The location of phase boundaries

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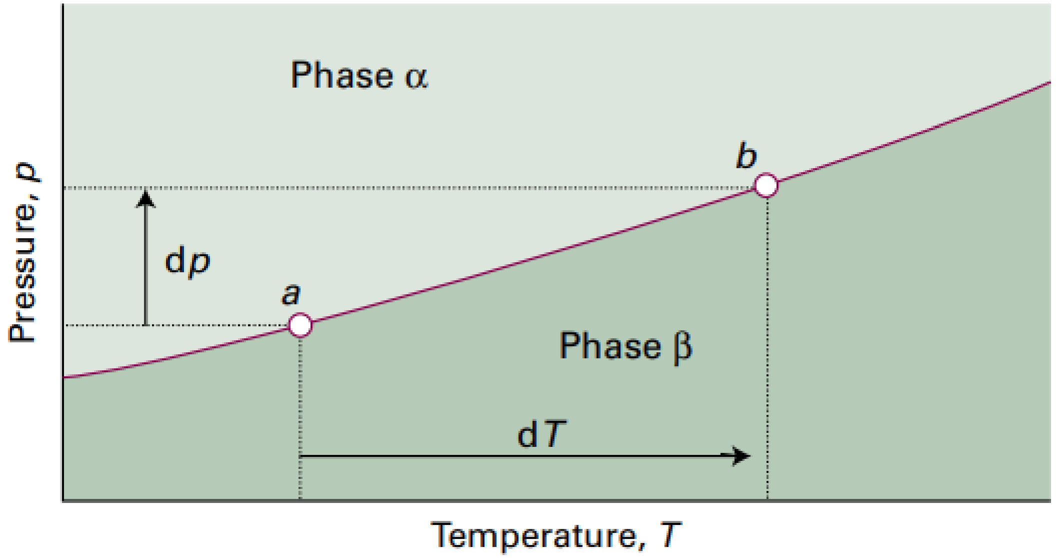

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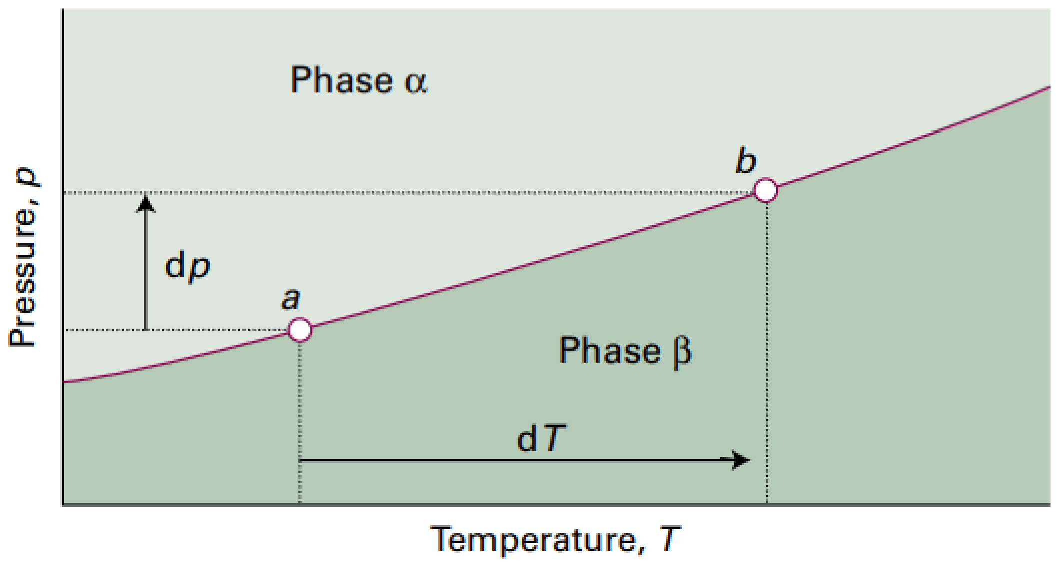
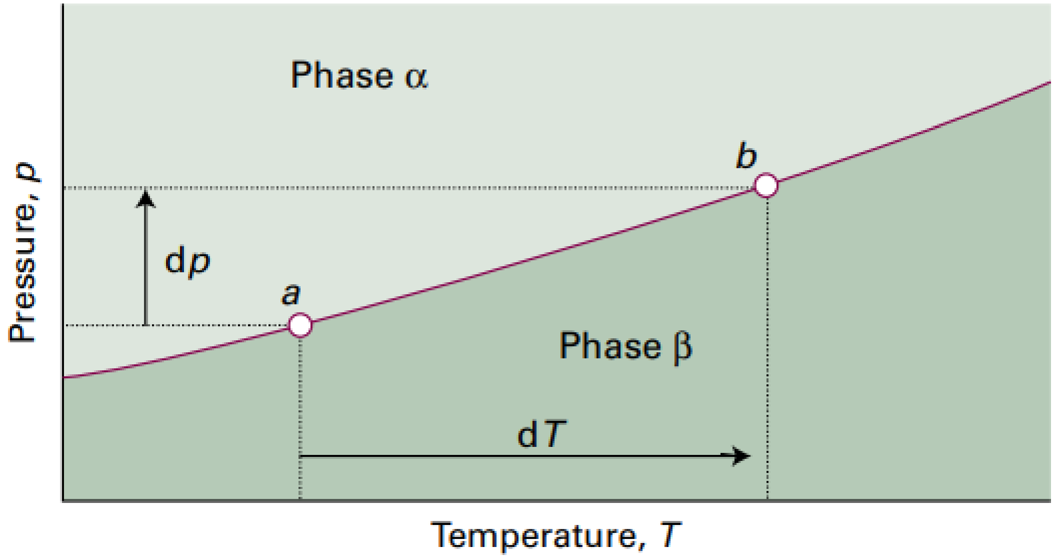


