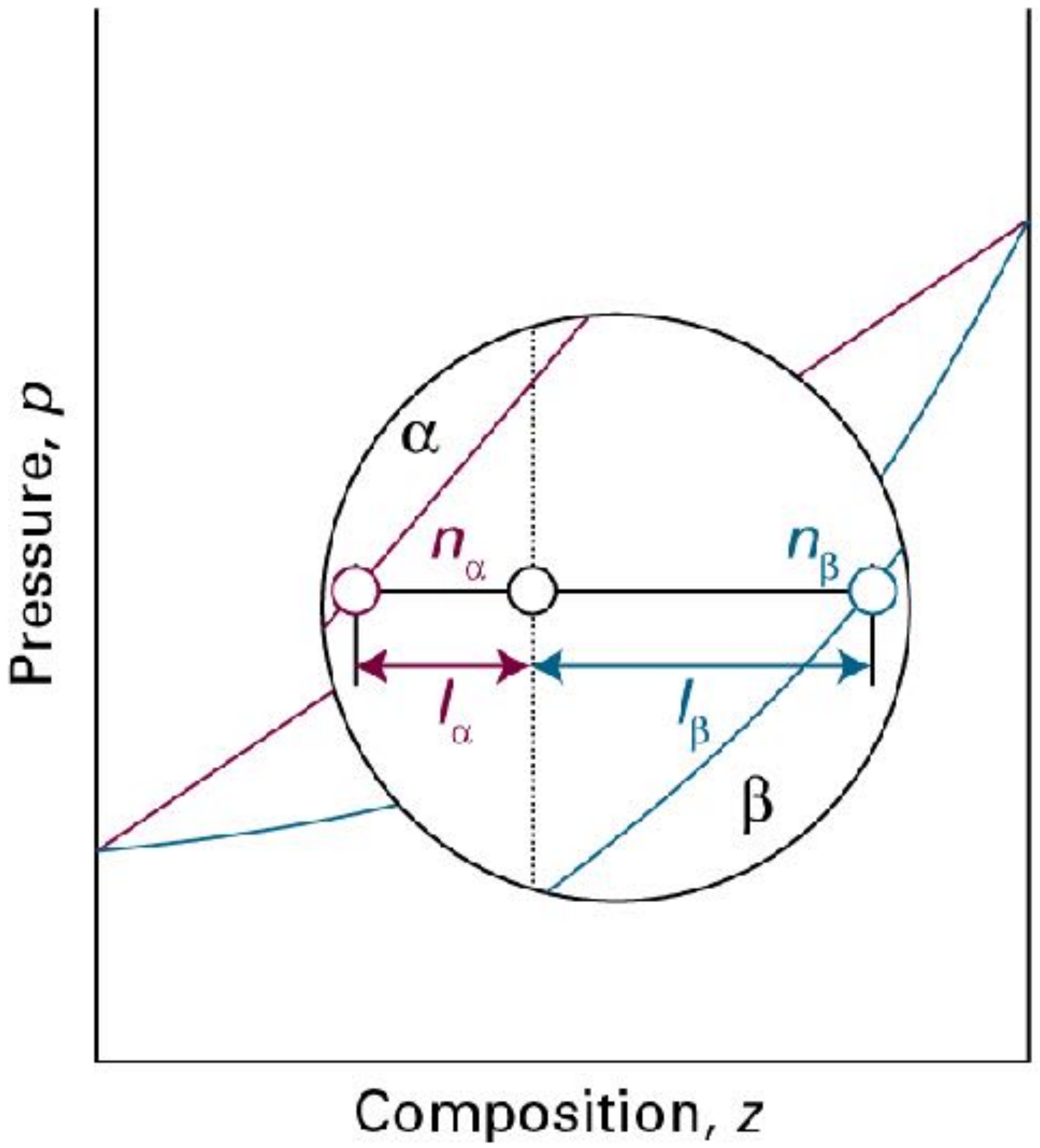
The lever rule



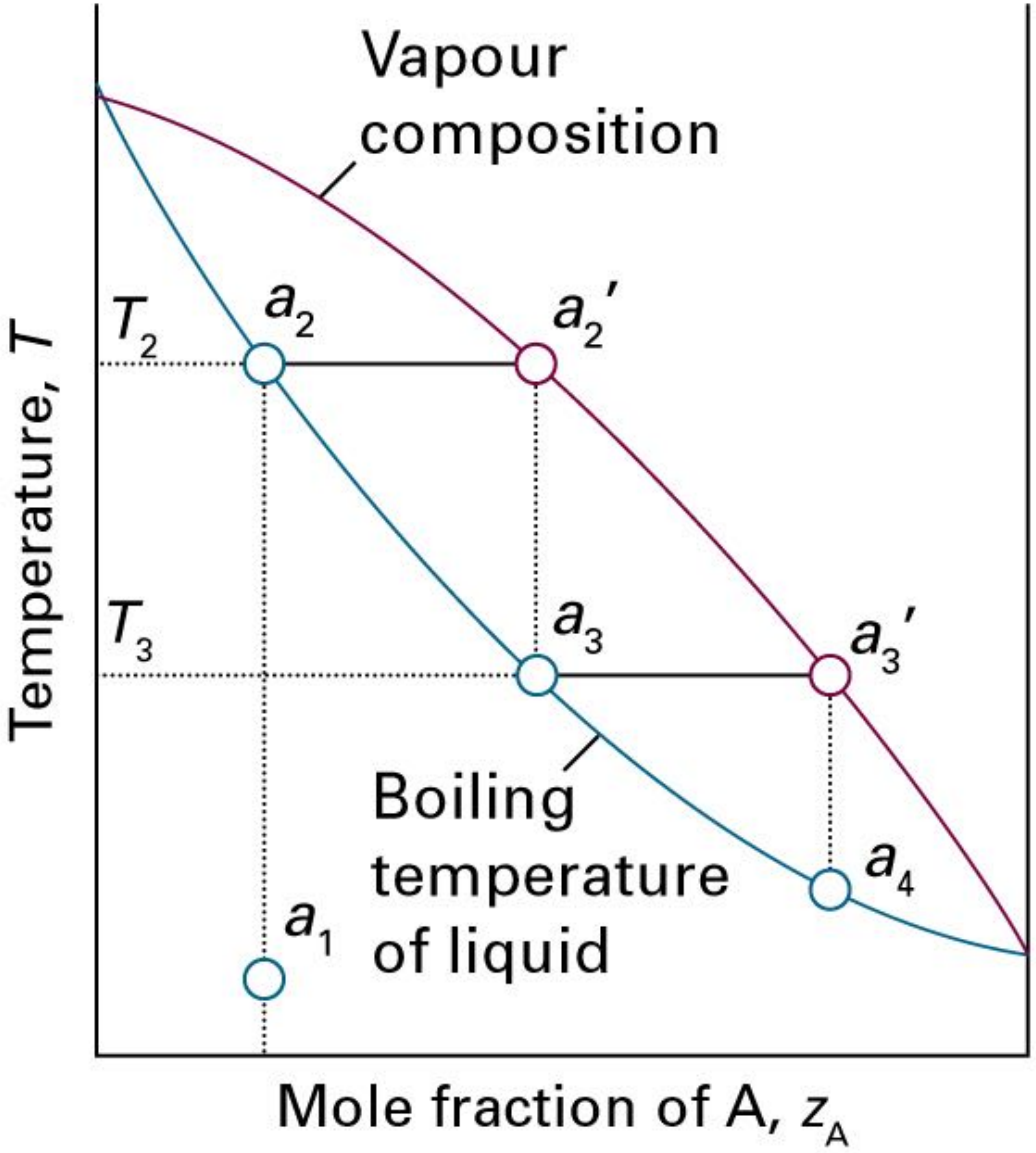
$$n = n_\alpha + n_\beta$$

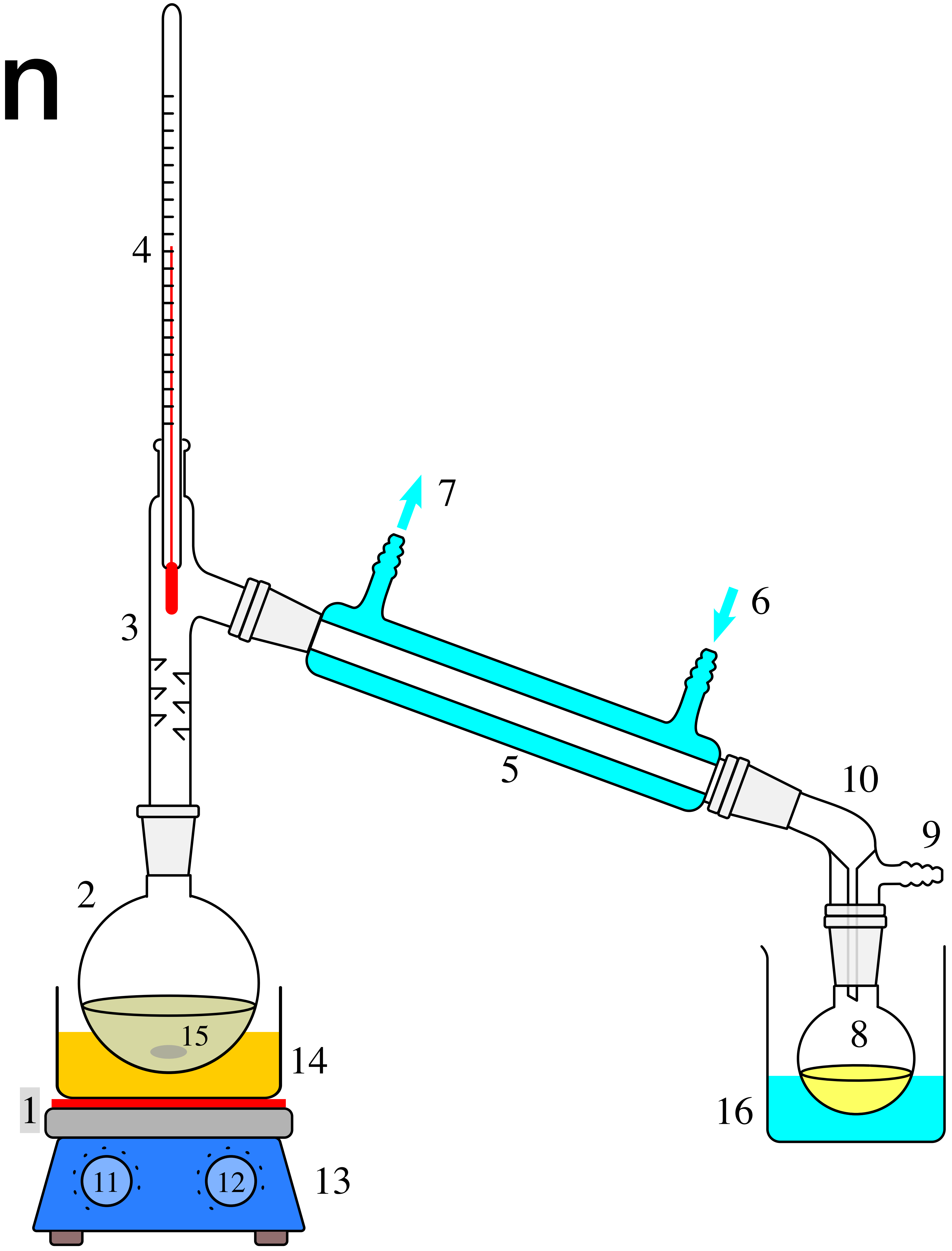
$$n_\alpha l_\alpha = n_\beta l_\beta$$





Distillation

