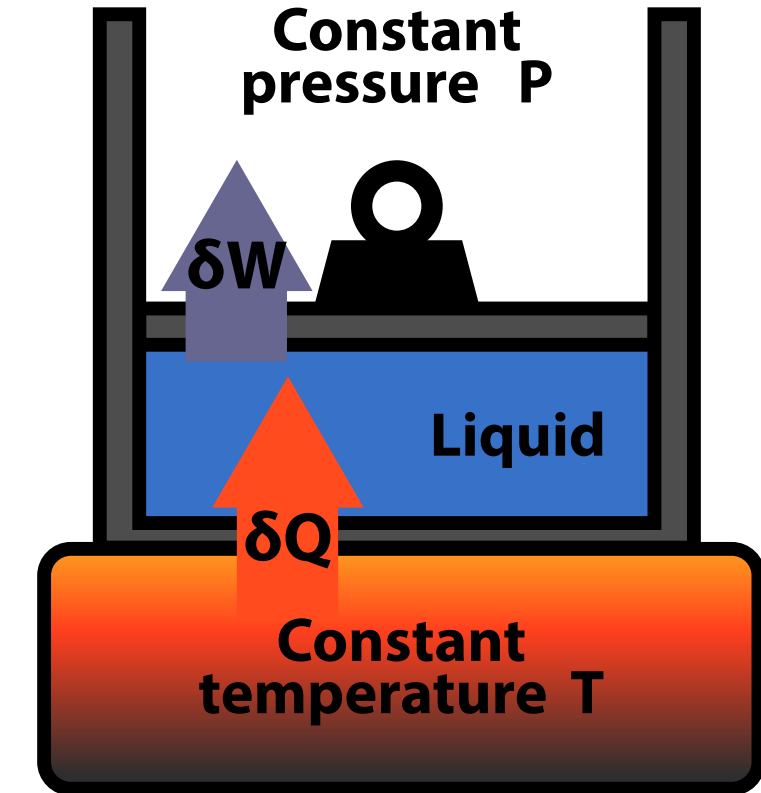# Phase transitions and phase equilibrium

Enthalpy of vaporization

The enthalpy of vaporization, (or latent heat of vaporization), is the amount of energy that must be added to a liquid substance to transform it into a gas while keeping the pressure constant.
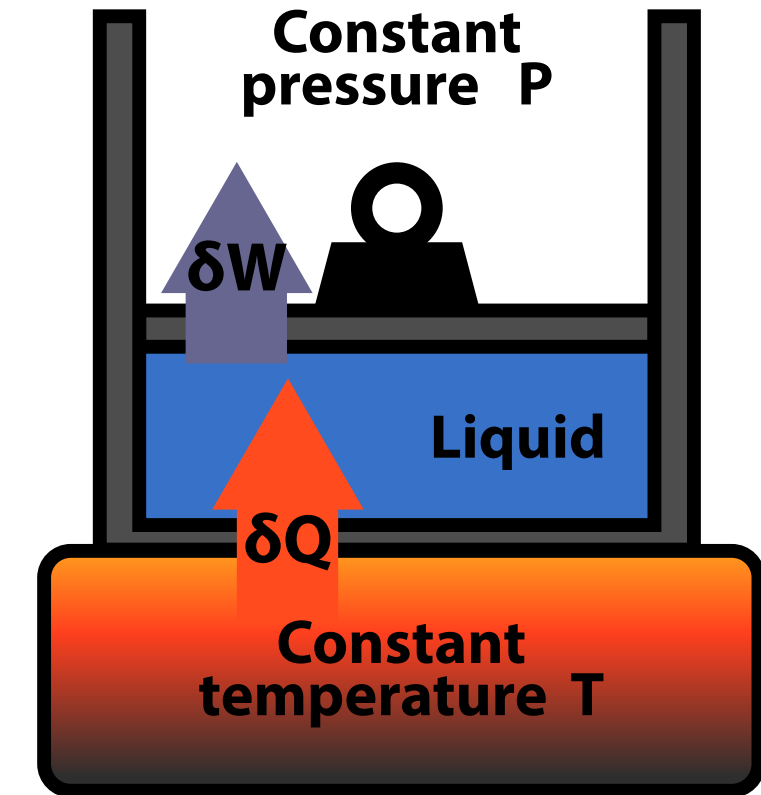
Enthalpy of vaporization

The enthalpy of vaporization, (or latent heat of vaporization), is the amount of energy that must be added to a liquid substance to transform it into a gas while keeping the pressure constant.

It is equal to the difference of internal energy between vapor and liquid, plus the work done against the external pressure.
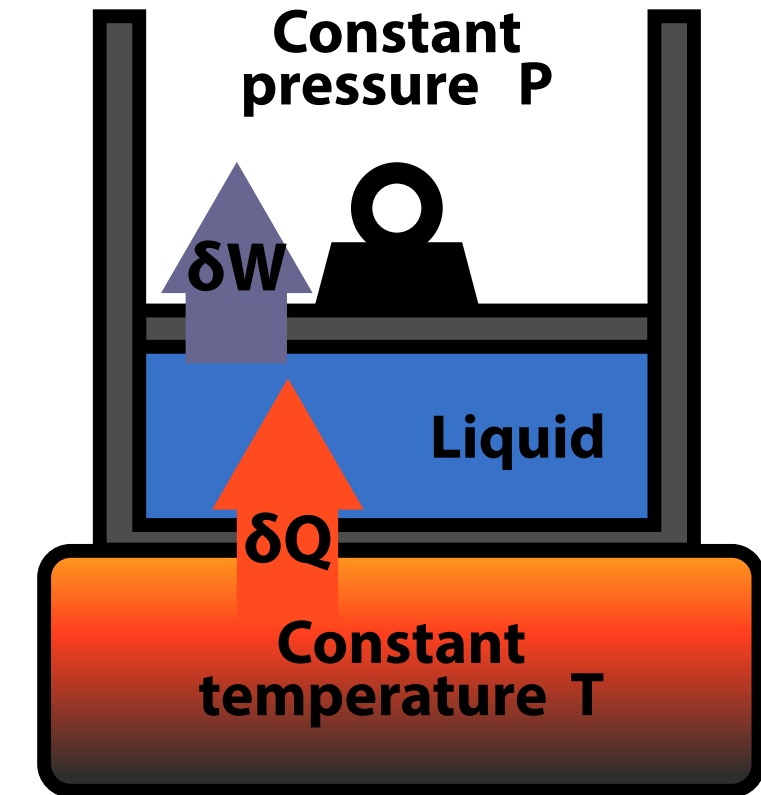
Enthalpy of vaporization

The enthalpy of vaporization, (or latent heat of vaporization), is the amount of energy that must be added to a liquid substance to transform it into a gas while keeping the pressure constant.

It is equal to the difference of internal energy between vapor and liquid, plus the work done against the external pressure.

It is a function of the pressure at which that transformation takes place.

Constant pressure P

δW

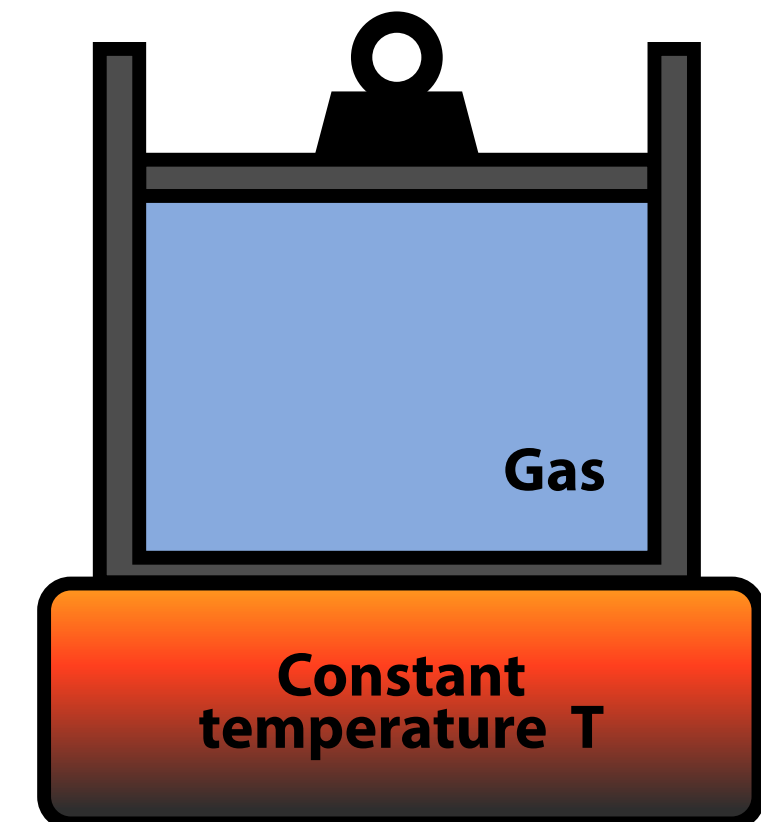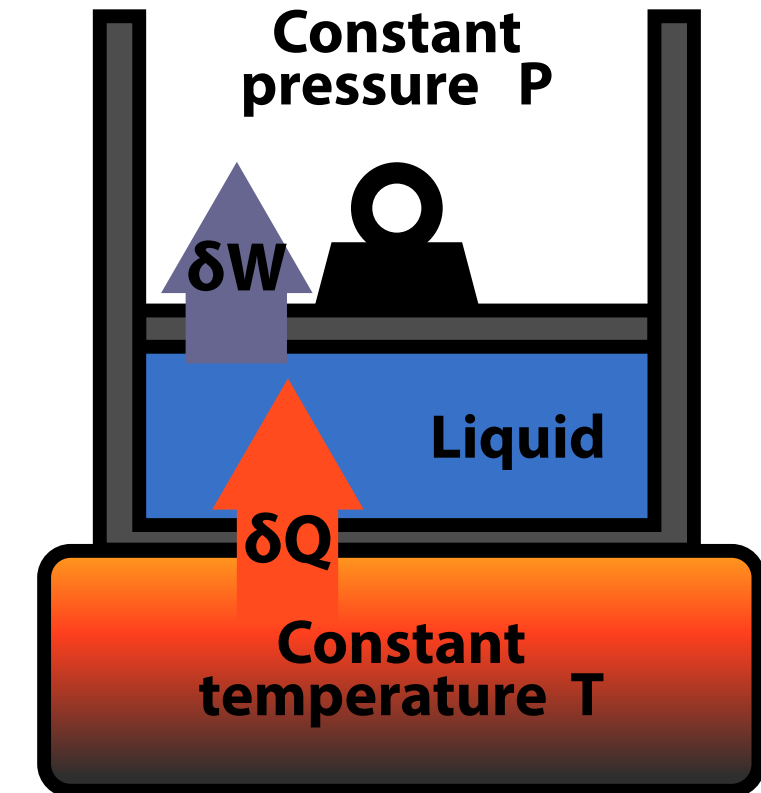**Liquid**

δQ

Constant temperature T

Enthalpy of vaporization

The enthalpy of vaporization, (or latent heat of vaporization), is the amount of energy that must be added to a liquid substance to transform it into a gas while keeping the pressure constant.

It is equal to the difference of internal energy between vapor and liquid, plus the work done against the external pressure.

We consider a liquid held at constant T and P while being supplied heat.

Constant pressure P

δW

Liquid

δQ

Constant temperature T
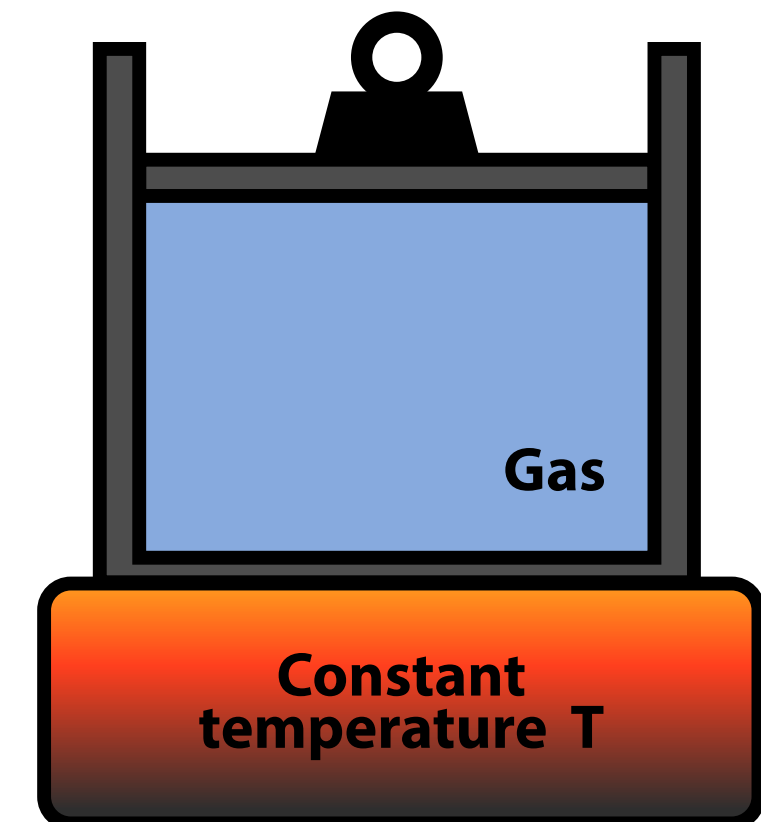
Gas

Constant temperature T

Enthalpy of vaporization

The enthalpy of vaporization, (or latent heat of vaporization), is the amount of energy that must be added to a liquid substance to transform it into a gas while keeping the pressure constant.

It is equal to the difference of internal energy between vapor and liquid, plus the work done against the external pressure.