Clapeyron equation

$$\frac{dp}{dT} = \frac{\Delta_{trs}S}{\Delta_{trs}V}$$

The location of phase boundaries

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



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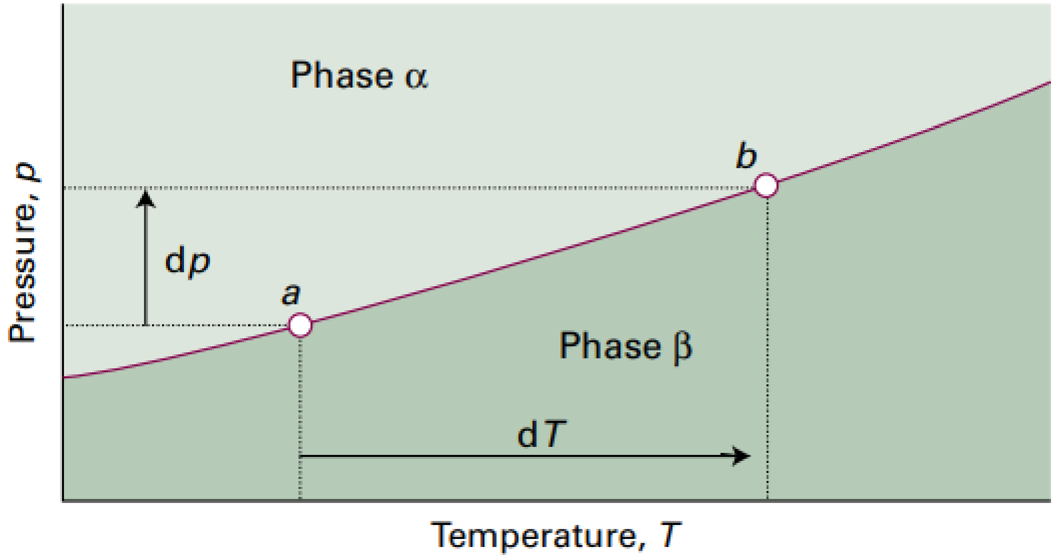

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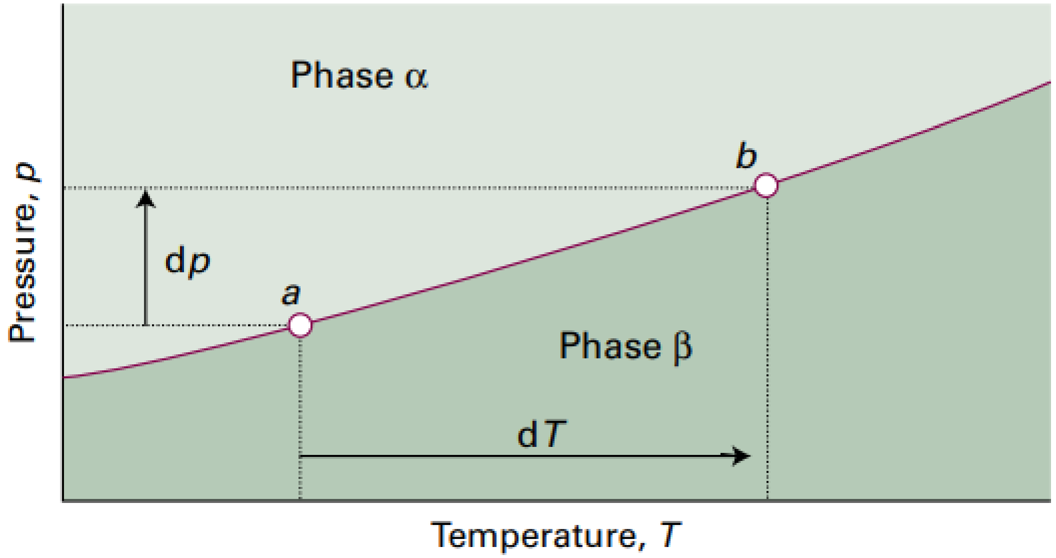