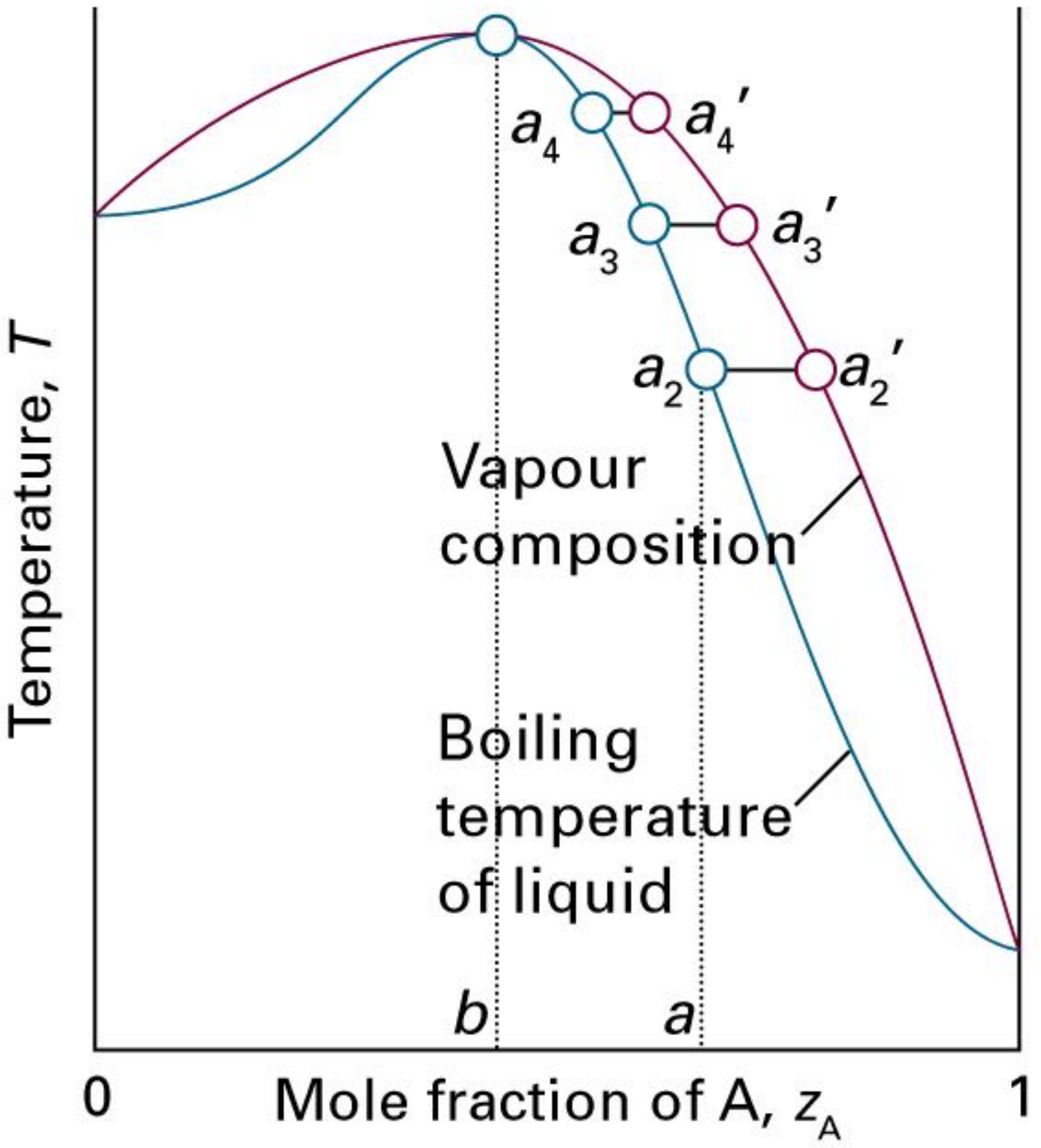




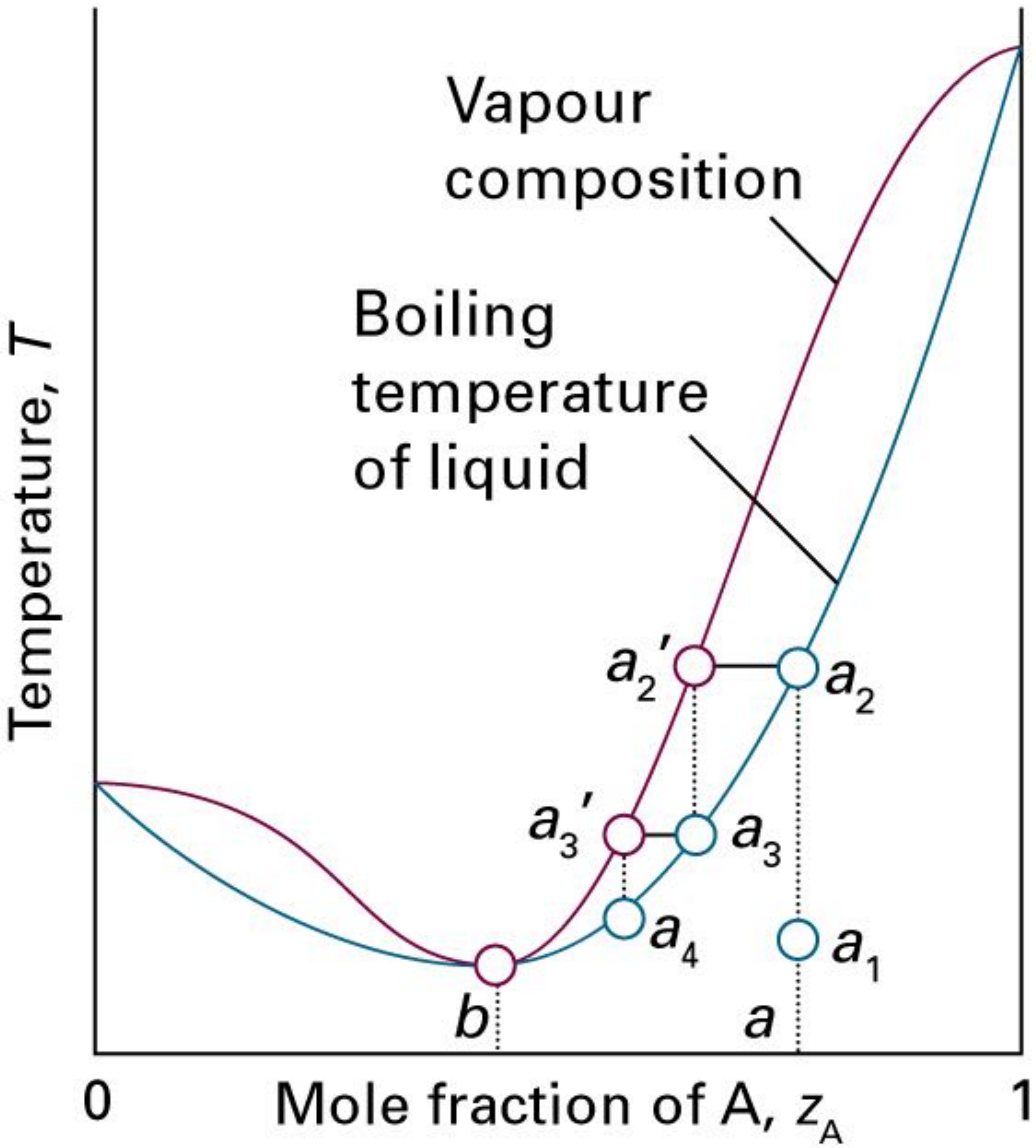
http://en.wikipedia.org/wiki/distillation

Azeotropes

high-boiling azeotrope



low-boiling azeotrope



Not all liquids are miscible