We consider a liquid held at constant *T* and *P* while being supplied heat. Gibbs equation (with no mass transfer):

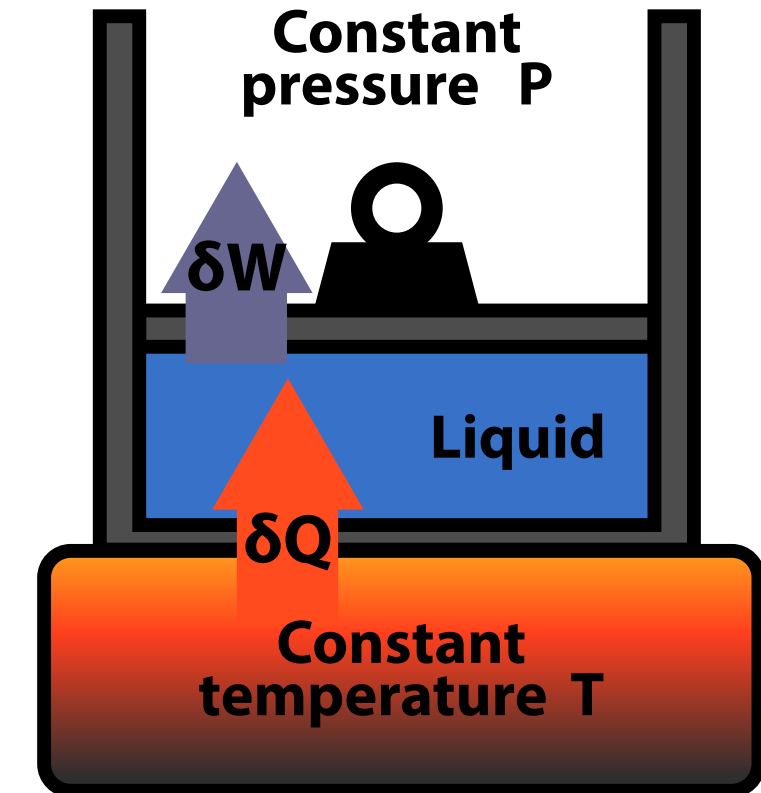$$Tds = du + Pdv = dh - vdP$$

Enthalpy of vaporization

The enthalpy of vaporization, (or latent heat of vaporization), is the amount of energy that must be added to a liquid substance to transform it into a gas while keeping the pressure constant.
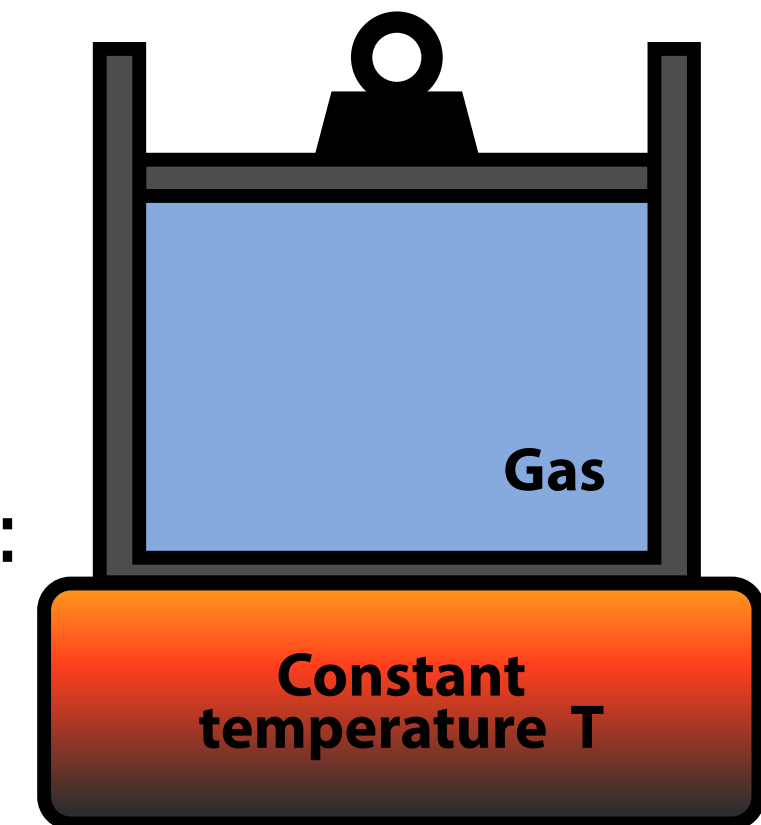
It is equal to the difference of internal energy between vapor and liquid, plus the work done against the external pressure.

We consider a liquid held at constant *T* and *P* while being supplied heat. Gibbs equation (with no mass transfer):

$$Tds = du + Pdv = dh - vdP$$

Integrating until the end of transition (with *T* and *P* constant):

$$T\int_1^2 ds = \int_1^2 dh$$

Enthalpy of vaporization

The enthalpy of vaporization, (or latent heat of vaporization), is the amount of energy that must be added to a liquid substance to transform it into a gas while keeping the pressure constant.
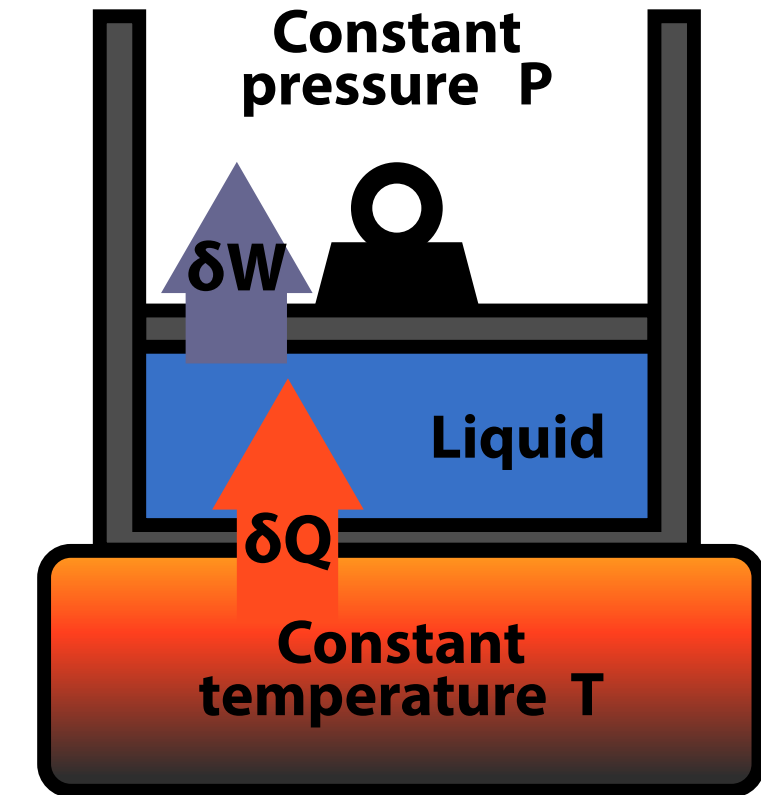
It is equal to the difference of internal energy between vapor and liquid, plus the work done against the external pressure.

We consider a liquid held at constant T and P while being supplied heat. Gibbs equation (with no mass transfer):

$$T ds = du + P dv = dh - v dP$$

Integrating until the end of transition (with T and P constant):

$$T \int_1^2 ds = \int_1^2 dh \Rightarrow T \Delta s = \Delta h_{\text{vap}}$$

Enthalpy of vaporization

The enthalpy of vaporization, (or latent heat of vaporization), is the amount of energy that must be added to a liquid substance to transform it into a gas while keeping the pressure constant.
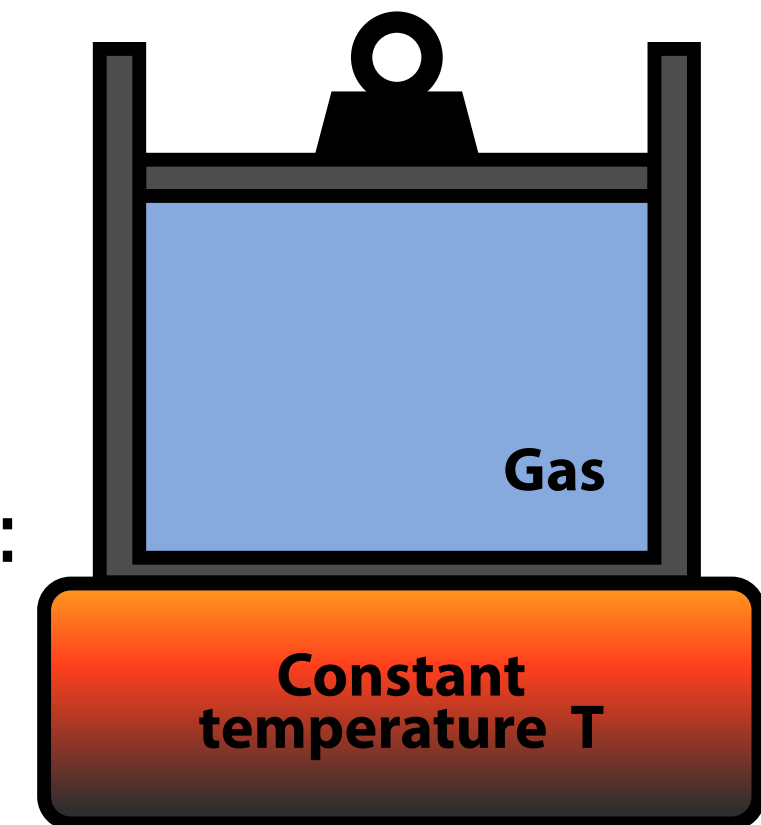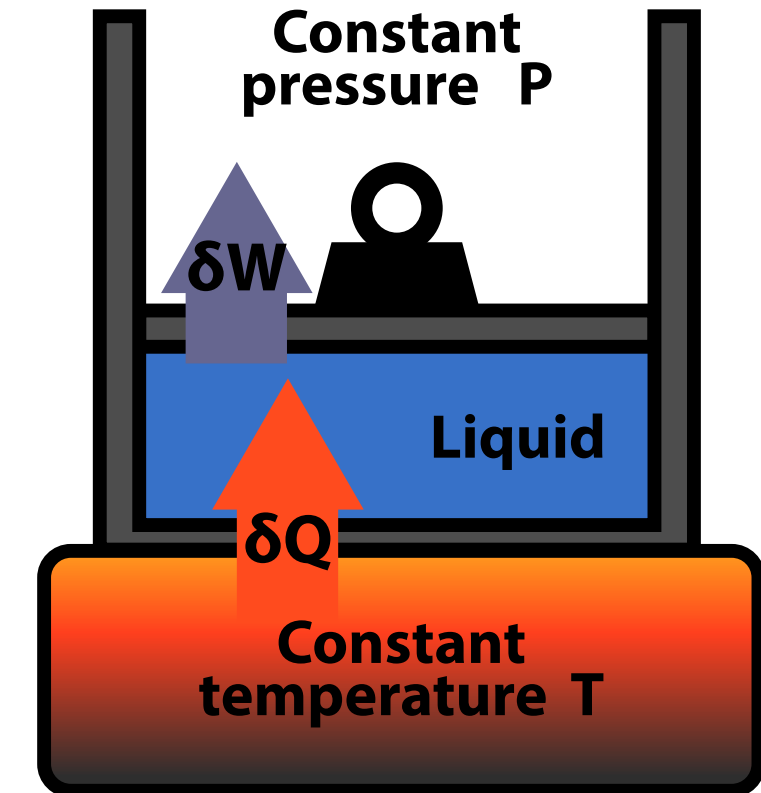
It is equal to the difference of internal energy between vapor and liquid, plus the work done against the external pressure.

We consider a liquid held at constant T and P while being supplied heat. Gibbs equation (with no mass transfer):

$$T ds = du + P dv = dh - v dP$$

Integrating until the end of transition (with T and P constant):

$$T \int_1^2 ds = \int_1^2 dh \Rightarrow T \Delta s = \Delta h_{\text{vap}} \quad \text{or} \quad T \Delta S = \Delta H_{\text{vap}}$$

Enthalpy of vaporization

The enthalpy of vaporization, (or latent heat of vaporization), is the amount of energy that must be added to a liquid substance to transform it into a gas while keeping the pressure constant.
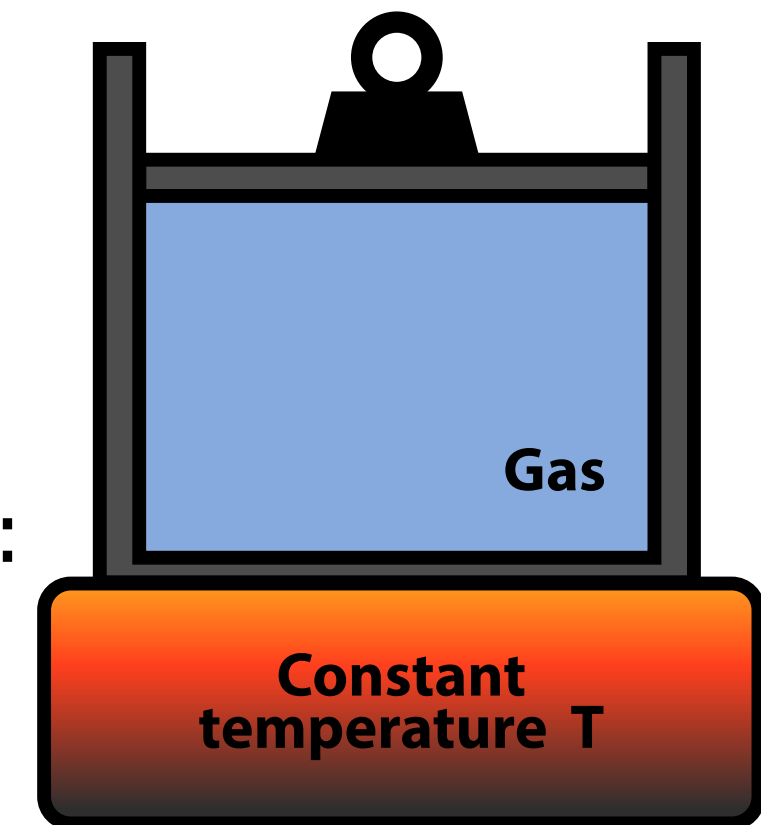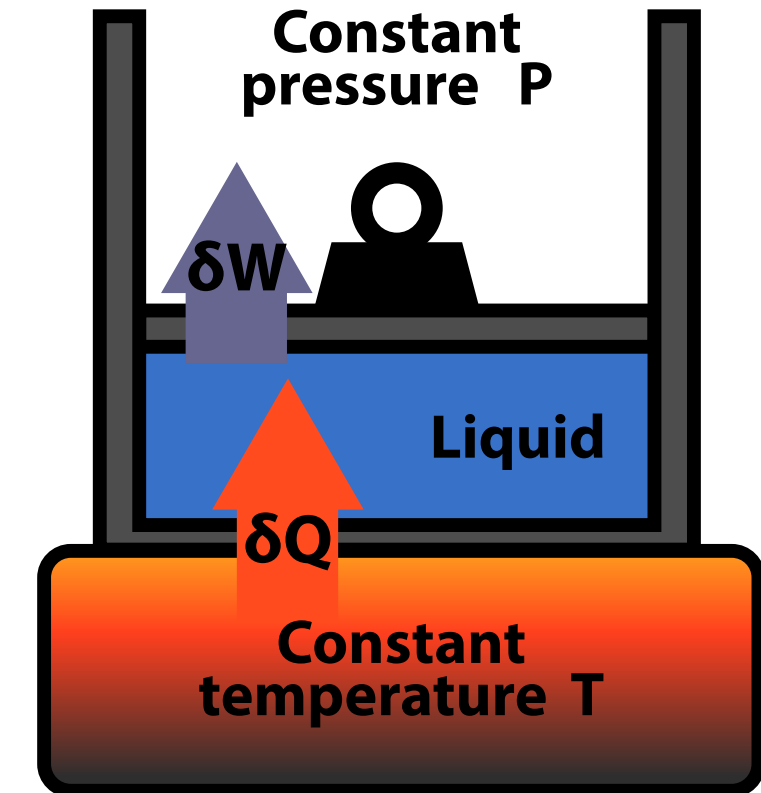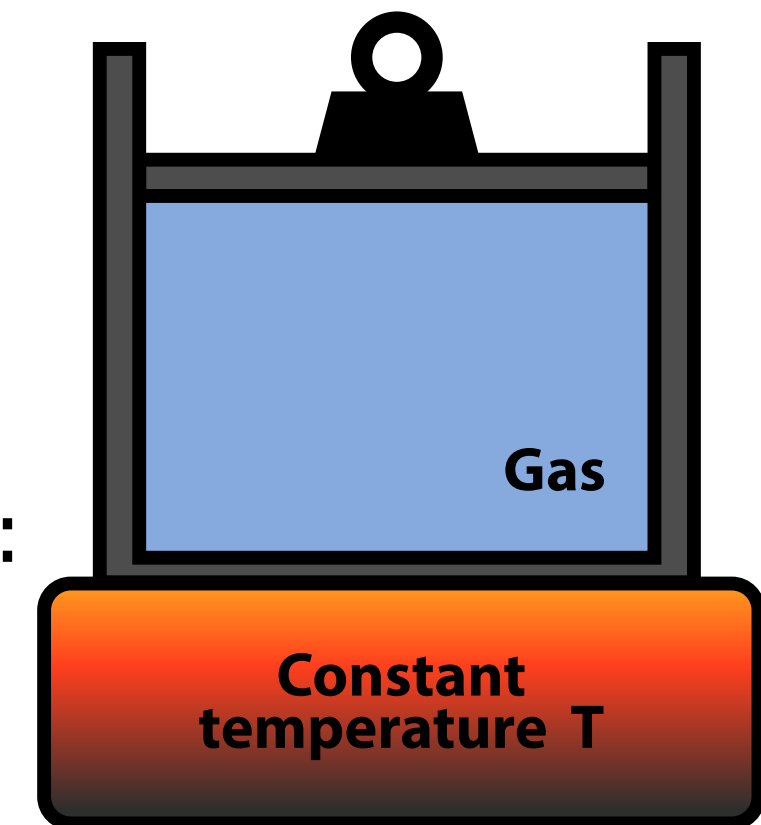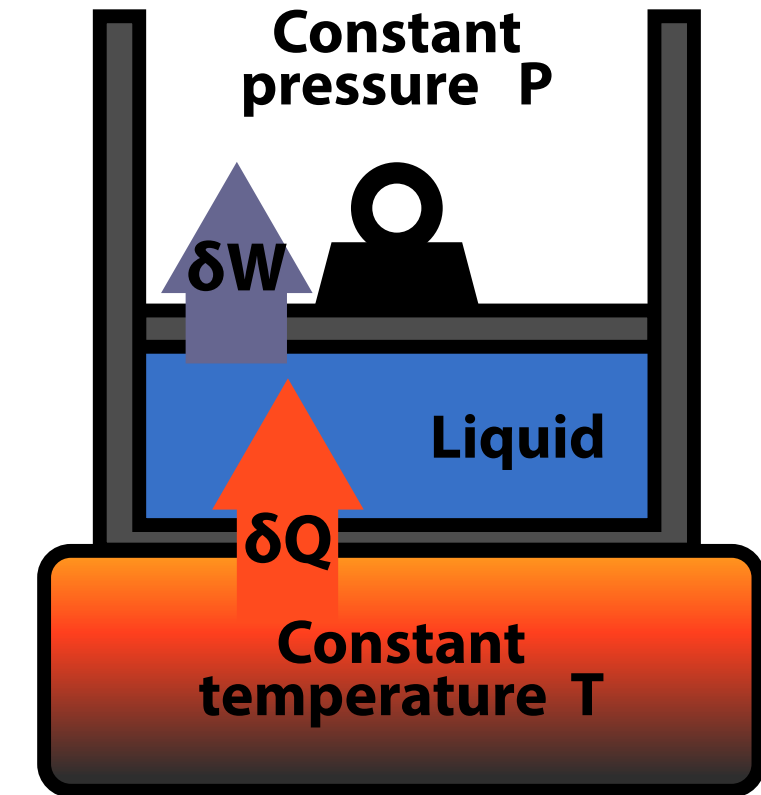
It is equal to the difference of internal energy between vapor and liquid, plus the work done against the external pressure.