The location of phase boundaries

$$dG = Vdp - SdT$$

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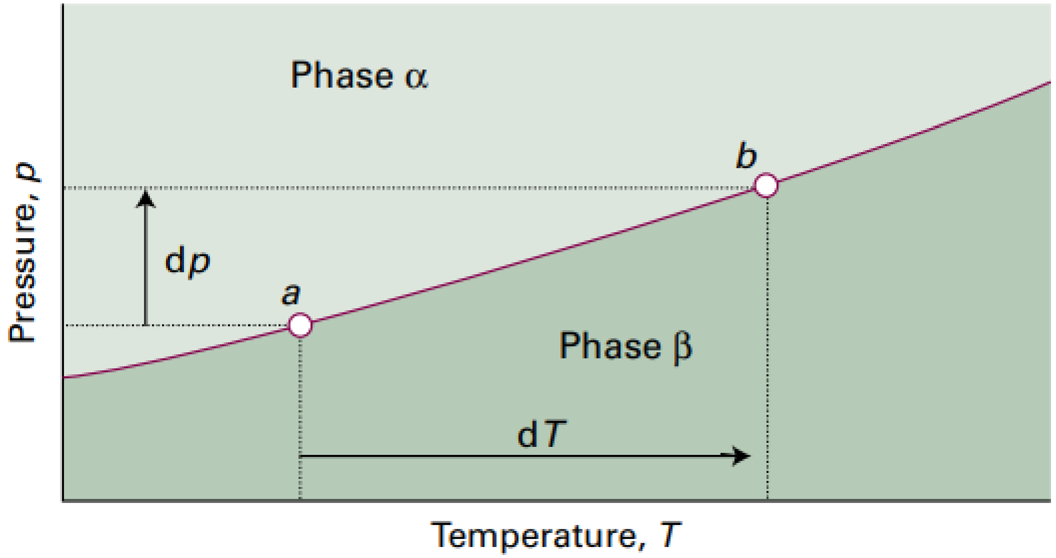

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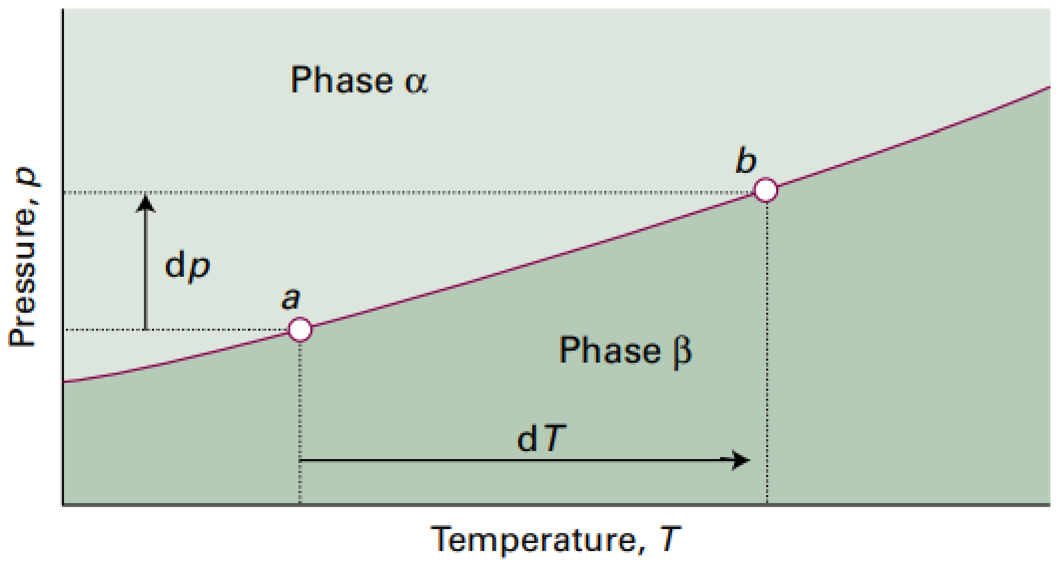

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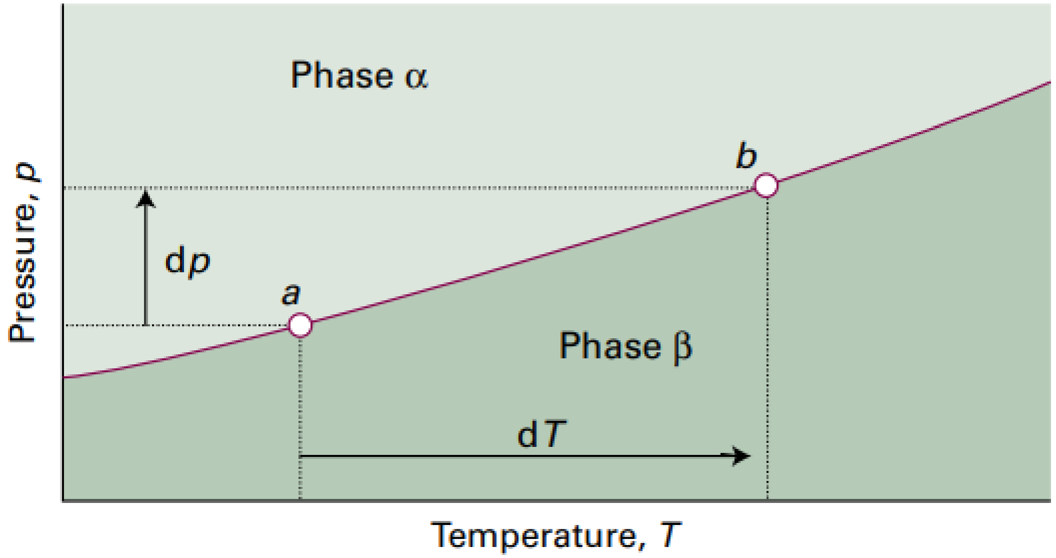