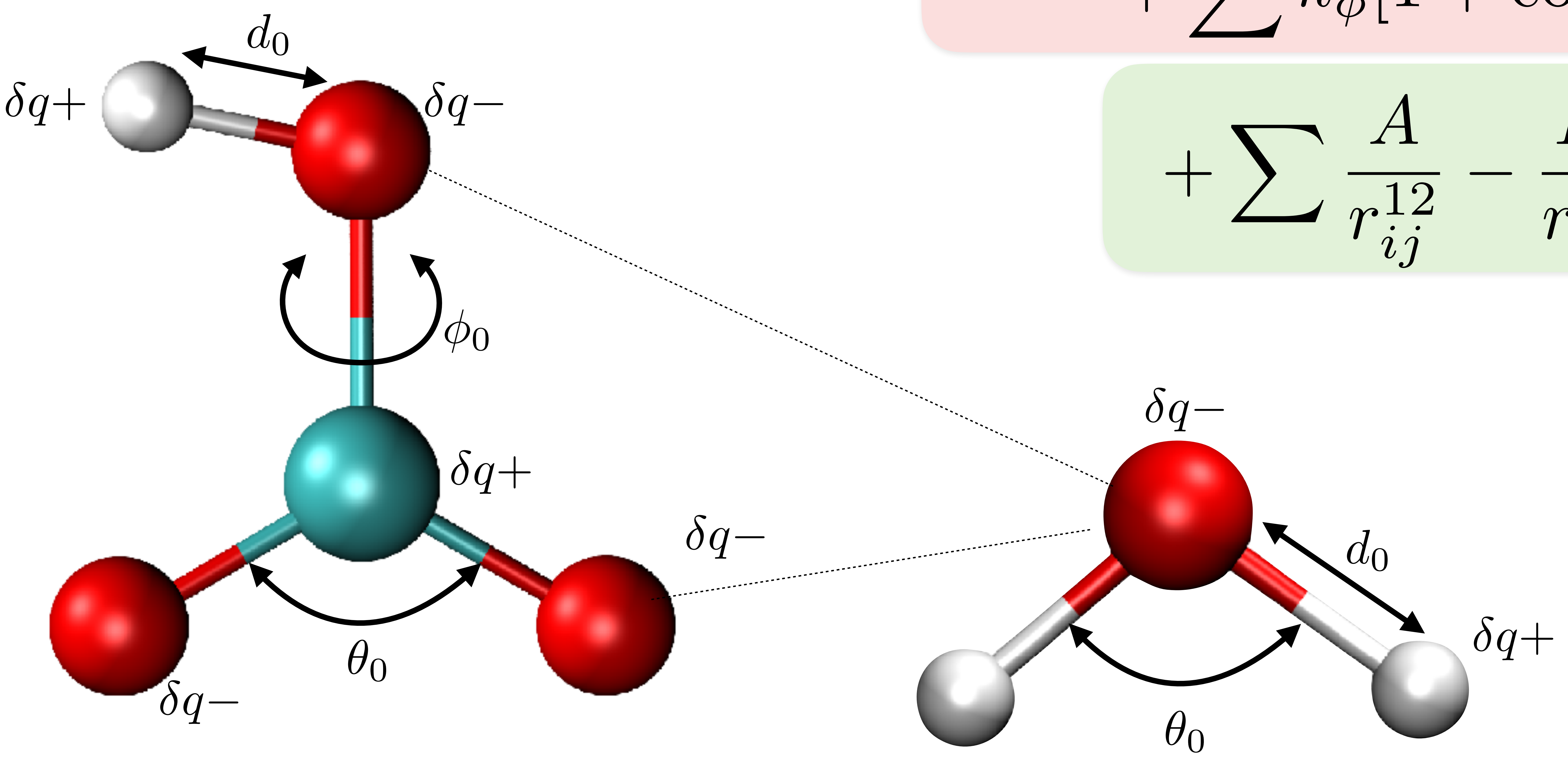
Image credit: https://peleg-design.com/products/dip-sea

Intramolecular forces

$$\mathbf{F}_i = -\frac{\partial \mathbf{U}}{\partial \mathbf{x}_i} + q_i \mathbf{E} = m_i \mathbf{a}_i$$