We consider a liquid held at constant T and P while being supplied heat. Gibbs equation (with no mass transfer):

$$Tds = du + Pdv = dh - vdP$$

Integrating until the end of transition (with T and P constant):

$$T\int_1^2 ds = \int_1^2 dh \Rightarrow T\Delta s = \Delta h_{\mathrm{vap}} \quad \text{or} \quad T\Delta S = \Delta H_{\mathrm{vap}} \Rightarrow \boxed{Q = \Delta H_{\mathrm{vap}}}$$

Constant pressure P

δW

Liquid

δQ

Constant temperature T

Gas

Constant temperature T

It can be shown that the variation of Gibbs energy is given by:

$$dG = g\,dm + V\,dP - S\,dT$$

Remembering *G = mg*, we can also express it as: $dG = m\,dg + g\,dm$

Gibbs-Duhem equation - variation of chemical potential

It can be shown that the variation of Gibbs energy is given by:

$$dG = g\,dm + V\,dP - S\,dT$$

Remembering *G = mg*, we can also express it as: $dG = m\,dg + g\,dm$

The variation of specific Gibbs energy is thus given by:

$$dg = v\,dP - S\,dT$$

known as the Gibbs–Duhem equation, used to calculate how the chemical potential *g* changes with pressure and temperature.

Clausius-Clapyeron equation

We consider a container filled with liquid A and gas B of the same substance, coexisting at thermodynamic equilibrium, $T_A = T_B = T$, $P_A = P_B = P$, and $g_A = g_B$.
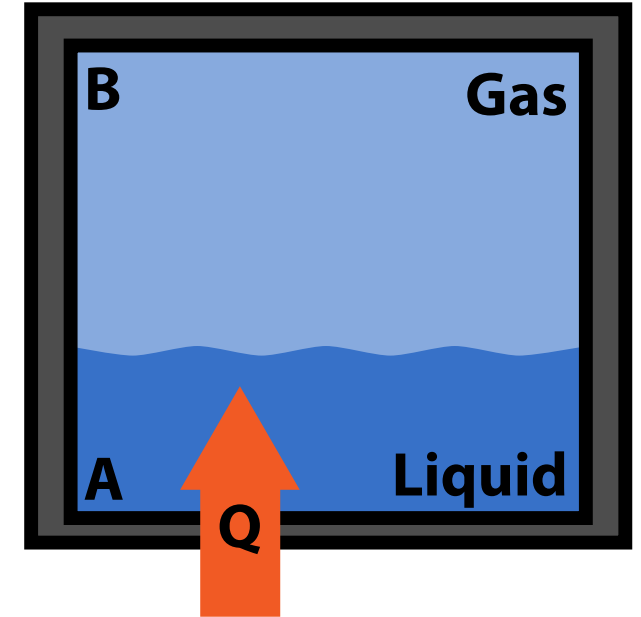
Clausius-Clapyeron equation

We consider a container filled with liquid A and gas B of the same substance, coexisting at thermodynamic equilibrium, $T_A = T_B = T$, $P_A = P_B = P$, and $g_A = g_B$.

Heat is slowly supplied to the system while the two phases remain at equilibrium. As T and P increase, some liquid vaporizes into gas.
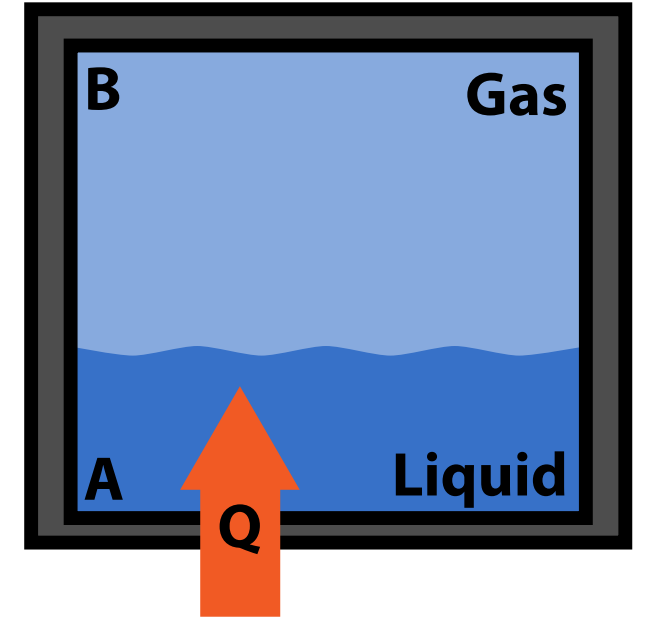
Clausius-Clapyeron equation

We consider a container filled with liquid A and gas B of the same substance, coexisting at thermodynamic equilibrium, $T_A = T_B = T$, $P_A = P_B = P$, and $g_A = g_B$.

Heat is slowly supplied to the system while the two phases remain at equilibrium. As T and P increase, some liquid vaporizes into gas.

Since the system remains at equilibrium, $g_A + dg_A = g_B + dg_B$: the variation of chemical potential is the same for the two phases, $dg_A = dg_B$.
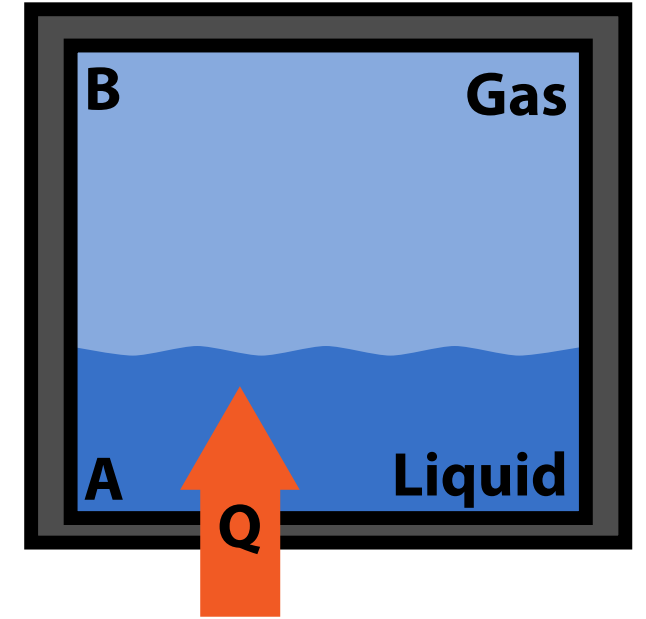
Clausius-Clapyeron equation

We consider a container filled with liquid A and gas B of the same substance, coexisting at thermodynamic equilibrium, $T_A = T_B = T$, $P_A = P_B = P$, and $g_A = g_B$.

Heat is slowly supplied to the system while the two phases remain at equilibrium. As T and P increase, some liquid vaporizes into gas.
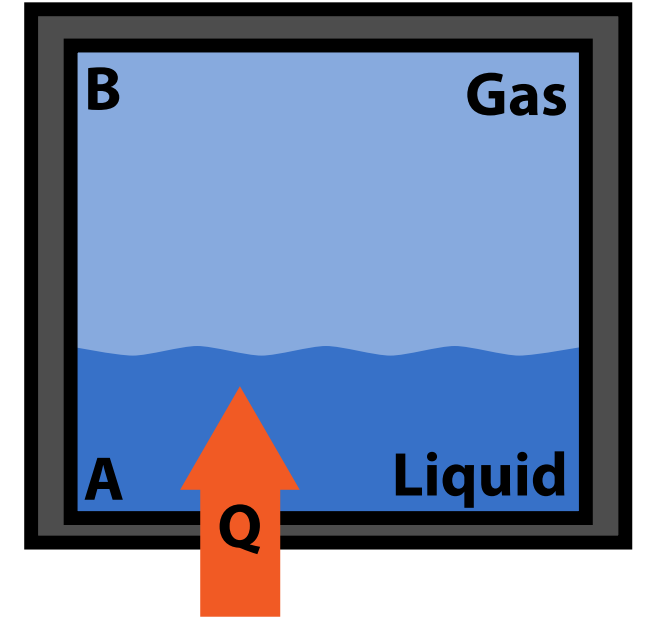
Since the system remains at equilibrium, $g_A + dg_A = g_B + dg_B$: the variation of chemical potential is the same for the two phases, $dg_A = dg_B$. Applying Gibbs–Duhem equation we have:

$$v_A dP - s_A dT = v_B dP - s_B dT$$

Clausius-Clapyeron equation

We consider a container filled with liquid A and gas B of the same substance, coexisting at thermodynamic equilibrium, $T_A = T_B = T$, $P_A = P_B = P$, and $g_A = g_B$.

Heat is slowly supplied to the system while the two phases remain at equilibrium. As T and P increase, some liquid vaporizes into gas.
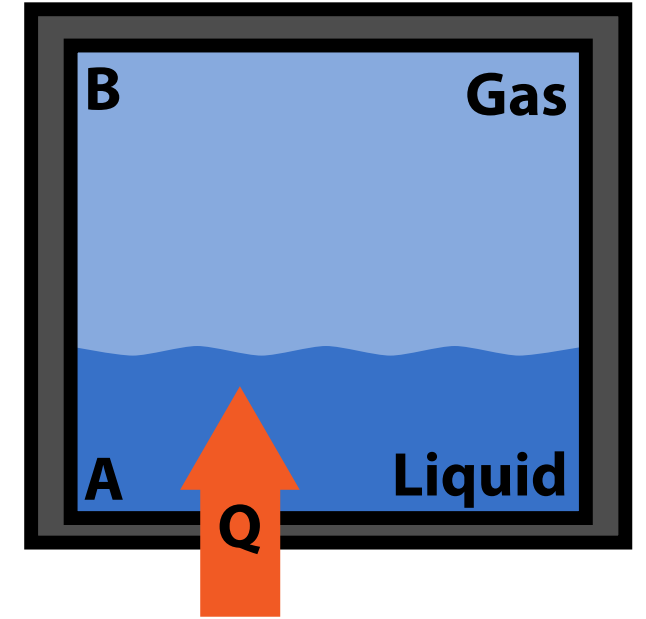
Since the system remains at equilibrium, $g_A + dg_A = g_B + dg_B$: the variation of chemical potential is the same for the two phases, $dg_A = dg_B$.
Applying Gibbs–Duhem equation we have:

$$v_A dP - s_A dT = v_B dP - s_B dT$$

Rearranging:

$$\frac{dP}{dT} = \frac{s_B - s_A}{v_B - v_A}$$

Clausius-Clapyeron equation

We consider a container filled with liquid A and gas B of the same substance, coexisting at thermodynamic equilibrium, $T_A = T_B = T$, $P_A = P_B = P$, and $g_A = g_B$.

Heat is slowly supplied to the system while the two phases remain at equilibrium. As T and P increase, some liquid vaporizes into gas.

Since the system remains at equilibrium, $g_A + dg_A = g_B + dg_B$: the variation of chemical potential is the same for the two phases, $dg_A = dg_B$.
Applying Gibbs–Duhem equation we have:
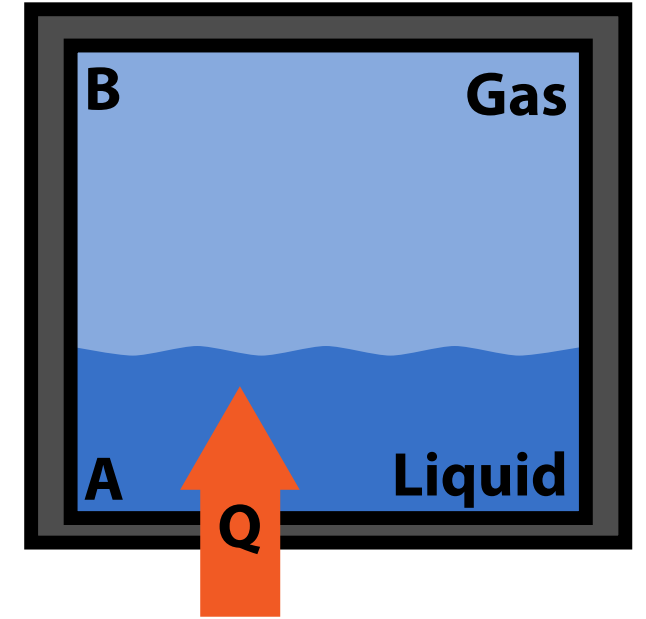
$$v_A dP - s_A dT = v_B dP - s_B dT$$

Rearranging, then using $T\Delta s = \Delta h_{\mathrm{vap}}$:

$$\frac{dP}{dT} = \frac{s_B - s_A}{v_B - v_A} = \frac{\Delta h_{\mathrm{vap}}}{T(v_B - v_A)}$$ **Clapyeron equation**

Clausius-Clapyeron equation

We consider a container filled with liquid A and gas B of the same substance, coexisting at thermodynamic equilibrium, $T_A = T_B = T$, $P_A = P_B = P$, and $g_A = g_B$.

Heat is slowly supplied to the system while the two phases remain at equilibrium. As T and P increase, some liquid vaporizes into gas.