$$d\mu(\alpha) = d\mu(\beta)$$

$$V_m(\alpha)dp - S_m(\alpha)dT = V_m(\beta)dp - S_m(\beta)dT$$

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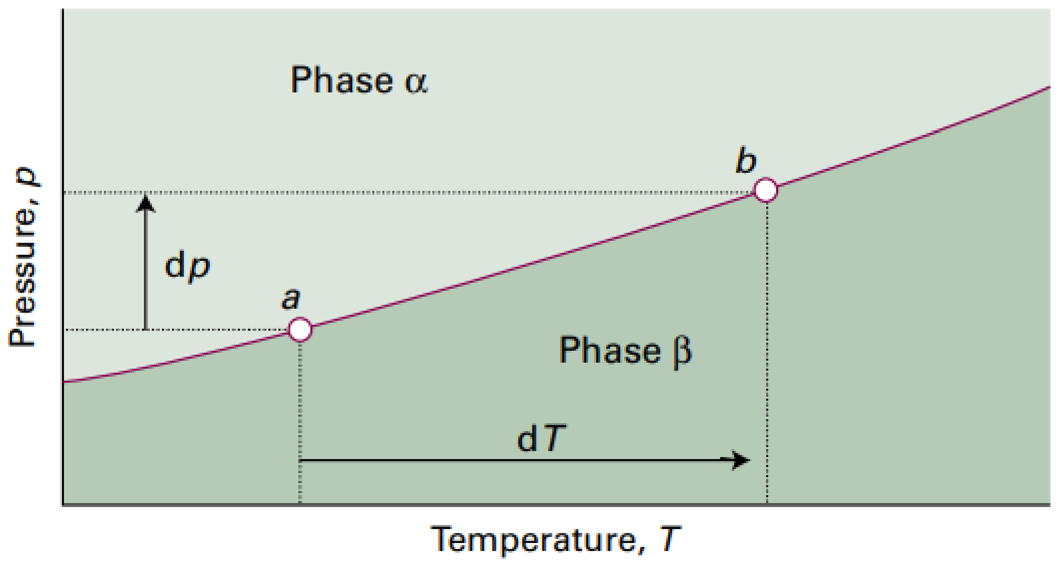

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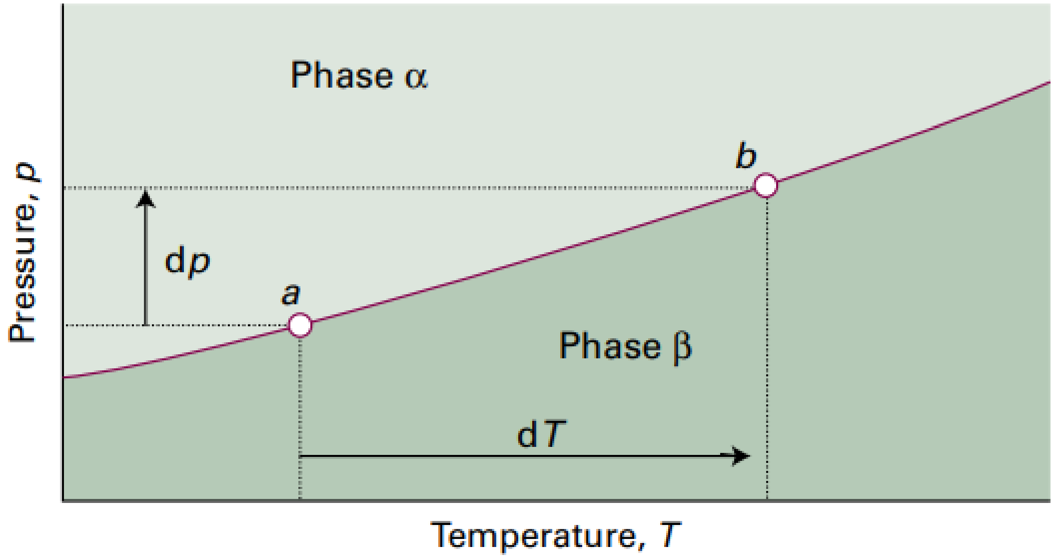

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$$\Delta_{trs}SdT = \Delta_{trs}Vdp$$