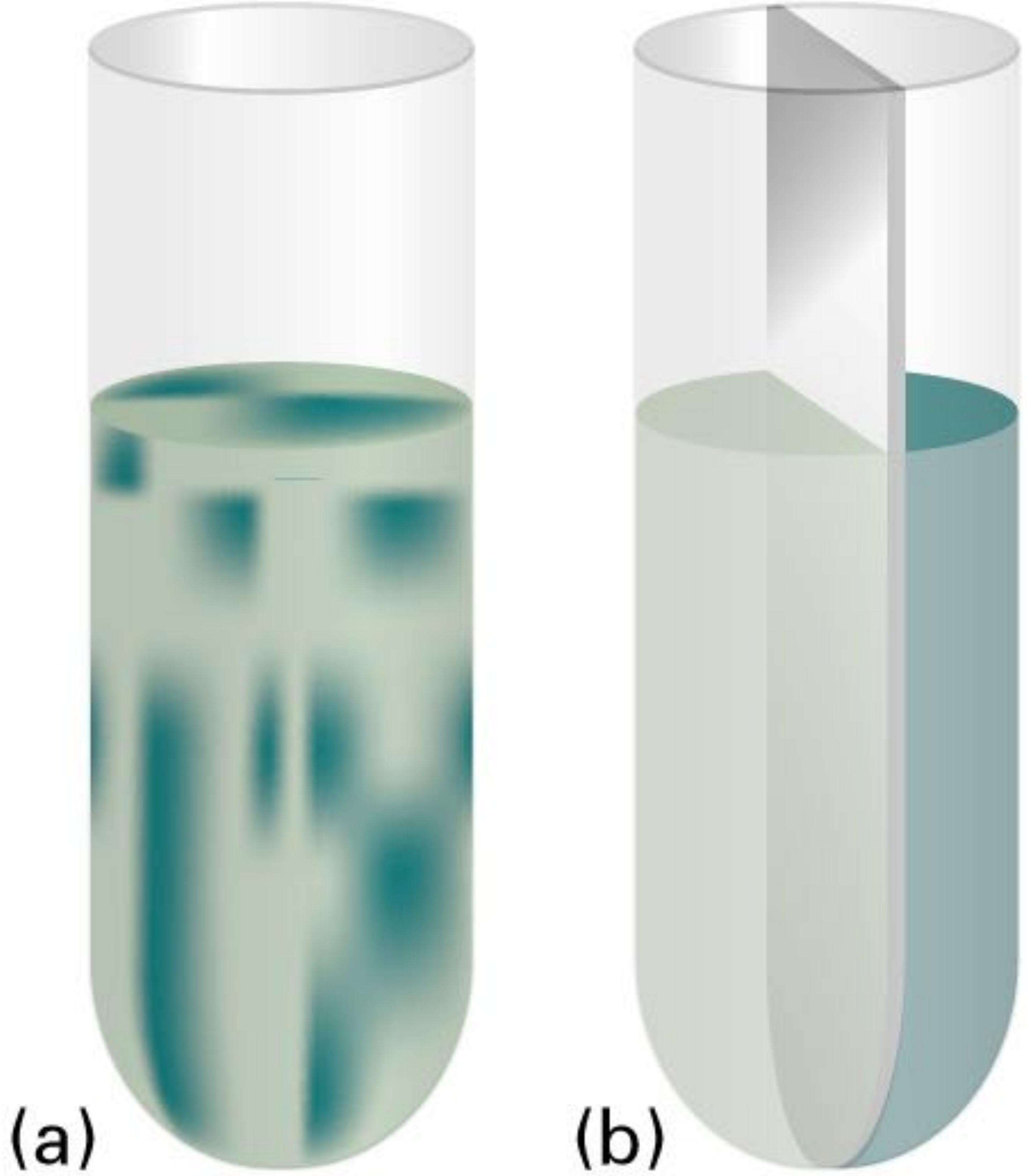
$$U = \sum k_b (b_{ij} - b_0)^2 + \sum k_\theta (\theta_{ijk} - \theta_0)^2 + \sum k_\phi [1 + \cos(n\phi_{ijkl} - \phi_0)]^2$$

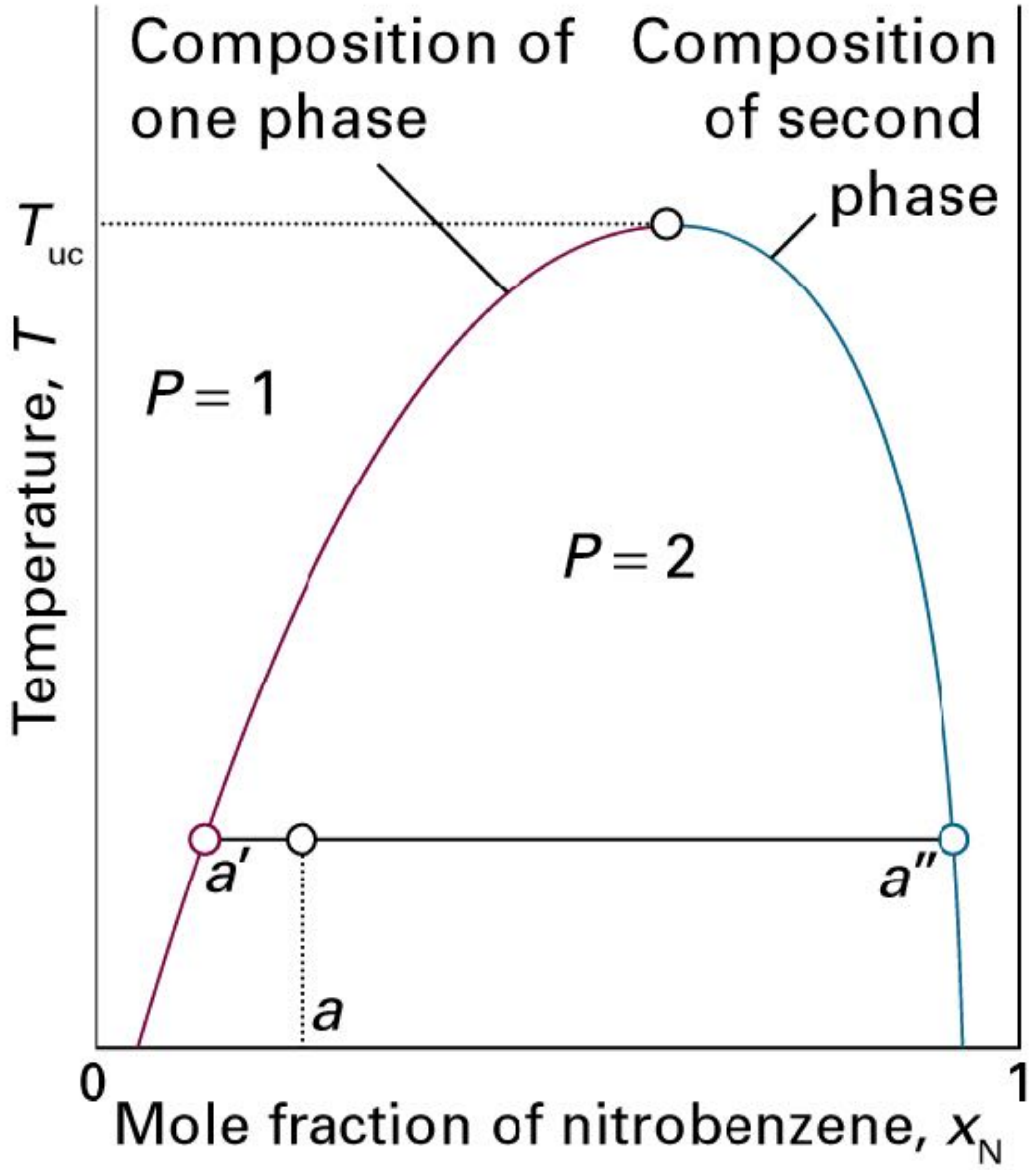
$$+ \sum \frac{A}{r_{ij}^{12}} - \frac{B}{r_{ij}^{6}} + \sum \frac{q_i q_j}{r_{ij}}$$