Since the system remains at equilibrium, $g_A + dg_A = g_B + dg_B$: the variation of chemical potential is the same for the two phases, $dg_A = dg_B$. Applying Gibbs–Duhem equation we have:
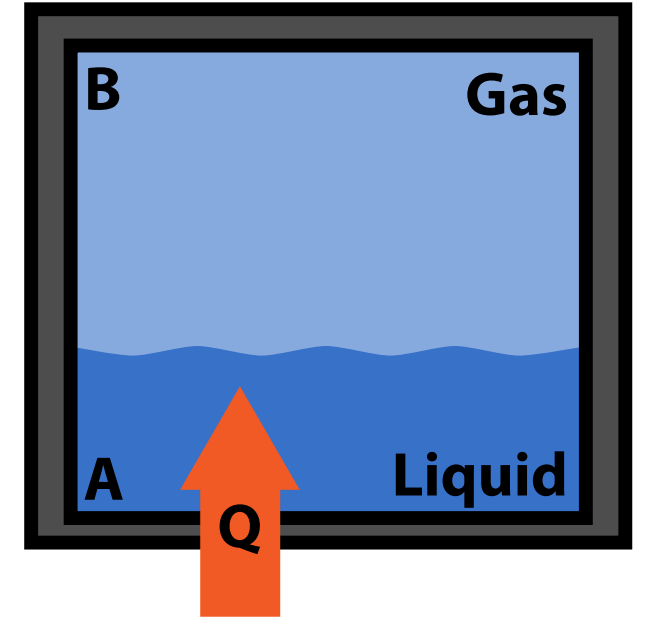
$$v_A dP - s_A dT = v_B dP - s_B dT$$

Rearranging, then using $T\Delta s = \Delta h_{\mathrm{vap}}$:

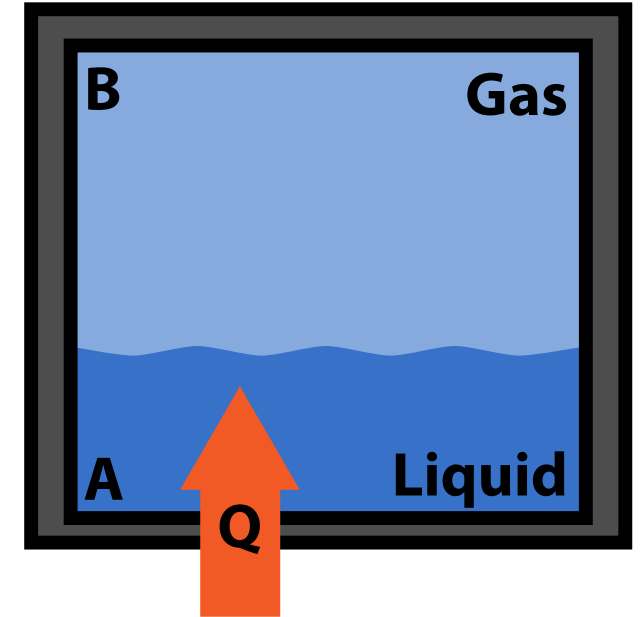$$\frac{dP}{dT} = \frac{s_B - s_A}{v_B - v_A} = \frac{\Delta h_{\mathrm{vap}}}{T(v_B - v_A)}$$ **Clapyeron equation**

With $v_A \approx 0$ and $v_B = RT/P$

$$\frac{dP}{dT} = \frac{\Delta h_{\mathrm{vap}} P}{RT^2}$$ **Clausius-Clapyeron equation**

Clausius-Clapyeron equation

We can visualize the process on the *P-T* phase diagram.
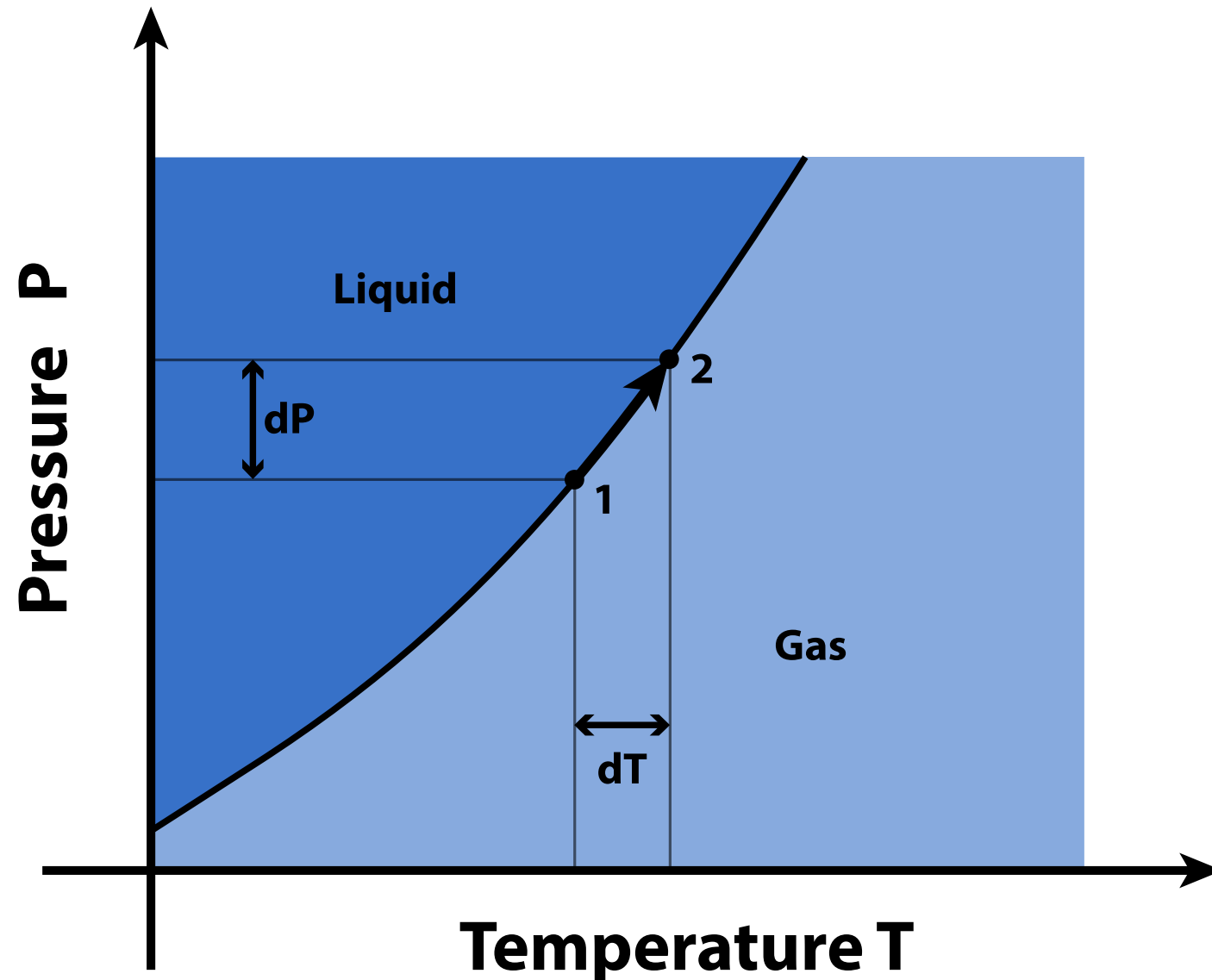
$$\frac{dP}{dT} = \frac{\Delta h_{\mathrm{vap}} P}{RT^2}$$ **Clausius-Clapyeron equation**

Clausius-Clapyeron equation

We can visualize the process on the *P-T* phase diagram. Integrating the Clausius-Clapyeron equation:

$$\int_1^2 \frac{dP}{P} = \int_1^2 \frac{\Delta h_{\text{vap}}}{RT^2}\, dT$$

$$\frac{dP}{dT} = \frac{\Delta h_{\text{vap}} P}{RT^2}$$

Clausius-Clapyeron equation

Clausius-Clapyeron equation

We can visualize the process on the *P-T* phase diagram.
Integrating the Clausius-Clapyeron equation:

$$\int_1^2 \frac{dP}{P} = \int_1^2 \frac{\Delta h_{\text{vap}}}{RT^2}\, dT \;\Rightarrow\; \log\left(P\right) = -\frac{\Delta h_{\text{vap}}}{RT} + C$$
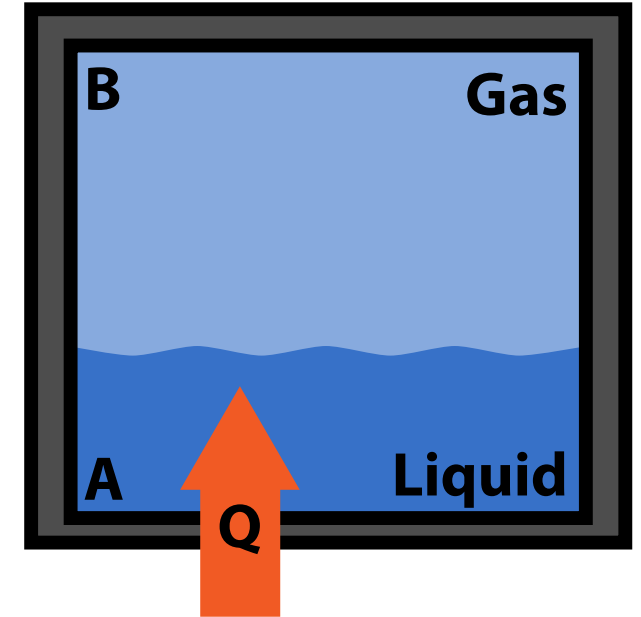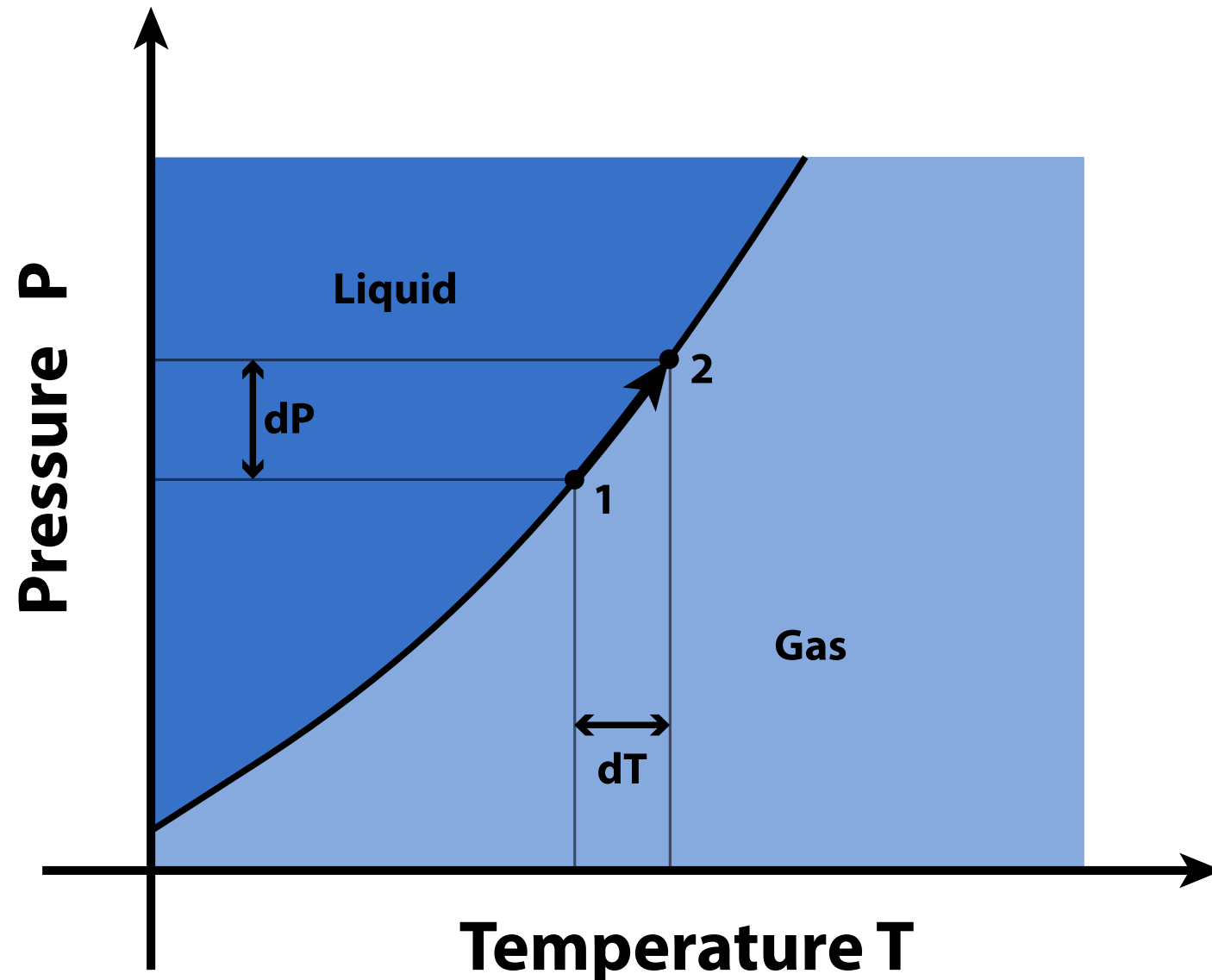

$$\frac{dP}{dT} = \frac{\Delta h_{\text{vap}} P}{RT^2}$$ **Clausius-Clapyeron equation**

Clausius-Clapyeron equation

We can visualize the process on the *P-T* phase diagram.
Integrating the Clausius-Clapyeron equation:

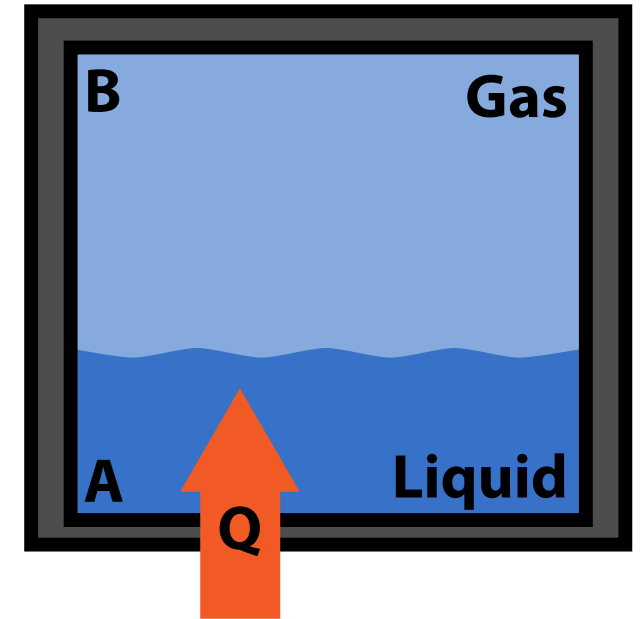$$\int_1^2 \frac{dP}{P} = \int_1^2 \frac{\Delta h_{\mathrm{vap}}}{RT^2}\, dT \;\Rightarrow\; \log\left(P\right) = -\frac{\Delta h_{\mathrm{vap}}}{RT} + C$$

$$\Rightarrow\quad P_{\mathrm{sat}} = C \exp\left(-\frac{\Delta h_{\mathrm{vap}}}{RT_{\mathrm{sat}}}\right)$$

$$\frac{dP}{dT} = \frac{\Delta h_{\mathrm{vap}} P}{RT^2}$$

Clausius-Clapyeron equation

Clausius-Clapeyron equation

We can visualize the process on the *P-T* phase diagram.
Integrating the Clausius-Clapeyron equation:

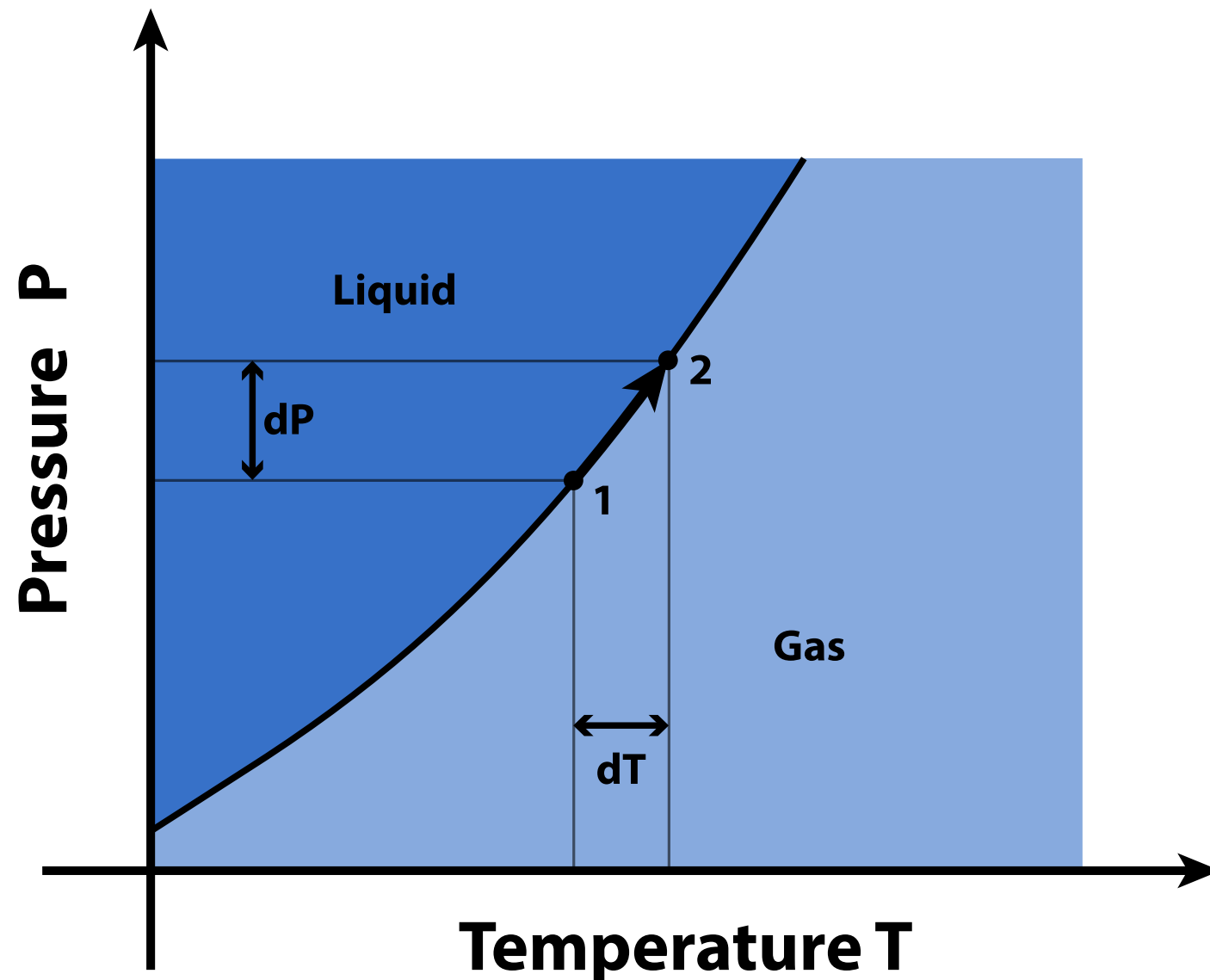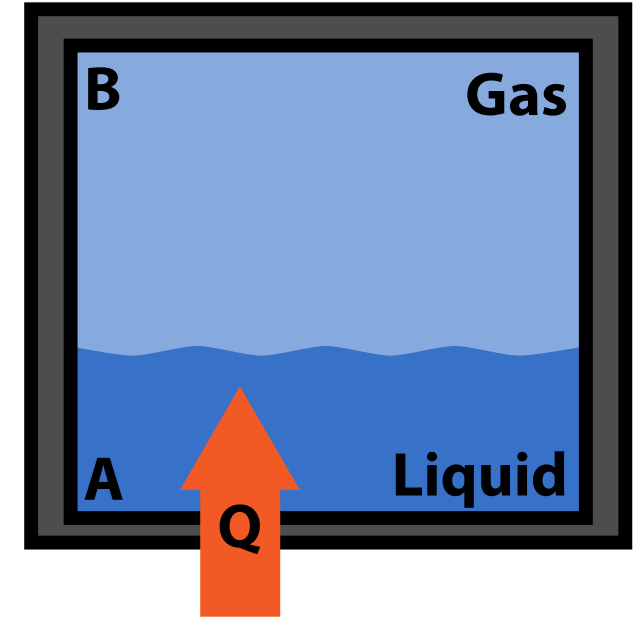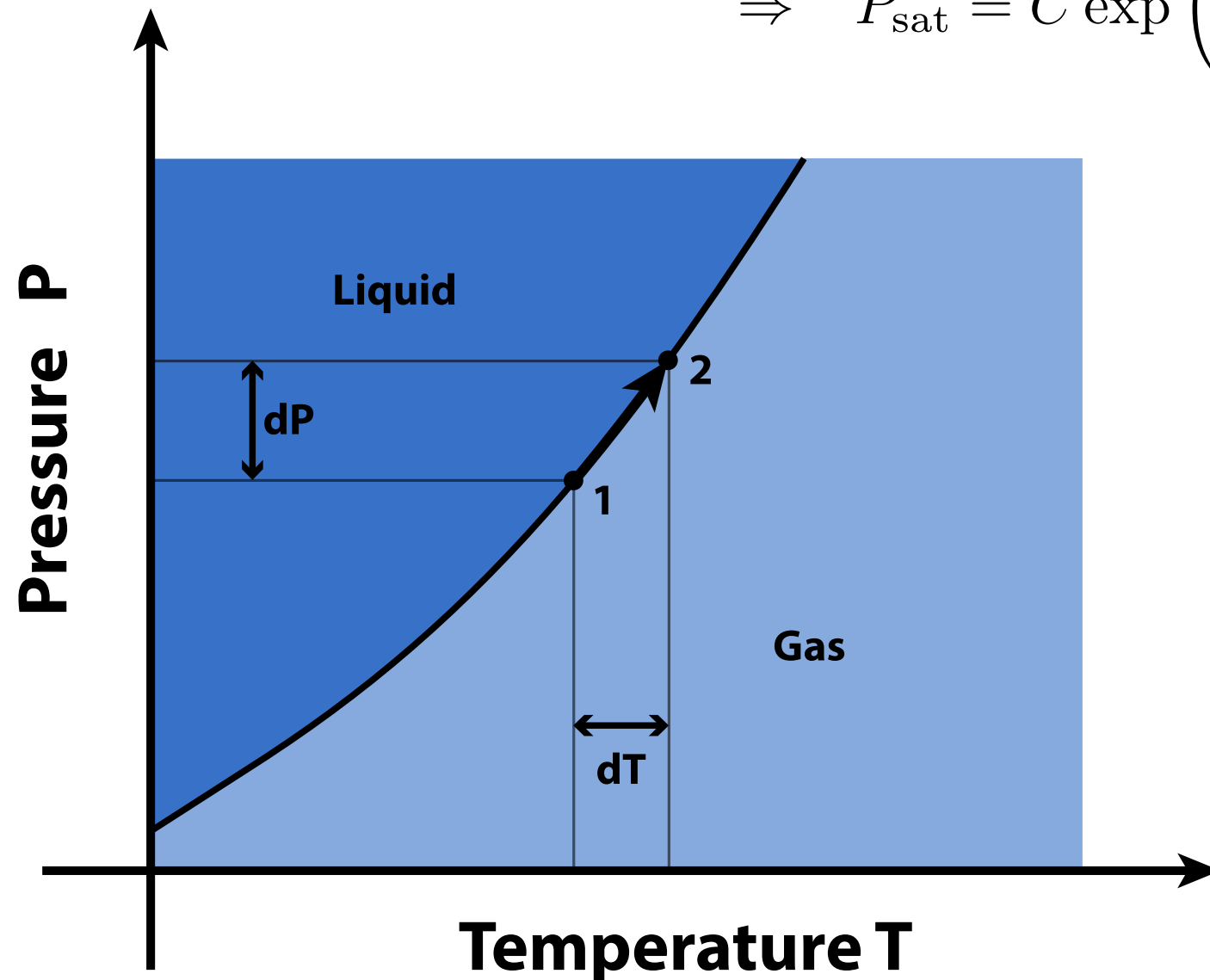$$\int_1^2 \frac{dP}{P} = \int_1^2 \frac{\Delta h_{\text{vap}}}{RT^2}\, dT \;\Rightarrow\; \log(P) = -\frac{\Delta h_{\text{vap}}}{RT} + C$$

$$\Rightarrow\quad P_{\text{sat}} = C \exp\left(-\frac{\Delta h_{\text{vap}}}{RT_{\text{sat}}}\right)$$
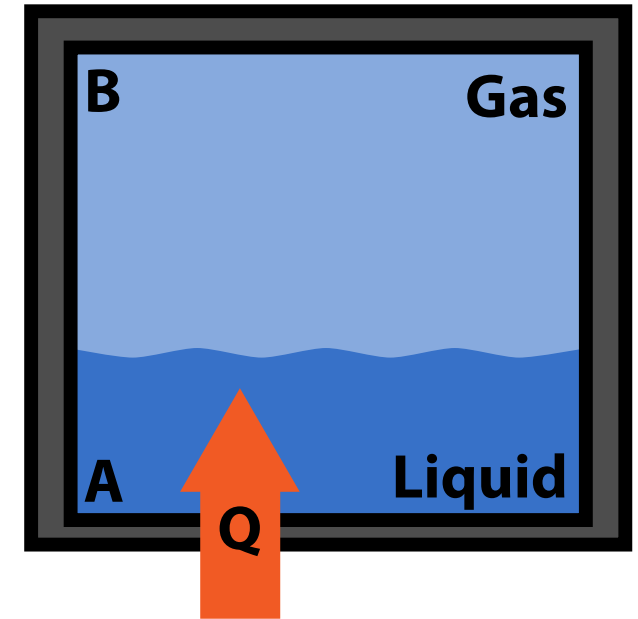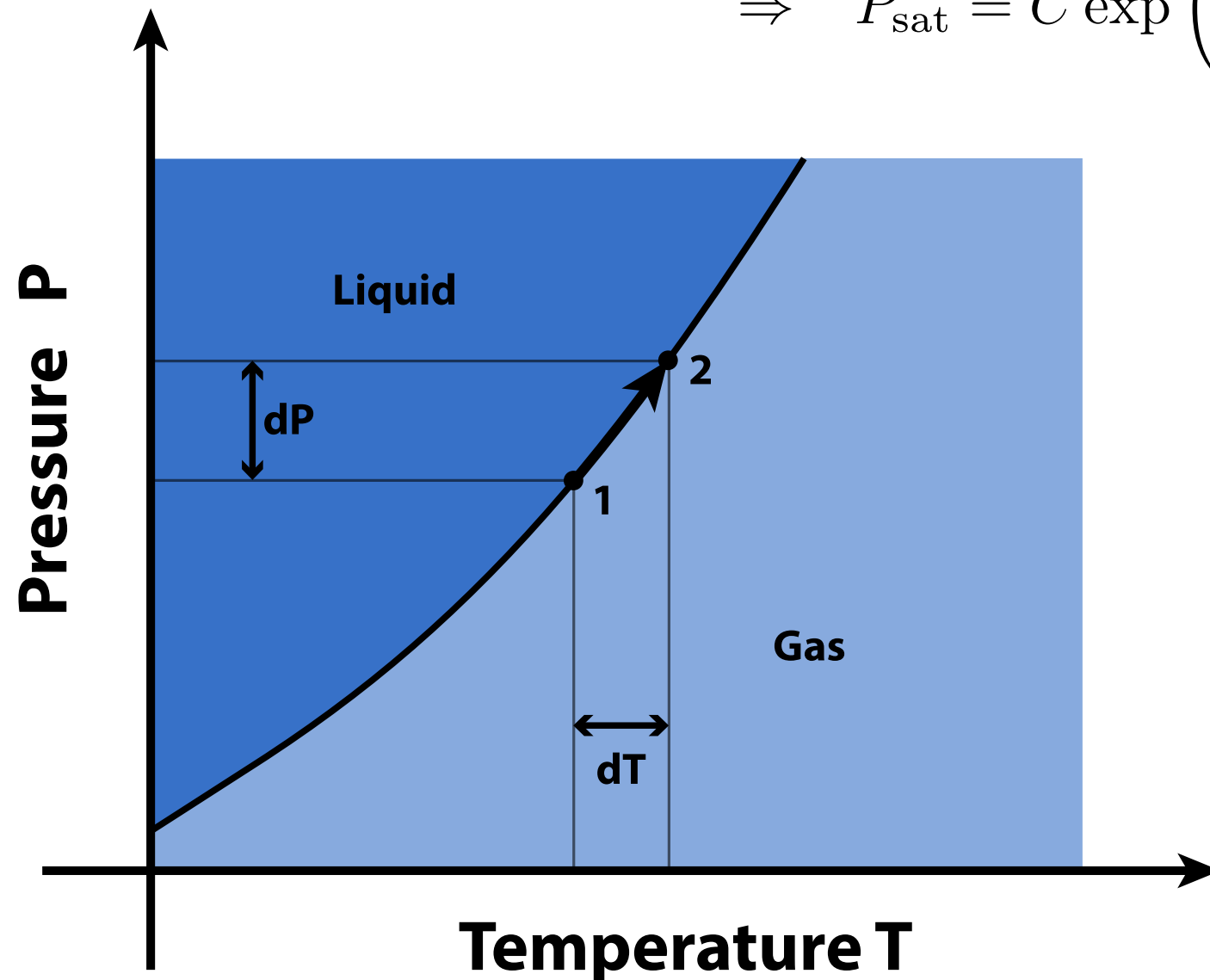
Where the properties (*P* and *T*)
at the phase equilibrium are known as
- Saturation pressure P_{sat}
- Saturation temperature T_{sat}

$$\frac{dP}{dT} = \frac{\Delta h_{\text{vap}} P}{RT^2}$$

Clausius-Clapeyron equation

Example 7.1

The saturation pressure of water at $T_1 = 100\ °C$ is $P_1 = 101.35\ kPa$. What is the saturation pressure at $T_2 = 105\ °C$? Assume the latent heat of vaporisation $\Delta h_{vap} = 2257.06\ kJ\ /\ kgK$.

Example 7.1

The saturation pressure of water at $T_1 = 100$ °C is $P_1 = 101.35$ kPa. What is the saturation pressure at $T_2 = 105$ °C? Assume the latent heat of vaporisation $\Delta h_{vap} = 2257.06$ kJ / kgK.

We use the relation $P_{\text{sat}} = C \exp \left(-\dfrac{\Delta h_{\text{vap}}}{RT_{\text{sat}}} \right)$ to calculate C from T_1 and P_1.

$$C = P_1 / \exp \left(-\frac{\Delta h_{\text{vap}}}{RT_1} \right) = 4.98510 \times 10^7 \text{ kPa}$$

Example 7.1

The saturation pressure of water at $T_1 = 100\ °C$ is $P_1 = 101.35\ kPa$.
What is the saturation pressure at $T_2 = 105\ °C$? Assume the latent heat of vaporisation $\Delta h_{vap} = 2257.06\ kJ\ /\ kgK$.