The location of phase boundaries

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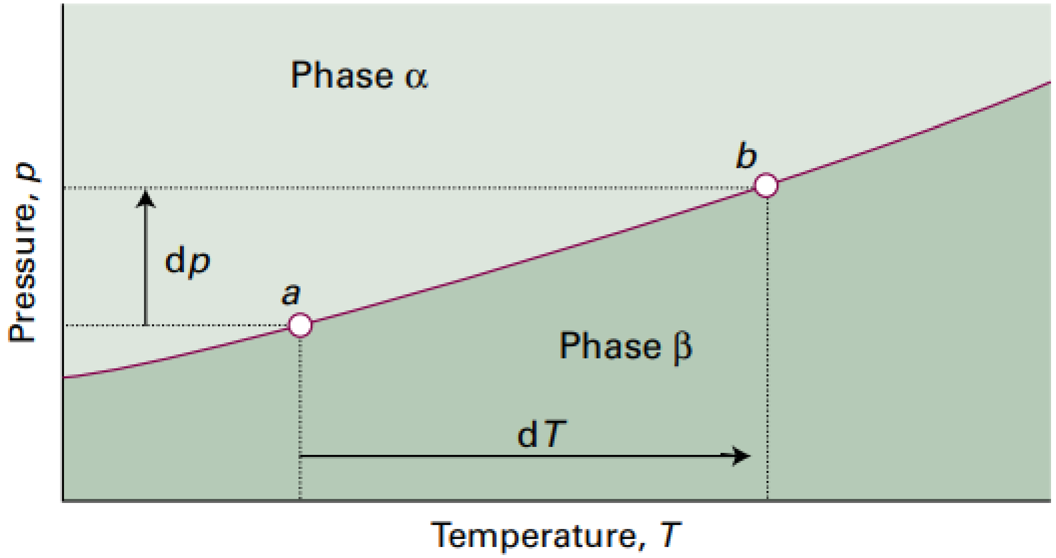

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$$\Delta_{trs}S\,dT = \Delta_{trs}V\,dp$$

Clapeyron equation

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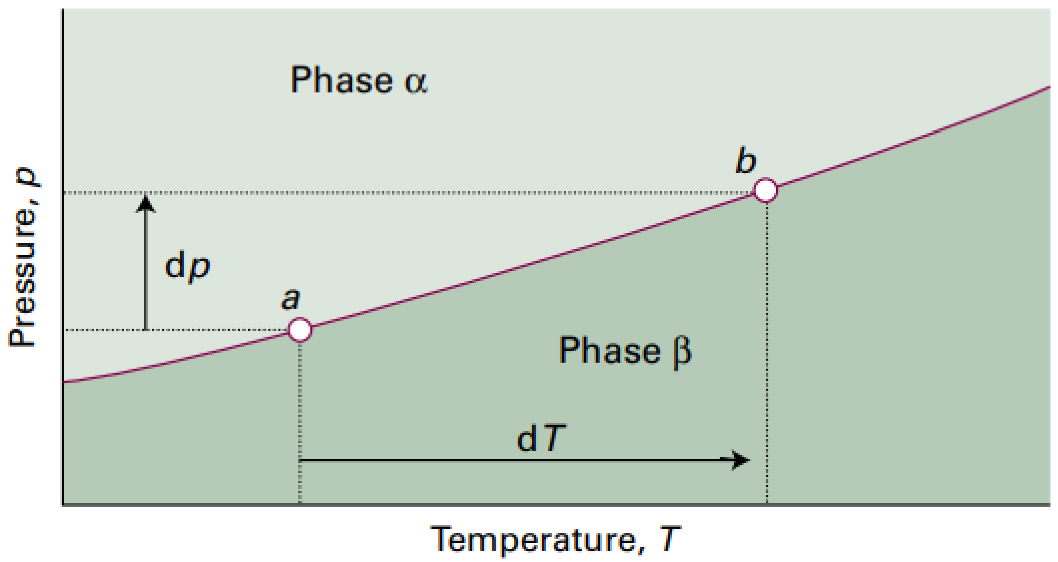

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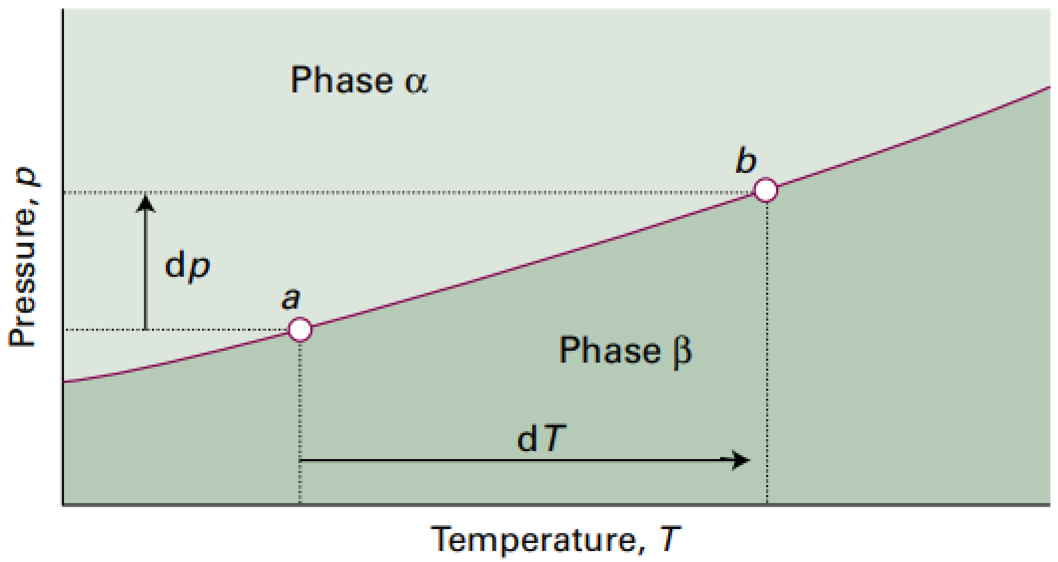