liquid-liquid phase diagram

miscibility gap

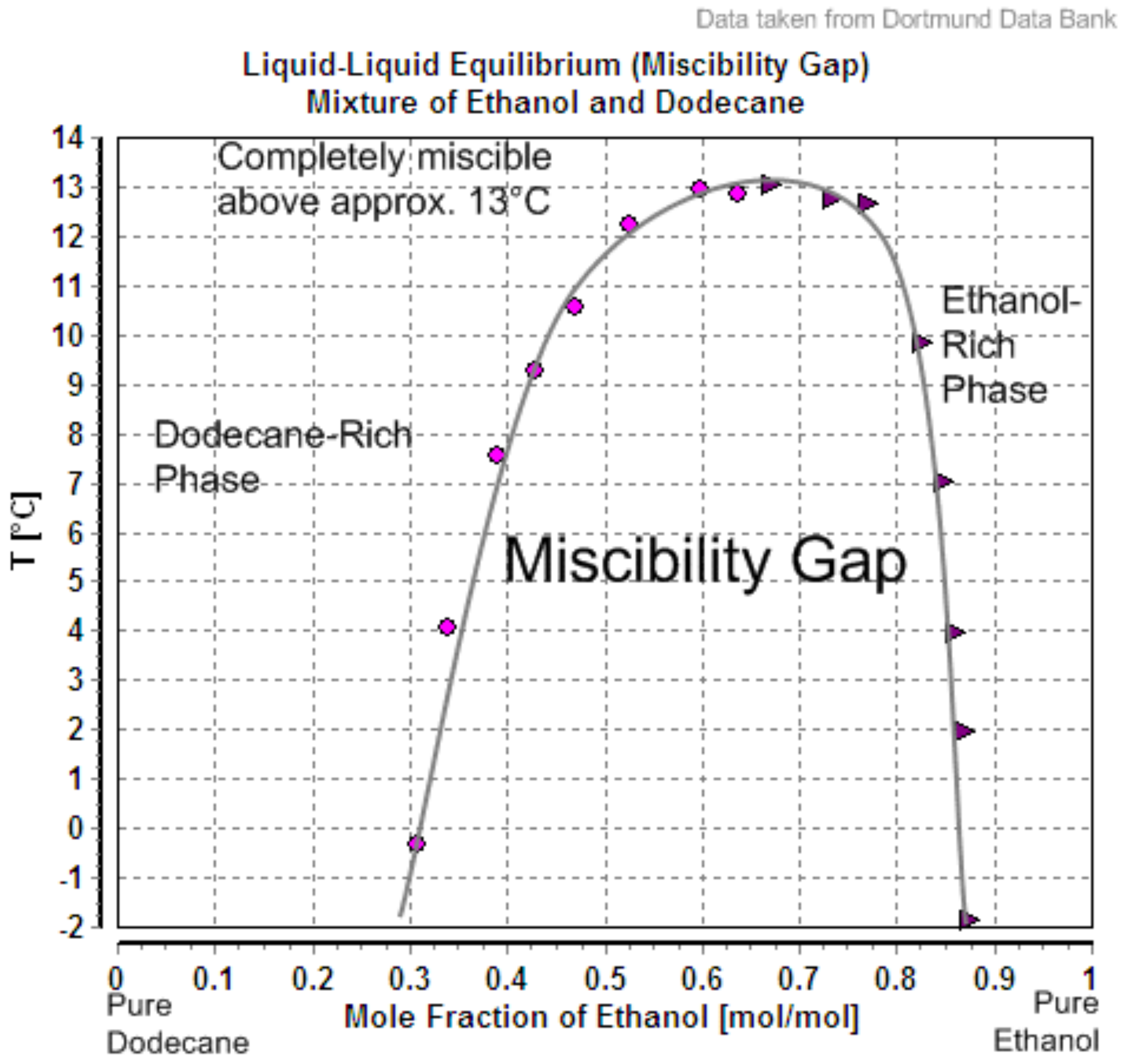


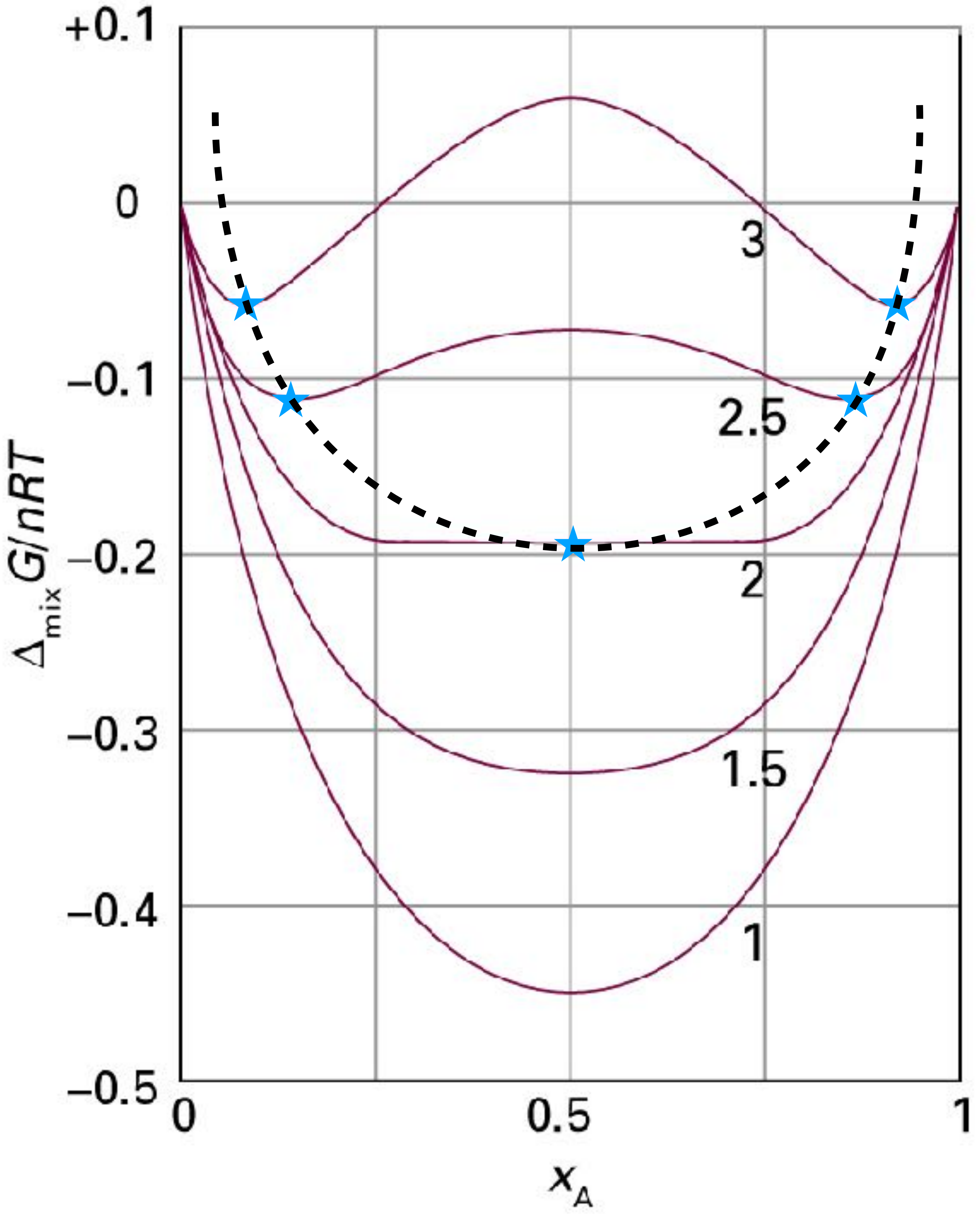


Excess free energy of mixing

$$\Delta_{mix}G = nRT\{\underbrace{x_A \ln x_A + x_B \ln x_B}_{ideal} + \xi x_A x_B\}$$