We use the relation $P_{\text{sat}} = C \exp\left(-\dfrac{\Delta h_{\text{vap}}}{RT_{\text{sat}}}\right)$ to calculate C from T_1 and P_1.

$$C = P_1 / \exp\left(-\frac{\Delta h_{\text{vap}}}{RT_1}\right) = 4.98510 \times 10^7\ \text{kPa}$$

Then we plug T_2 the same relation to obtain P_2.

$$P_2 = C \exp\left(-\frac{\Delta h_{\text{vap}}}{RT_2}\right) = 120.527\ \text{kPa}$$

Liquid-Solid and Gas-Solid Equilibria

The previous derivation remains valid for gas-solid phase transitions.
For liquid-solid transitions, we must use Clapyeron equation.
Below, the specific enthalpy for the generic transition is denoted by Δh_{tr}
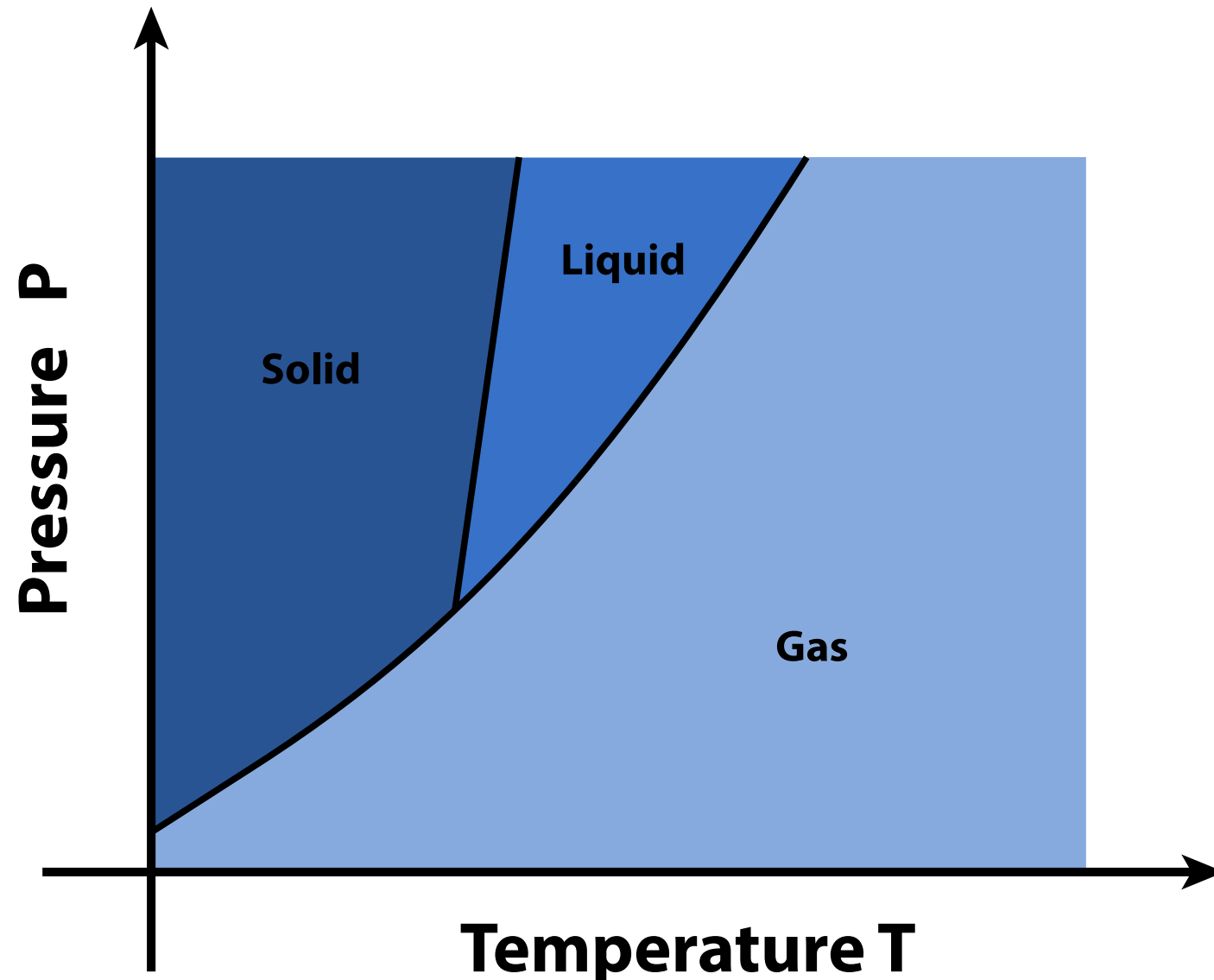
$$\frac{dP}{dT} = \frac{\Delta h_{\mathrm{tr}}}{T(v_B - v_A)}$$ **Clapyeron equation**

$$\frac{dP}{dT} = \frac{\Delta h_{\mathrm{tr}}\, P}{RT^2}$$ **Clausius-Clapyeron equation**

Liquid-Solid and Gas-Solid Equilibria

The previous derivation remains valid for gas-solid phase transitions.
For liquid-solid transitions, we must use Clapyeron equation.
Below, the specific enthalpy for the generic transition is denoted by Δh_{tr}

In most cases the solid has a lower specific volume than that of the liquid. The slope $\dfrac{dP}{dT}$ of the phase equilibrium curve is thus > 0

$$\frac{dP}{dT} = \frac{\Delta h_{\text{tr}}}{T(v_B - v_A)} \qquad \textbf{Clapyeron equation}$$

$$\frac{dP}{dT} = \frac{\Delta h_{\text{tr}}\, P}{RT^2} \qquad \textbf{Clausius-Clapeyron equation}$$

Liquid-Solid and Gas-Solid Equilibria

The previous derivation remains valid for gas-solid phase transitions.
For liquid-solid transitions, we must use Clapyeron equation.
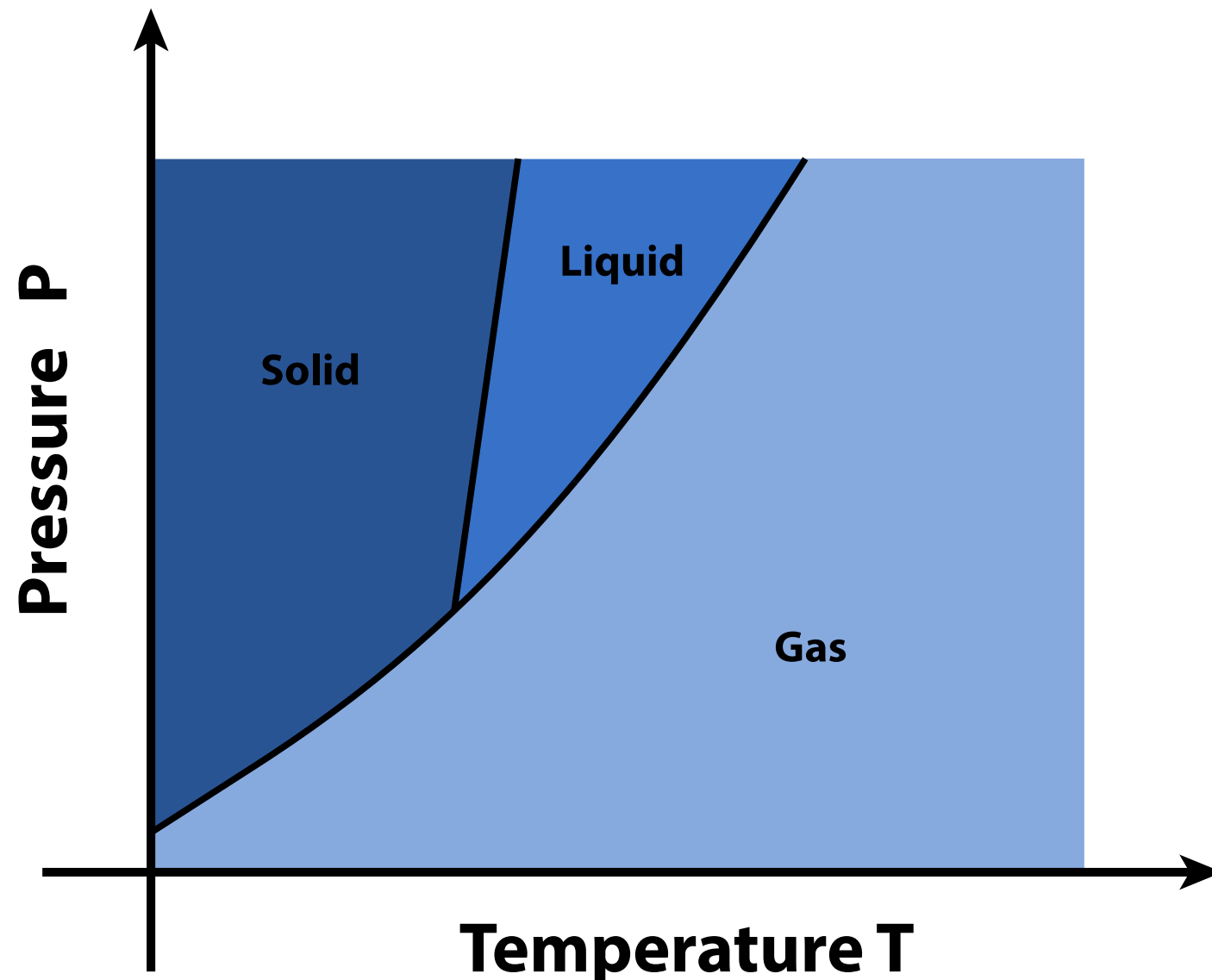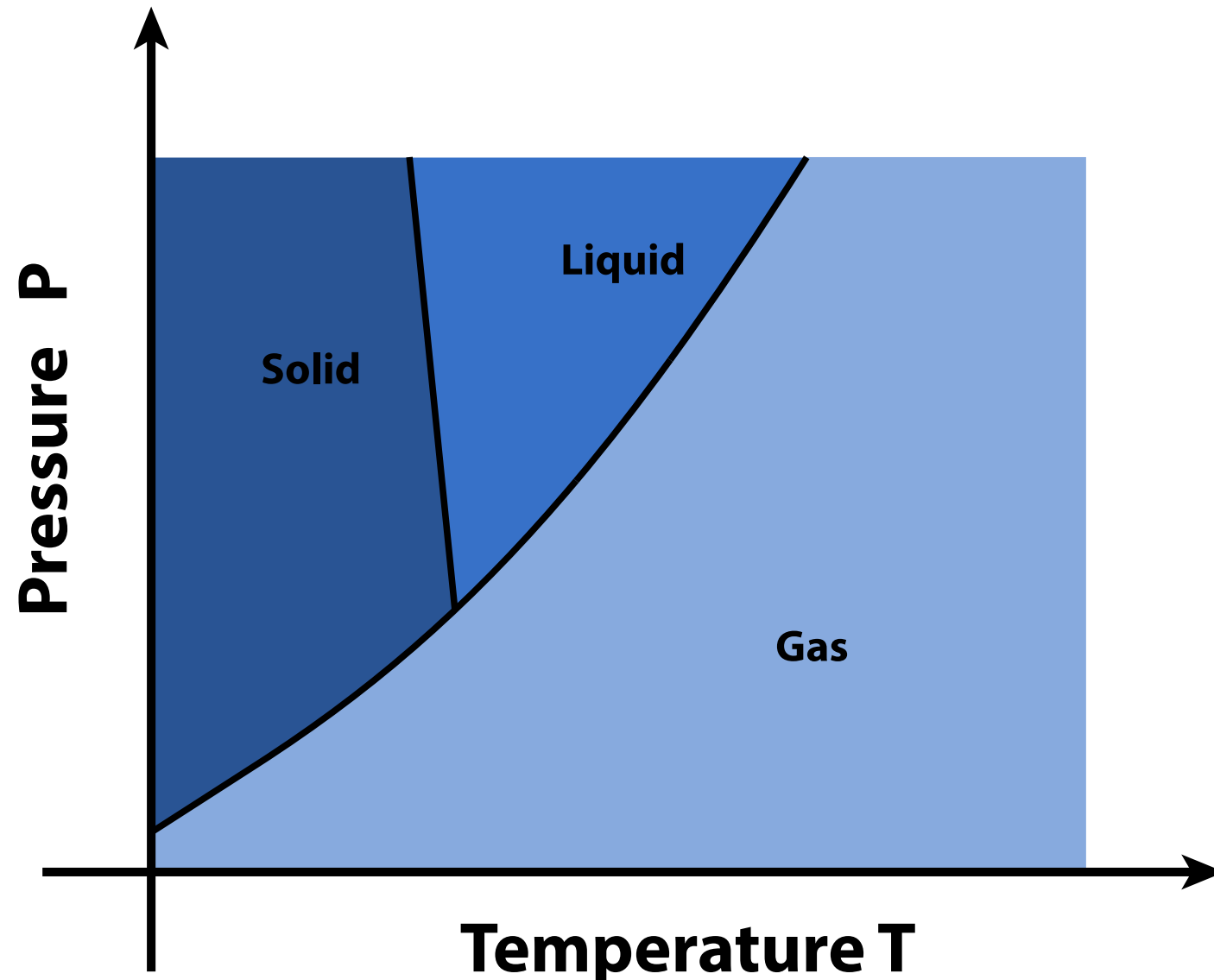Below, the specific enthalpy for the generic transition is denoted by Δh_{tr}

In most cases the solid has a lower specific volume than that of the liquid. The slope $\dfrac{dP}{dT}$ of the phase equilibrium curve is thus > 0

Otherwise the slope is < 0 (e.g. water)

$$\frac{dP}{dT} = \frac{\Delta h_{\mathrm{tr}}}{T(v_B - v_A)}$$ **Clapyeron equation**

$$\frac{dP}{dT} = \frac{\Delta h_{\mathrm{tr}}\, P}{RT^2}$$ **Clausius-Clapeyron equation**