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$$\Delta_{trs}S dT = \Delta_{trs}V dp$$

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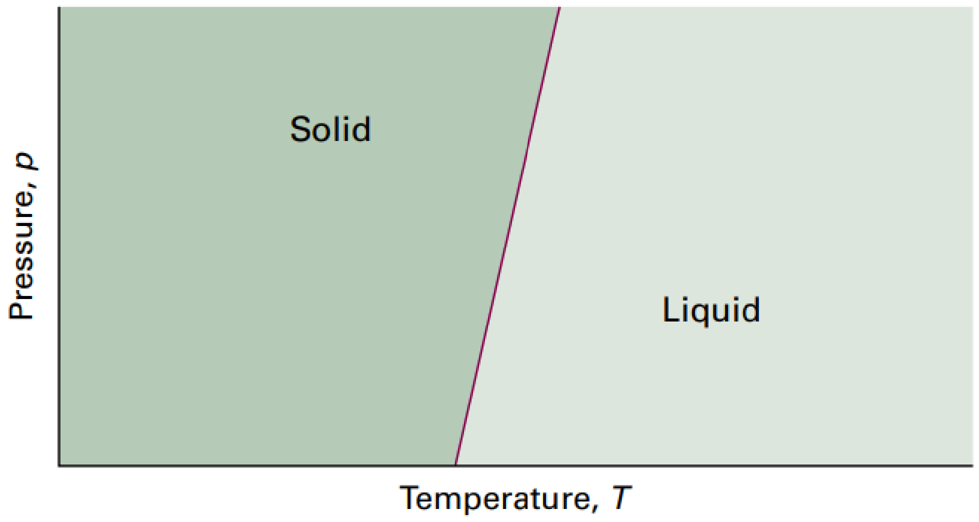
$$\boxed{\frac{dp}{dT} = \frac{\Delta_{trs}S}{\Delta_{trs}V}} \qquad \frac{dT}{dp} = \frac{\Delta_{trs}V}{\Delta_{trs}S}$$

A relationship between p and T along the phase boundaries

Solid-liquid boundary

$$\boxed{\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta_{\mathrm{trs}}S}{\Delta_{\mathrm{trs}}V}}$$



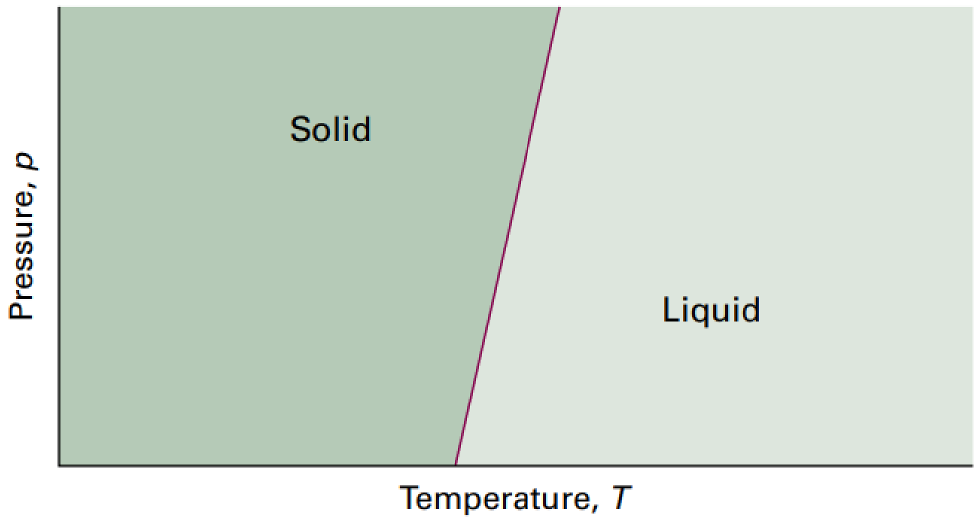
Solid-liquid boundary

$$\boxed{\frac{dp}{dT} = \frac{\Delta_{trs}S}{\Delta_{trs}V}}$$

Melting (fusion)