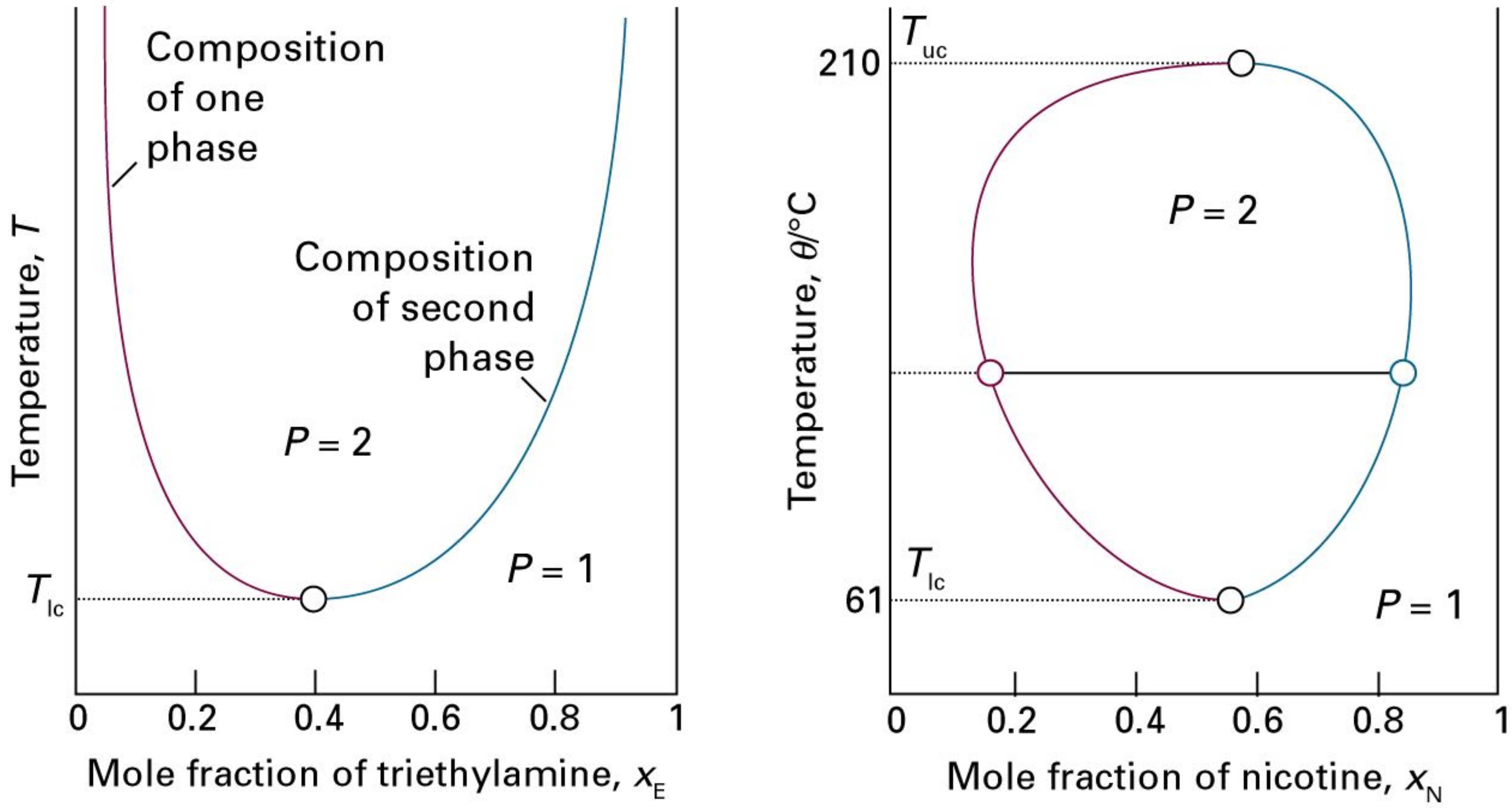
$$\Delta_{mix}G^{ex} = nRT\xi x_A x_B$$



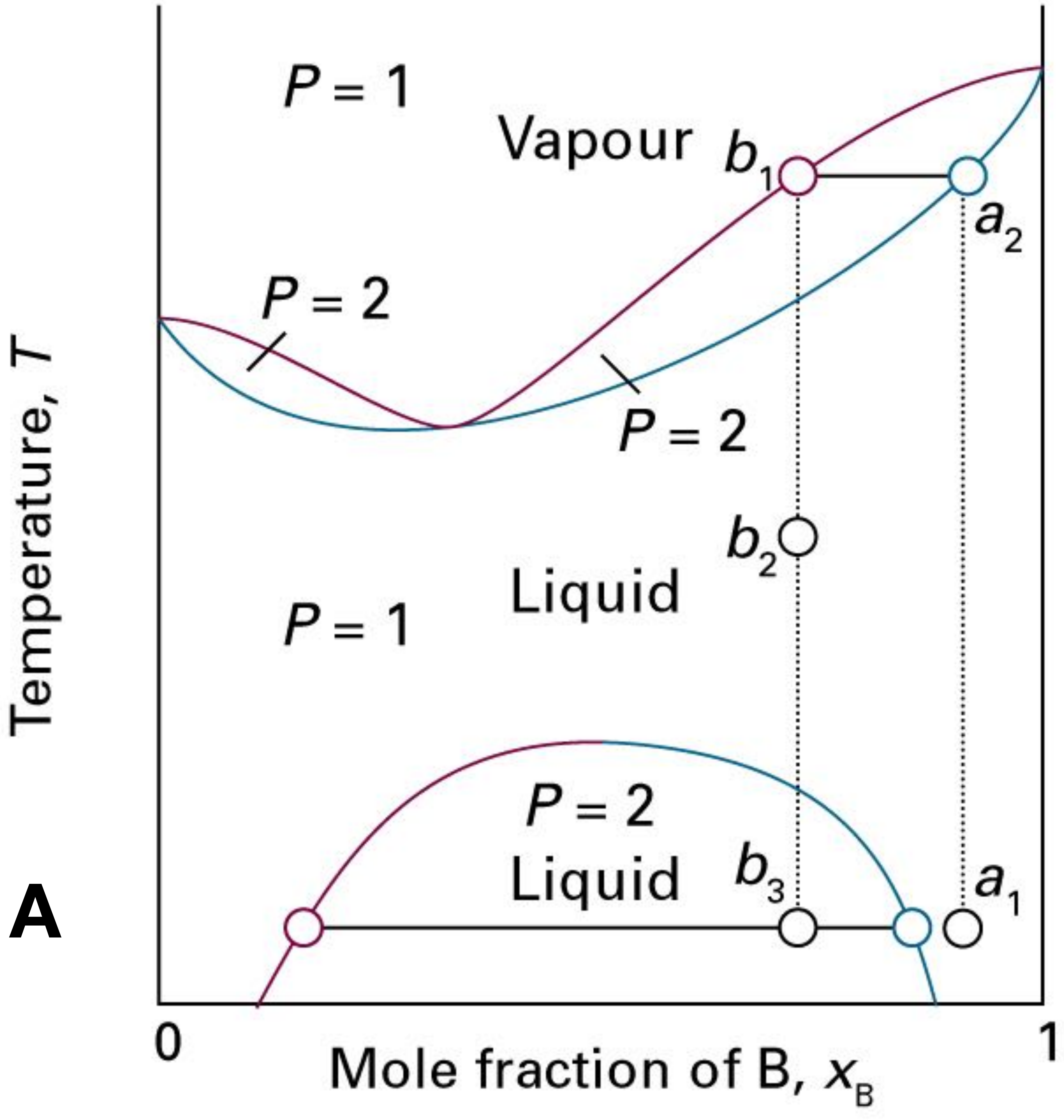


liquid-liquid phase diagram

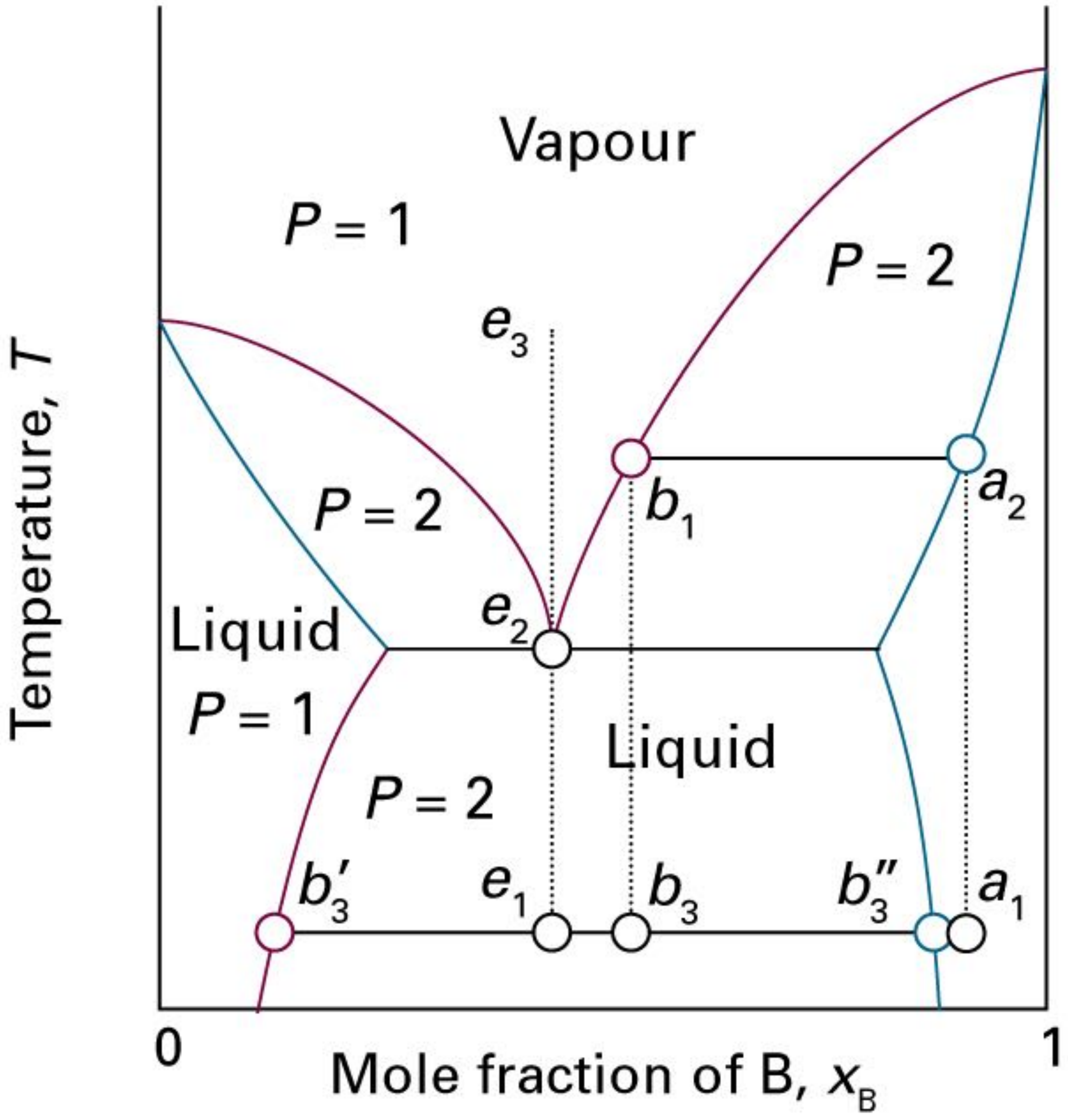
miscibility gap