Phase Change on P-v and T-v Diagrams

The region of coexistence of vapour and liquid is known as *vapour dome*.
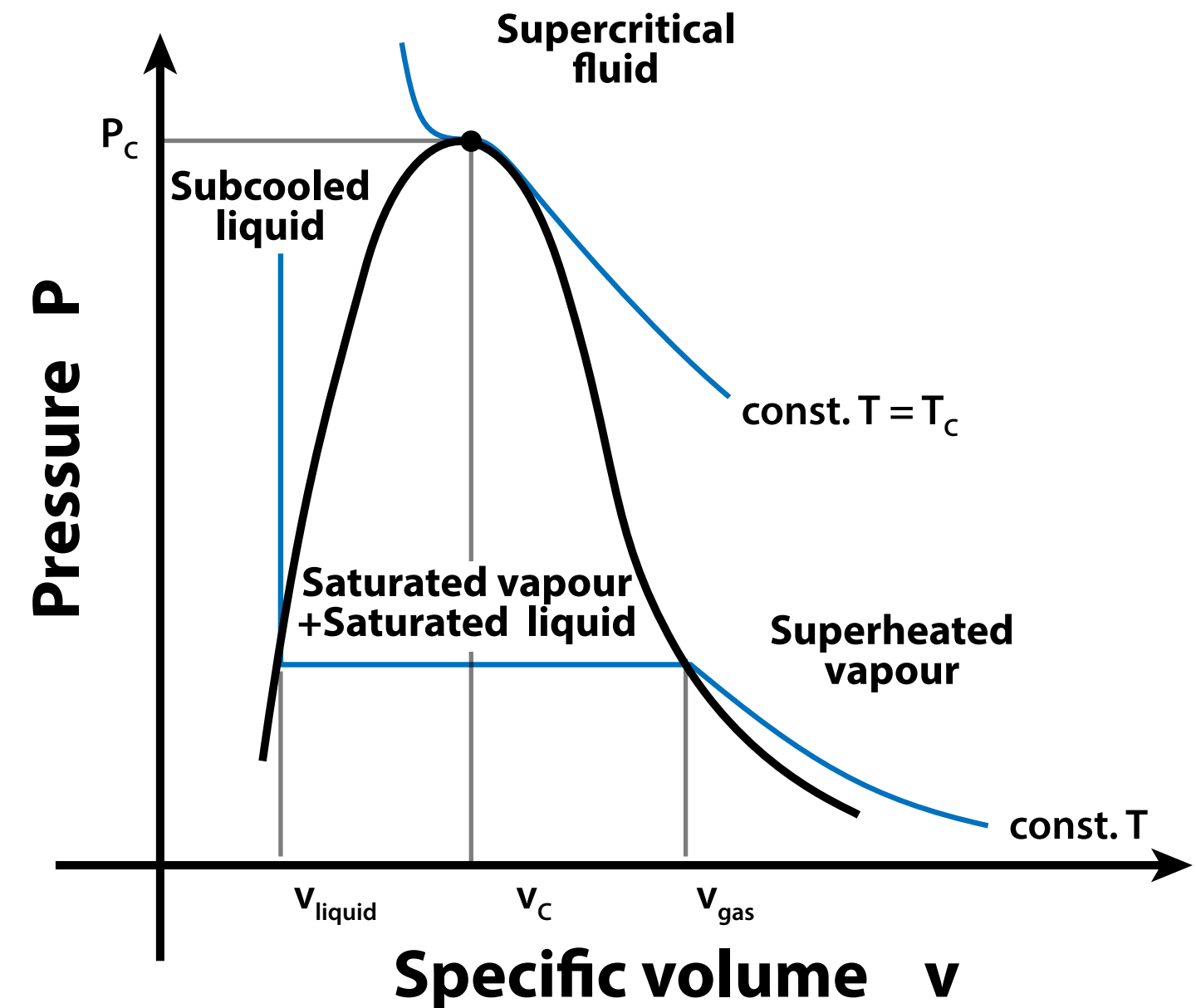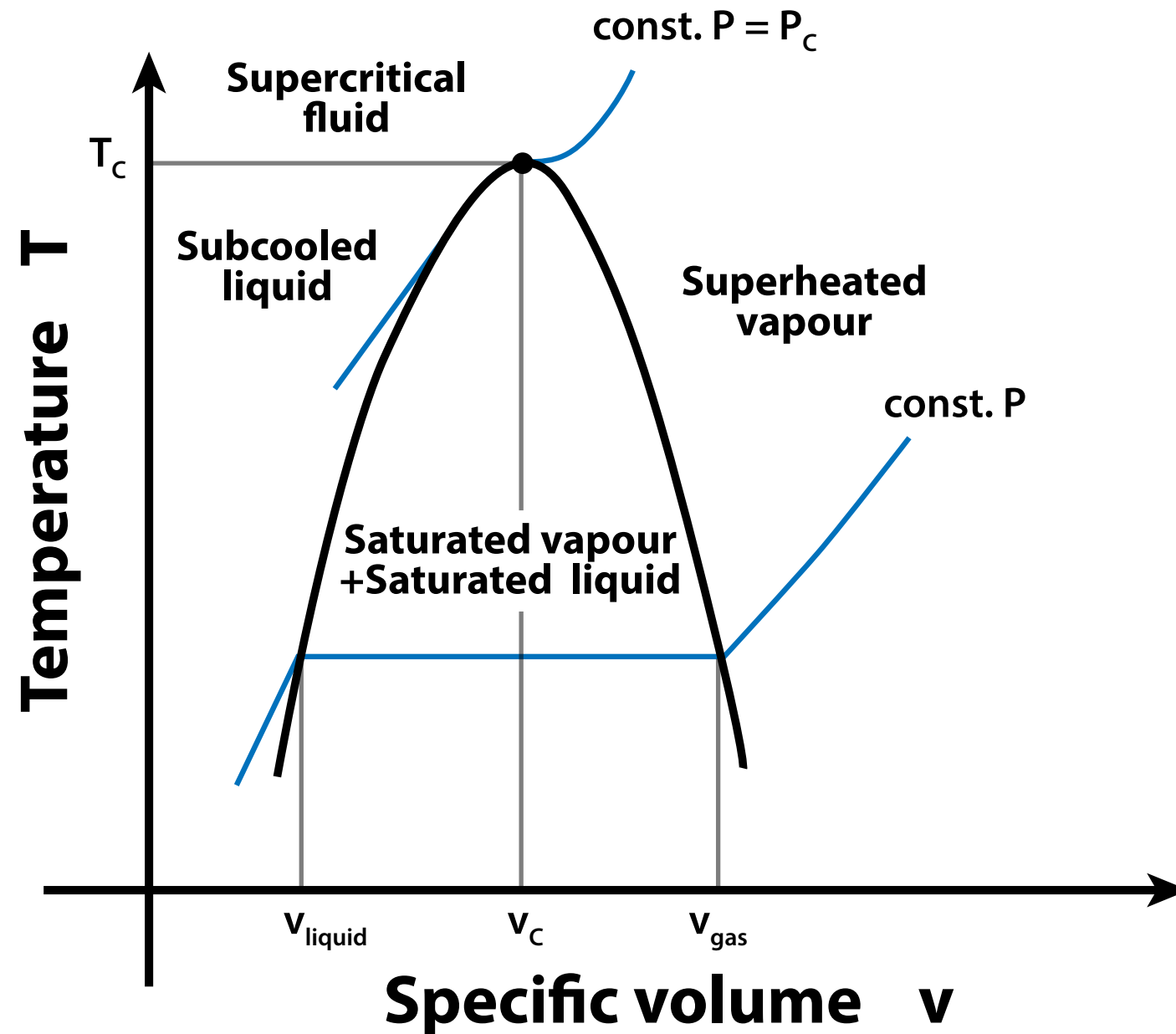
Quality of a mixture

The quality of a mixture of vapour and liquid is defined as:

$$x = \frac{m_\text{vapour}}{m_\text{mixture}}$$

Since $m_\text{mixture} = m_\text{vapour} + m_\text{liquid}$, we have:

$$1 - x = \frac{m_\text{liquid}}{m_\text{mixture}}$$

Quality of a mixture

The quality of a mixture of vapour and liquid is defined as:

$$x = \frac{m_{\text{vapour}}}{m_{\text{mixture}}}$$

Since $m_{\text{mixture}} = m_{\text{vapour}} + m_{\text{liquid}}$, we have:

$$1 - x = \frac{m_{\text{liquid}}}{m_{\text{mixture}}}$$

The properties of the mixture are the weighted average of the properties of the individual phases. For example, for the specific volume we have:

$$v_{\text{mixture}} = x v_{\text{vapour}} + (1 - x) v_{\text{liquid}}$$

For the specific internal energy:

$$u_{\text{mixture}} = x u_{\text{vapour}} + (1 - x) u_{\text{liquid}}$$

For the specific entropy:

$$s_{\text{mixture}} = x s_{\text{vapour}} + (1 - x) s_{\text{liquid}}$$

Van der Waals equation

The Van der Waals equation of state generalizes the ideal gas law, and predicts more realistically the behavior of fluids over a wider range of parameters *T* and *V*.

The equation is written as:

$$\left(P + \frac{a}{\overline{v}^2}\right)(\overline{v} - b) = R_u T$$

where $\overline{v} = V/N$ is the specific molar volume, and *a* and *b* are known as Van der Waals constants and are tabulated for different substances.

Van der Waals equation

The Van der Waals equation of state generalizes the ideal gas law, and predicts more realistically the behavior of fluids over a wider range of parameters *T* and *V*.

The equation is written as:

$$\left(P + \frac{a}{\overline{v}^2}\right)(\overline{v} - b) = R_u T$$

where $\overline{v} = V/N$ is the specific molar volume, and *a* and *b* are known as Van der Waals constants and are tabulated for different substances.

Van der Waals equation

The Van der Waals equation of state generalizes the ideal gas law, and predicts more realistically the behavior of fluids over a wider range of parameters *T* and *V*.

The equation is written as:

$$\left(P + \frac{a}{\bar{v}^2}\right)(\bar{v} - b) = R_u T$$

where $\bar{v} = V/N$ is the specific molar volume, and *a* and *b* are known as Van der Waals constants and are tabulated for different substances.

The equation gives the behavior of incompressible fluids at high pressure, as well as the ideal gas behavior at low pressure, and the critical point.

Van der Waals equation

The Van der Waals equation of state generalizes the ideal gas law, and predicts more realistically the behavior of fluids over a wider range of parameters *T* and *V*.

The equation is written as:

$$\left(P + \frac{a}{\bar{v}^2} \right) \left(\bar{v} - b \right) = R_u T$$

where $\bar{v} = V/N$ is the specific molar volume, and *a* and *b* are known as Van der Waals constants and are tabulated for different substances.

The equation gives the behavior of incompressible fluids at high pressure, as well as the ideal gas behavior at low pressure, and the critical point.

However, in the region of the vapour dome, the equation does not predict correctly the experimental observation that during an isothermal process the pressure is constant with respect to the volume.

Van der Waals equation and the critical point

We notice from the P-v diagram that the critical isotherm at the critical point has zero first and second derivative. It is a stationary point that is also an inflection point.
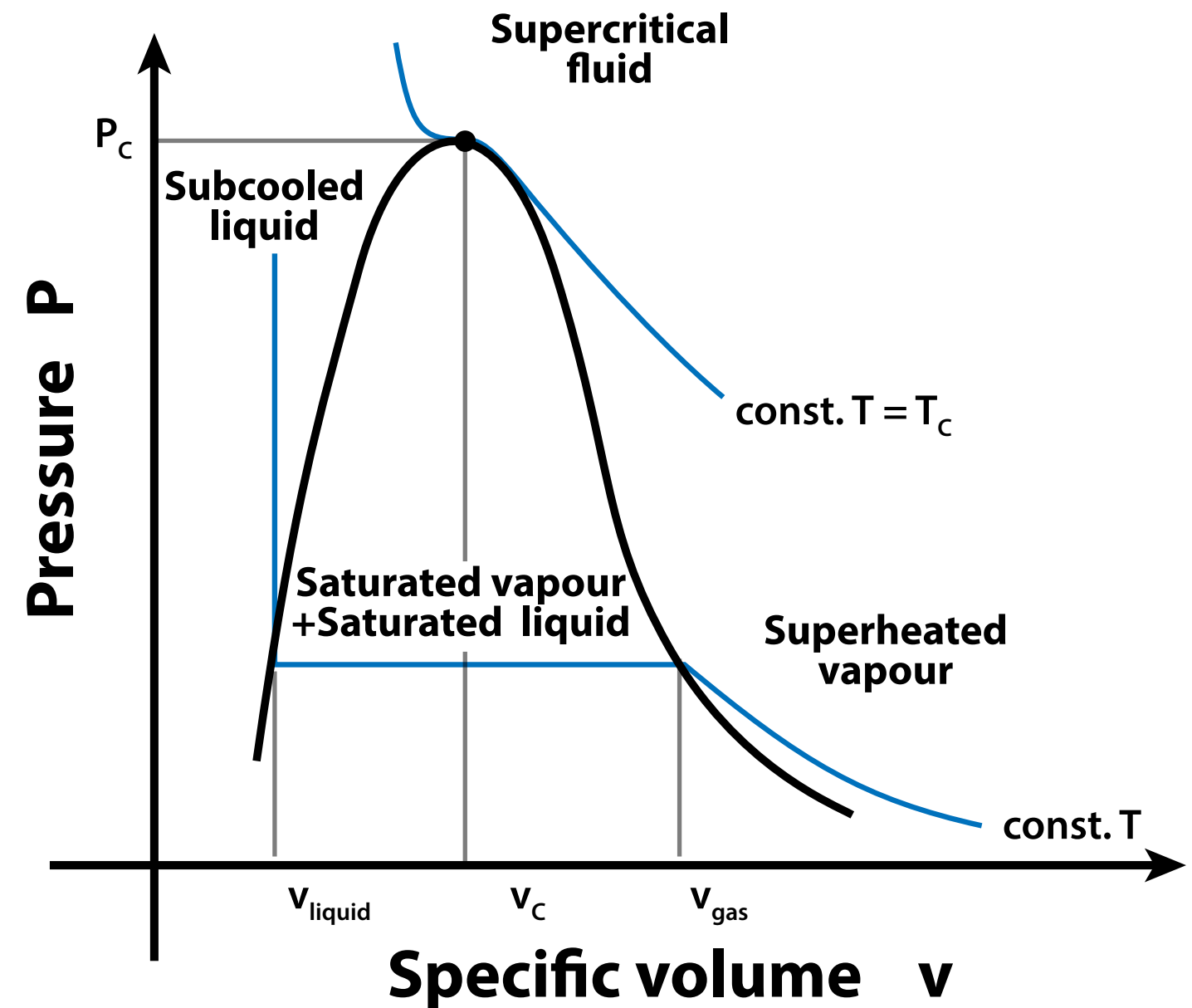
Van der Waals equation and the critical point

We notice from the P-v diagram that the critical isotherm at the critical point has zero first and second derivative. It is a stationary point that is also an inflection point.

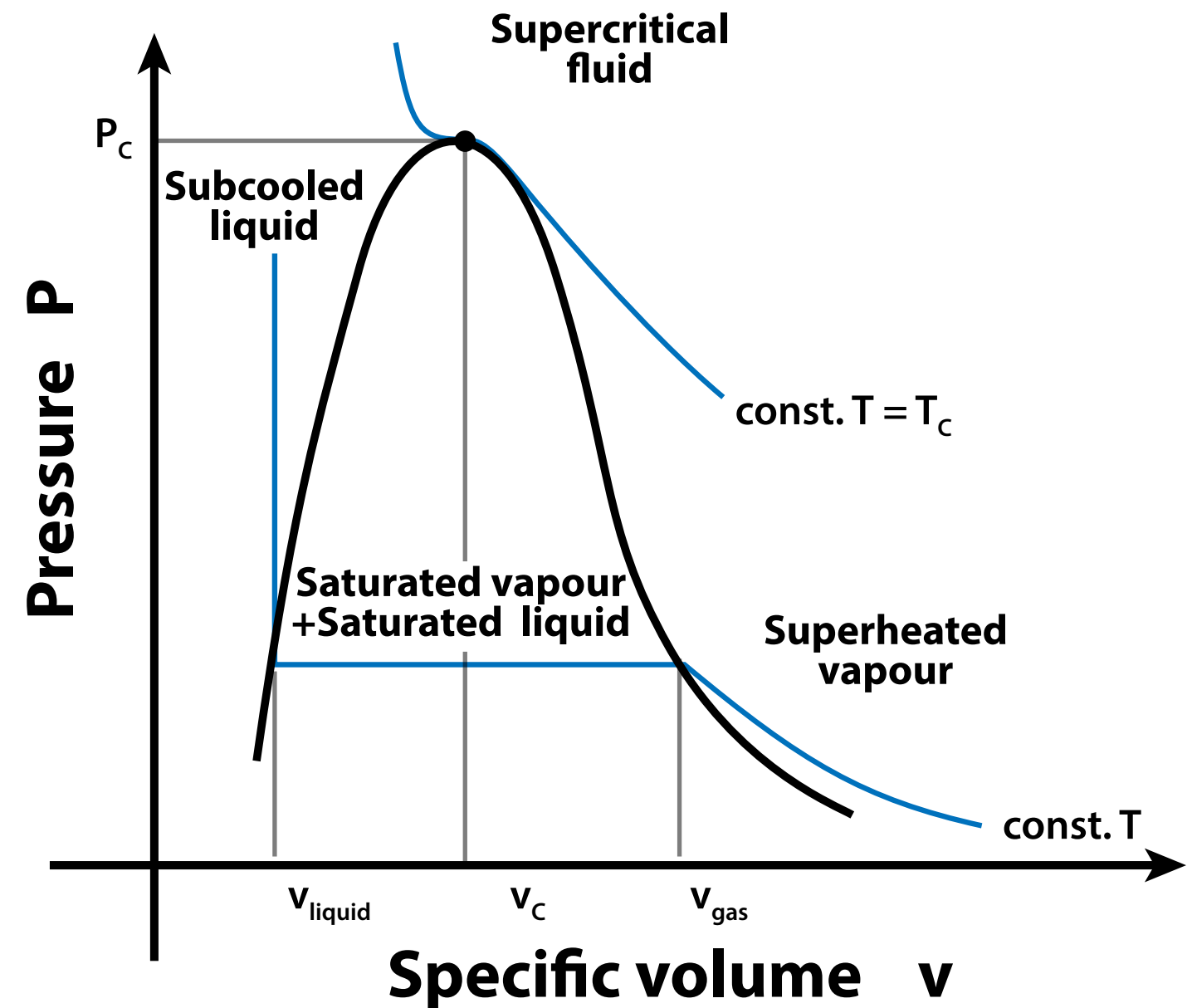Starting from the equation and applying the two additional conditions

$$\left(\frac{\partial P}{\partial \overline{v}}\right)_T = 0 \quad \text{and} \quad \left(\frac{\partial^2 P}{\partial \overline{v}^2}\right)_T = 0$$

at $T = T_c$, $P = P_c$ and $\overline{v} = \overline{v}_c$, we get:

$$a = \frac{27}{64}\frac{R_u T_c^2}{P_c}$$

$$b = \frac{1}{8}\frac{R_u T_c}{P_c}$$

$$\overline{v}_c = \frac{3}{8}\frac{R_u T_c}{P_c}$$

Van der Waals equation and the compressibility factor

We define the reduced pressure $P_r = P/P_c$, the reduced temperature $T_r = T/T_c$, and reduced specific molar volume $\bar{v}_r = \bar{v}/\bar{v}_c$.