$$\frac{dp}{dT} = \frac{\Delta_{fus}H}{T\Delta_{fus}V}$$

Slope of solid–liquid boundary



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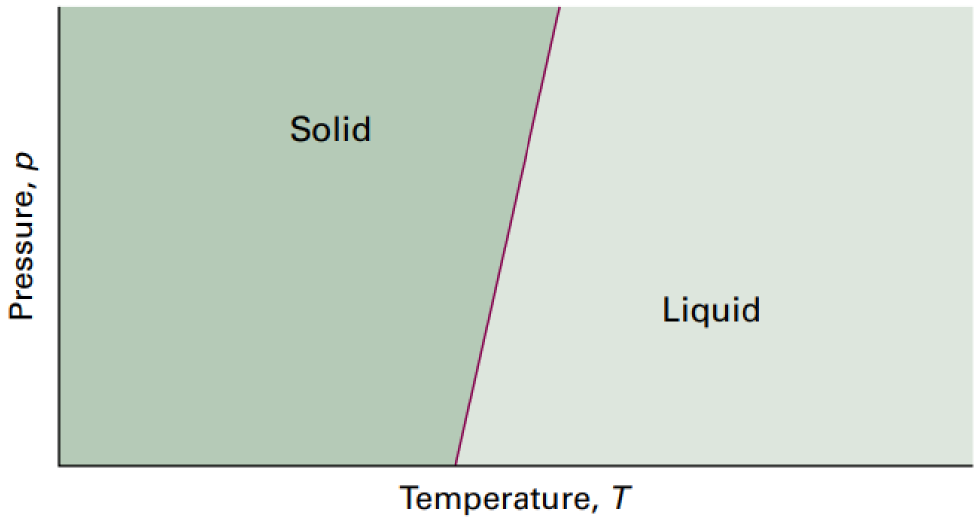

$$\int_{p^*}^{p} dp = \frac{\Delta_{fus}H}{\Delta_{fus}V}\int_{T^*}^{T}\frac{dT}{T}$$

melting temperature is T* when the pressure is p*
melting temperature is T when the pressure is p

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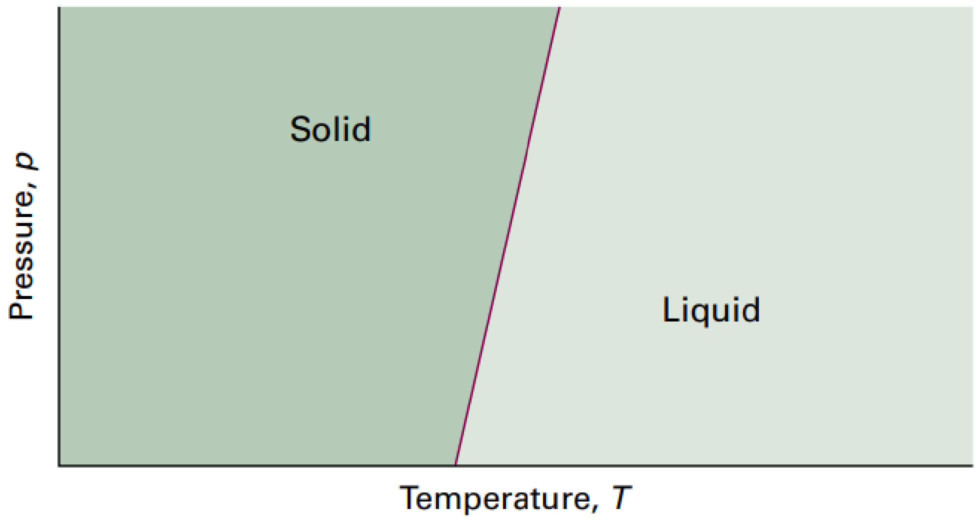

$$\int_{p^*}^{p} dp = \frac{\Delta_{fus}H}{\Delta_{fus}V}\int_{T^*}^{T}\frac{dT}{T}$$

$$p = p^* + \frac{\Delta_{fus}H}{\Delta_{fus}V}\ln\frac{T}{T^*}$$

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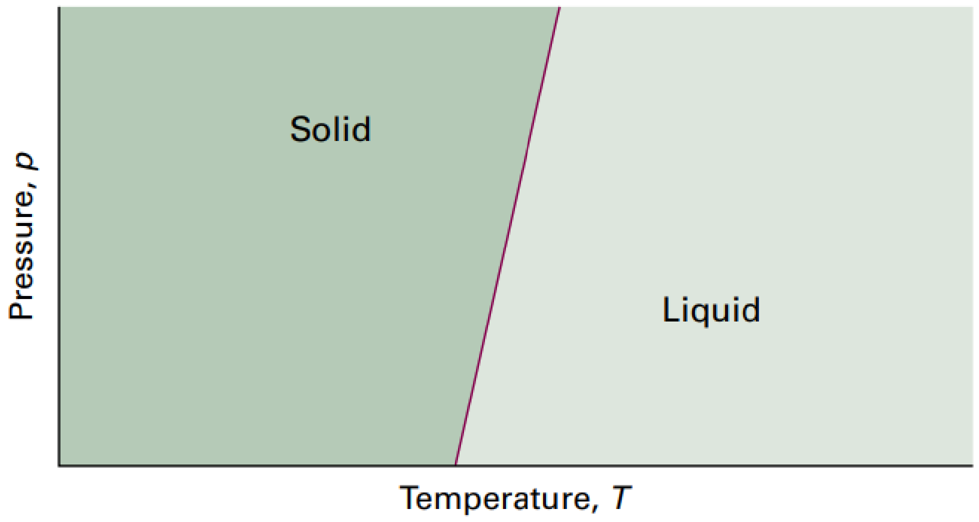