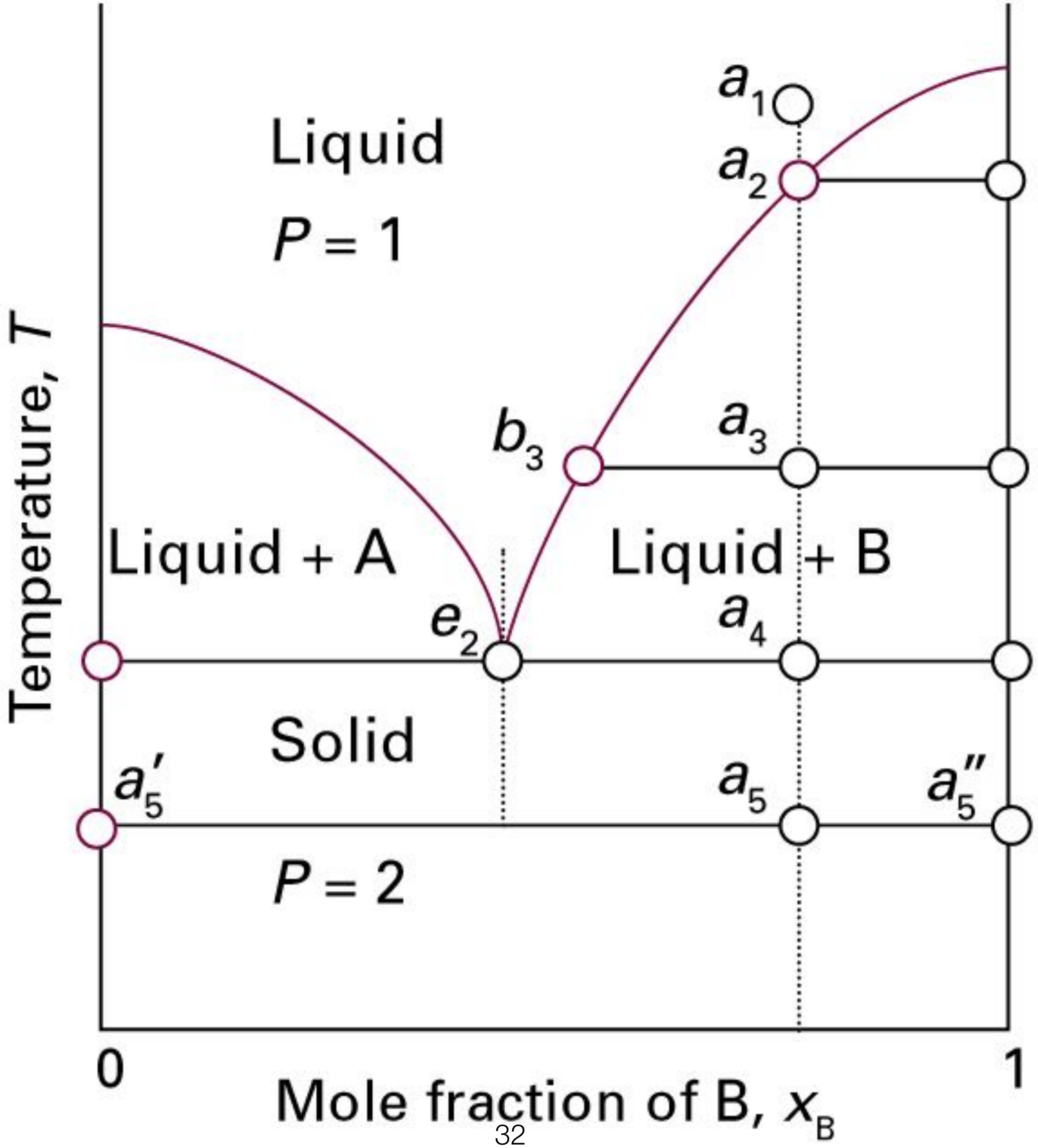
Phase A

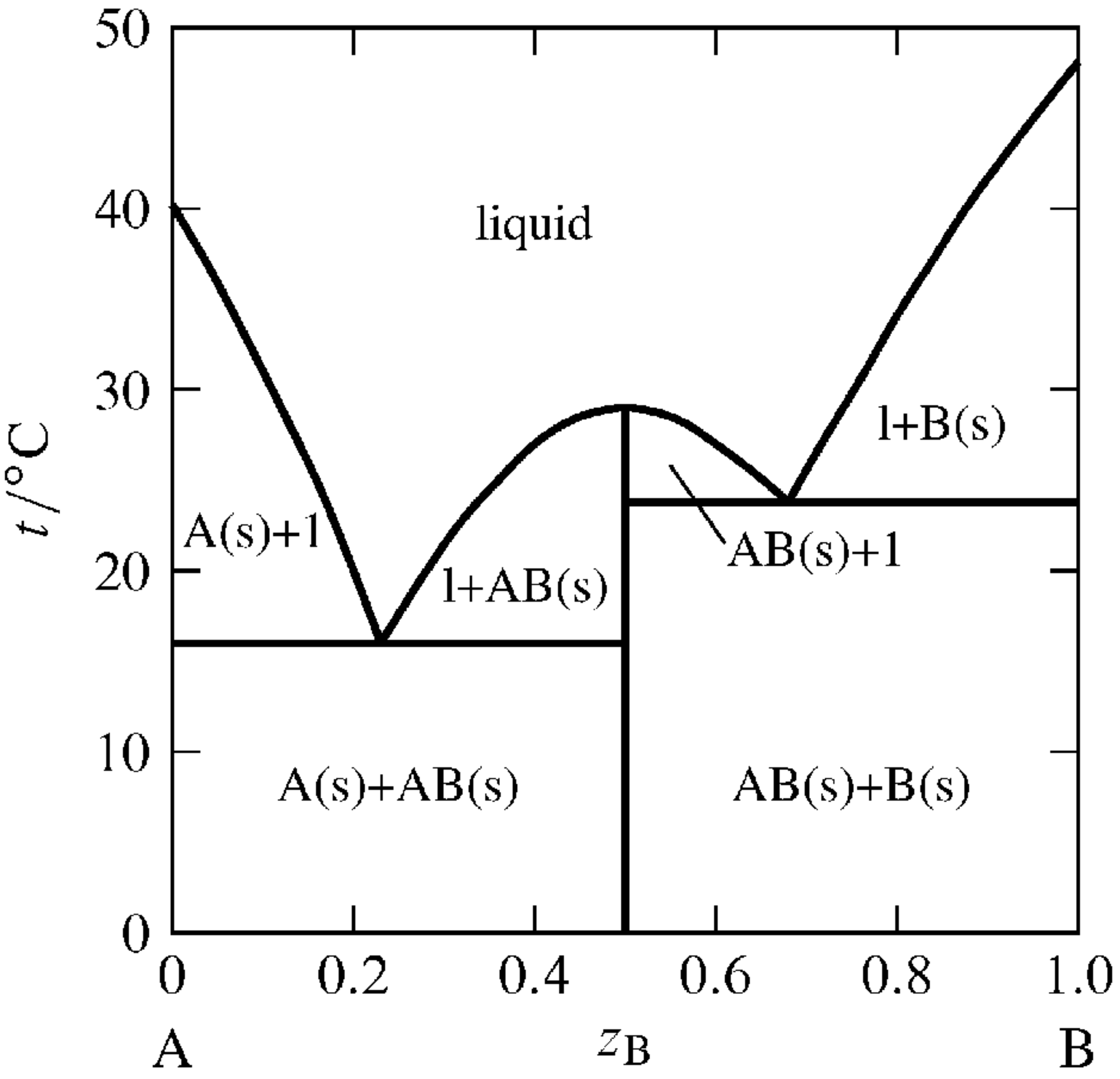


Phase B


Vapour
P = 1
P = 2
e3
b1
a2
P = 2
e2
Liquid
P = 1
Liquid
P = 2
b′3
e1
b3
b″3
a1
Temperature, T
0
1
Mole fraction of B, xB