Using these definitions and the relations below, we can express the Van der Waals equation as:

$$P_r = \frac{8T_r}{3\bar{v}_r - 1} - \frac{3}{\bar{v}_r^2}$$

This equation is a *universal equation of state*: it is applicable to all gasses. In fact, the compressibility factor, defined as $Z = Pv/(RT)$, has for all gasses the same dependence on P_r and T_r.

$$a = \frac{27}{64}\frac{R_u T_c^2}{P_c}$$

$$b = \frac{1}{8}\frac{R_u T_c}{P_c}$$

$$\bar{v}_c = \frac{3}{8}\frac{R_u T_c}{P_c}$$

Example 7.14

Calculate the specific volume of steam at a temperature *T = 600 °C* and pressure *P = 10 MPa* using the generalised compressibility charts.

Example 7.14

Calculate the specific volume of steam at a temperature $T = 600\ °C$ and pressure $P = 10\ MPa$ using the generalised compressibility charts.

We read from Appendix 1 the gas constant for water $R = 0.4615\ kJ\ /\ kgK$ and from Table 7.1 the critical temperature $T_c = 647.3\ K$, and the critical pressure $P_c = 22.09\ MPa$.

Example 7.14

Calculate the specific volume of steam at a temperature $T = 600$ °C and pressure $P = 10$ MPa using the generalised compressibility charts.

We read from Appendix 1 the gas constant for water $R = 0.4615$ kJ / kgK and from Table 7.1 the critical temperature $T_c = 647.3$ K, and the critical pressure $P_c = 22.09$ MPa.

Then we compute the reduced temperature $T_r = T/T_c = 1.35$, and the reduced pressure $P_r = P/P_c = 0.45$.

Example 7.14

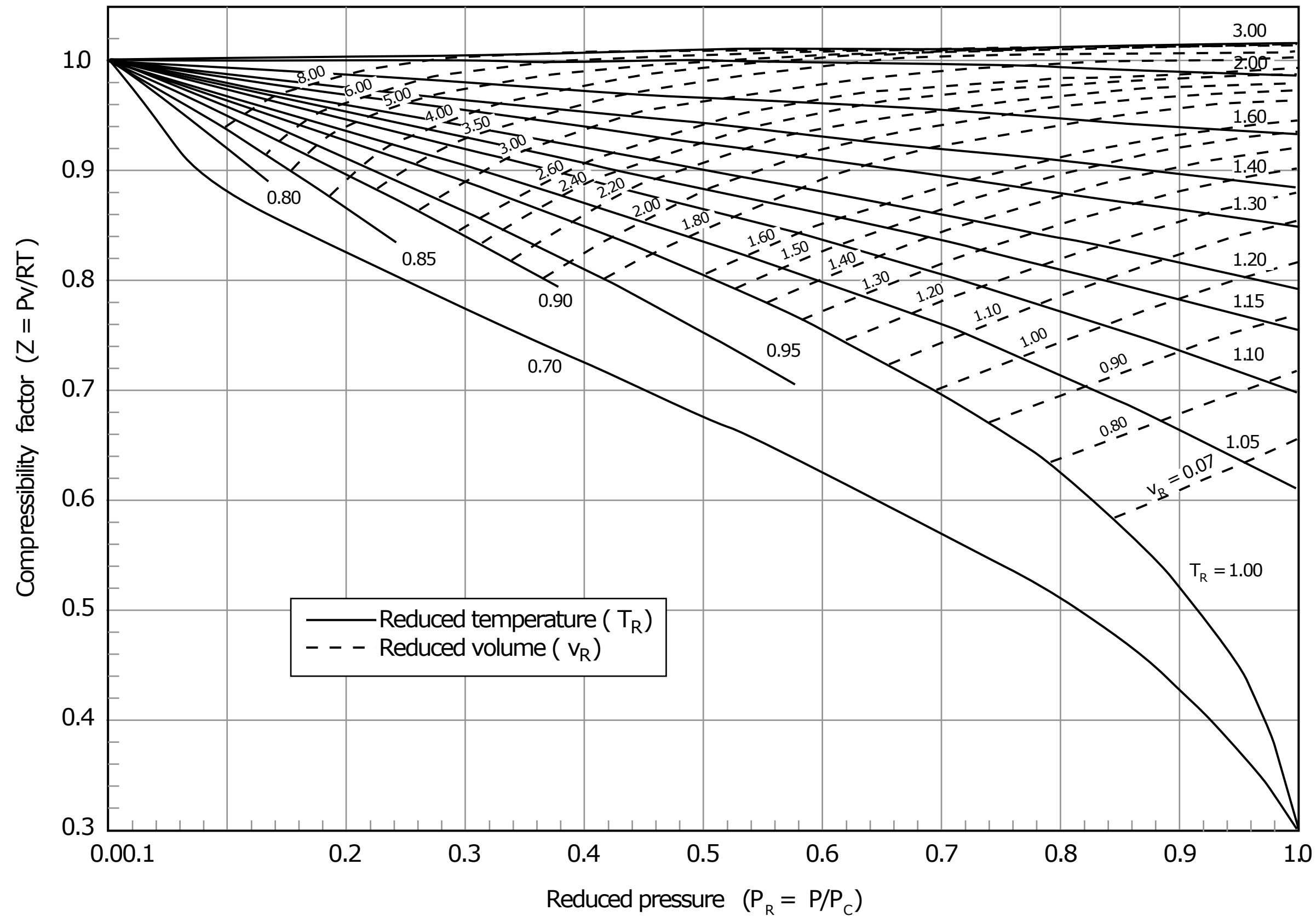Calculate the specific volume of steam at a temperature $T = 600\ °C$ and pressure $P = 10\ MPa$ using the generalised compressibility charts.

We read from Appendix 1 the gas constant for water $R = 0.4615\ kJ\ /\ kgK$ and from Table 7.1 the critical temperature $T_c = 647.3\ K$, and the critical pressure $P_c = 22.09\ MPa$.
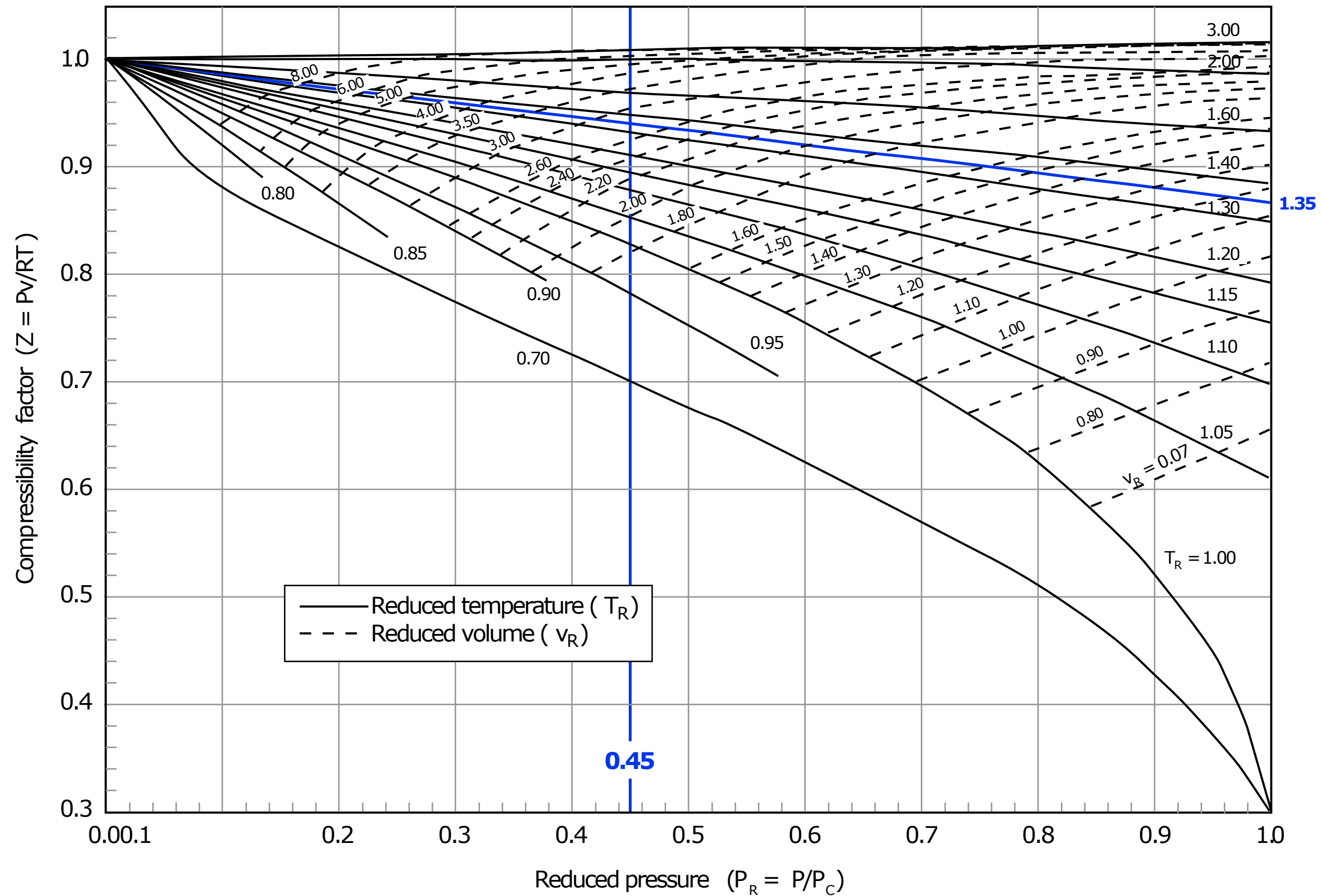
Then we compute the reduced temperature $T_r = T/T_c = 1.35$, and the reduced pressure $P_r = P/P_c = 0.45$.

Then we extract the required information from the generalised compressibility charts (Appendix 10).
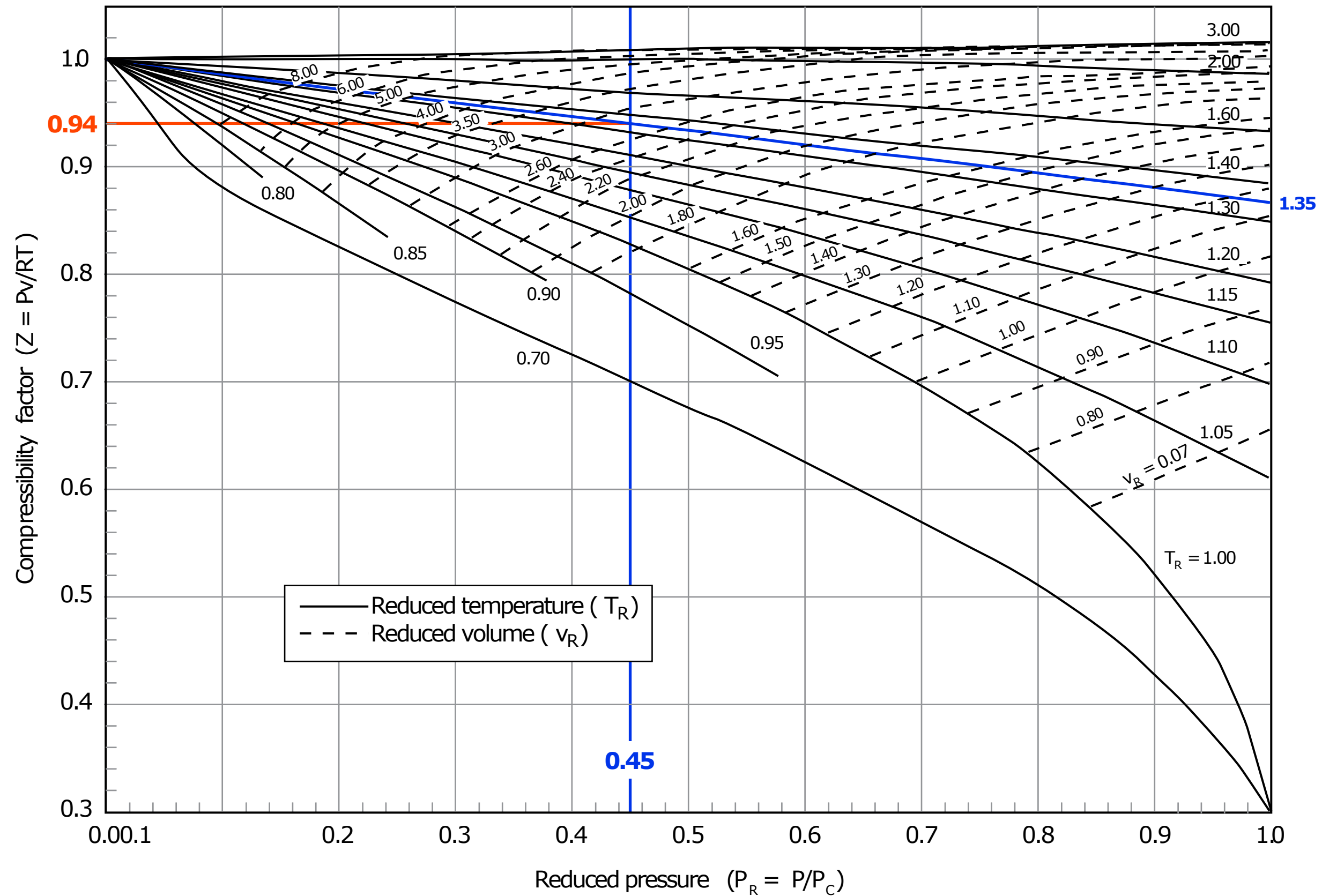
Example 7.14 - generalised compressibility charts

Example 7.14 - generalised compressibility charts

Example 7.14 - generalised compressibility charts

Example 7.14

Calculate the specific volume of steam at a temperature $T = 600\ °C$ and pressure $P = 10\ MPa$ using the generalised compressibility charts.

___

We read from Appendix 1 the gas constant for water $R = 0.4615\ kJ/kgK$ and from Table 7.1 the critical temperature $T_c = 647.3\ K$, and the critical pressure $P_c = 22.09\ MPa$.

Then we compute the reduced temperature $T_r = T/T_c = 1.35$, and the reduced pressure $P_r = P/P_c = 0.45$.

Then we extract the required information from the generalised compressibility charts (Appendix 10). We obtain $Z = 0.94$.

Using $Z = 0.94$, we get $v = ZRT/P = 0.0378\ m^3/kg$.