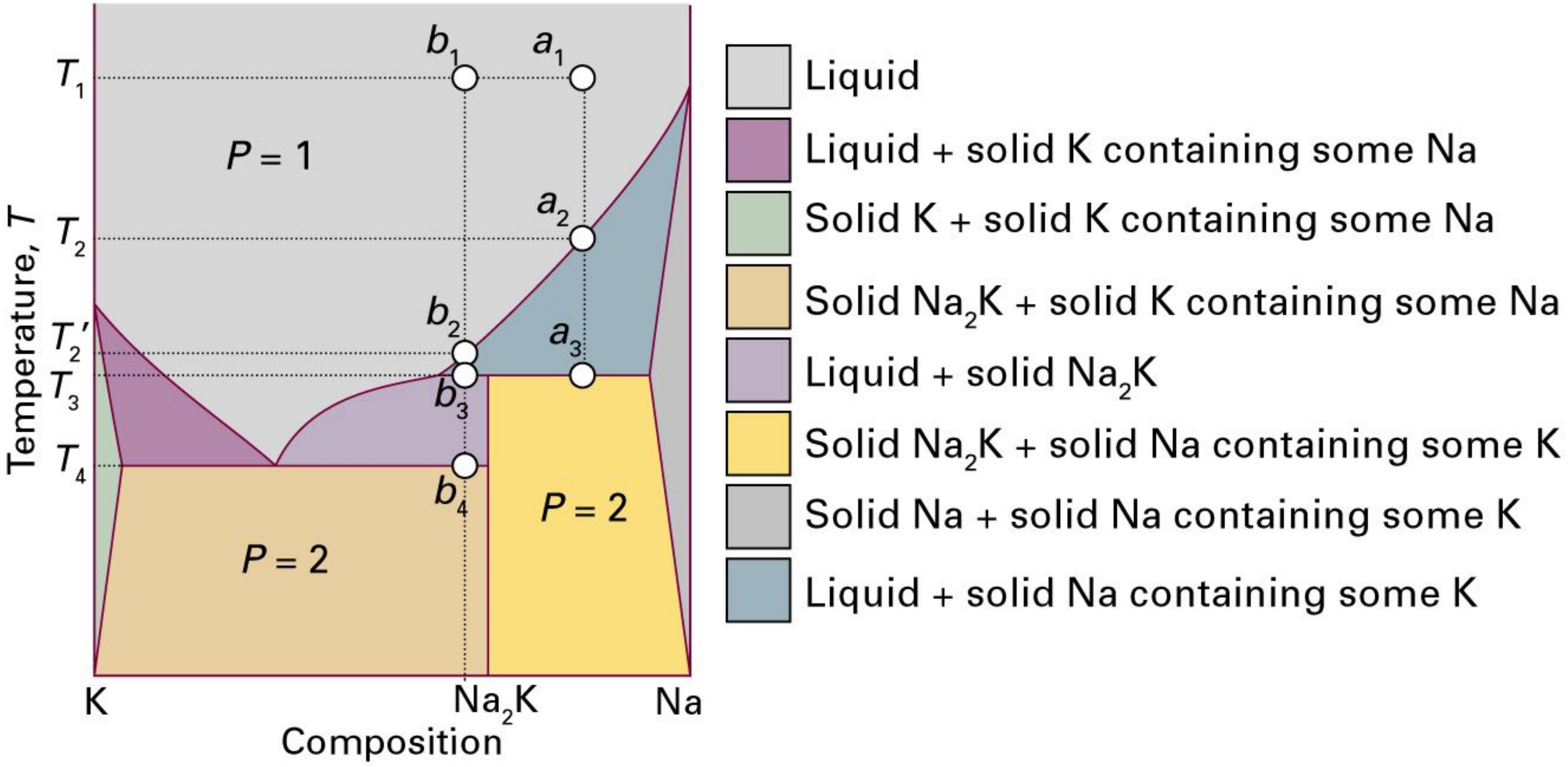
Solid-liquid phase diagram



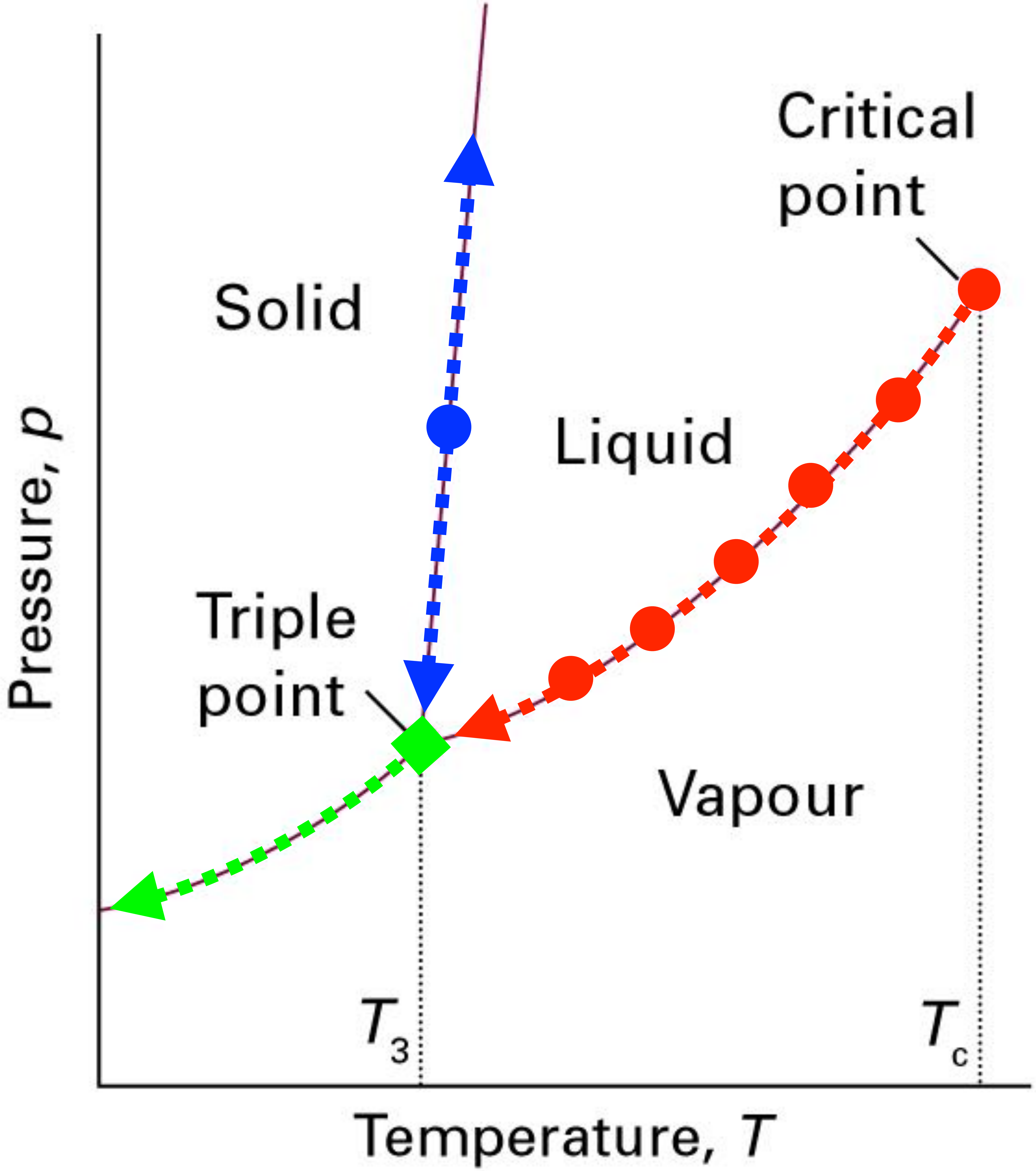


50
40
30
20
10
0
t/°C
liquid
A(s)+1
l+AB(s)
l+B(s)
AB(s)+1
A(s)+AB(s)
AB(s)+B(s)
0
0.2
0.4
0.6
0.8
1.0
A
zB
B

Na-K phase diagram



- Incongruent melting
- Zone refining


Critical
point
Solid
Liquid
Triple
point
Vapour
Pressure, p
T_3
T_c
Temperature, T