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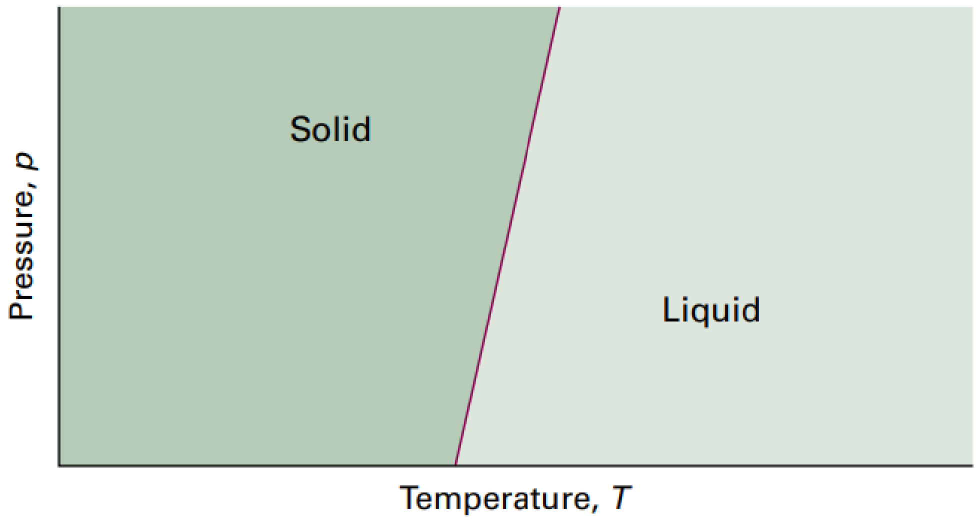

$$\int_{p^*}^{p} dp = \frac{\Delta_{fus}H}{\Delta_{fus}V}\int_{T^*}^{T}\frac{dT}{T}$$

$$\ln\frac{T}{T^*} = \ln\left(1+\frac{T-T^*}{T^*}\right)$$

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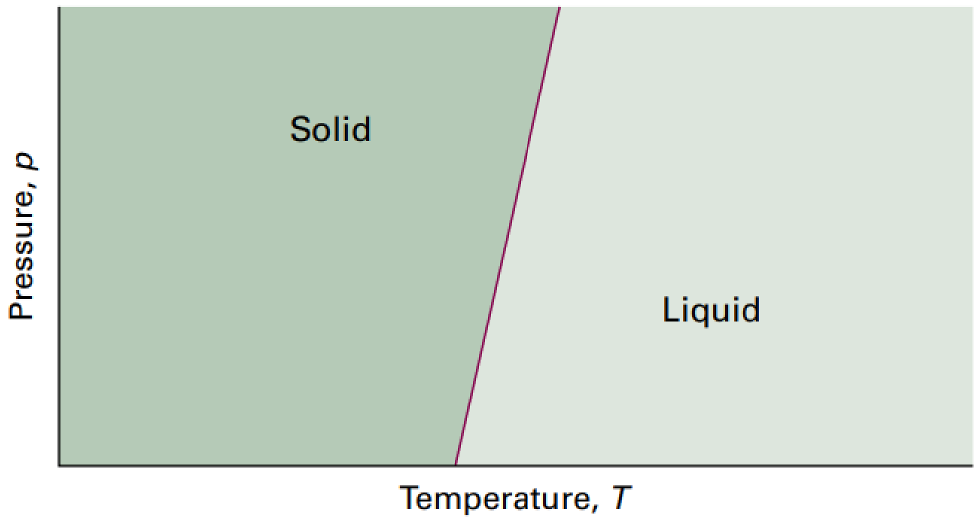

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Slope of solid–liquid boundary

$$\int_{p^*}^{p} \mathrm{d}p = \frac{\Delta_{\mathrm{fus}} H}{\Delta_{\mathrm{fus}} V} \int_{T^*}^{T} \frac{\mathrm{d}T}{T}$$

$$\ln \frac{T}{T^*} = \ln\left(1 + \frac{T - T^*}{T^*}\right)$$

$$\ln(1 + x) = x - \tfrac{1}{2}x^2 + \cdots$$

Taylor series expansion of ln(1 + x) around x = 0

$$p = p^* + \frac{\Delta_{\mathrm{fus}} H}{\Delta_{\mathrm{fus}} V} \ln \frac{T}{T^*}$$

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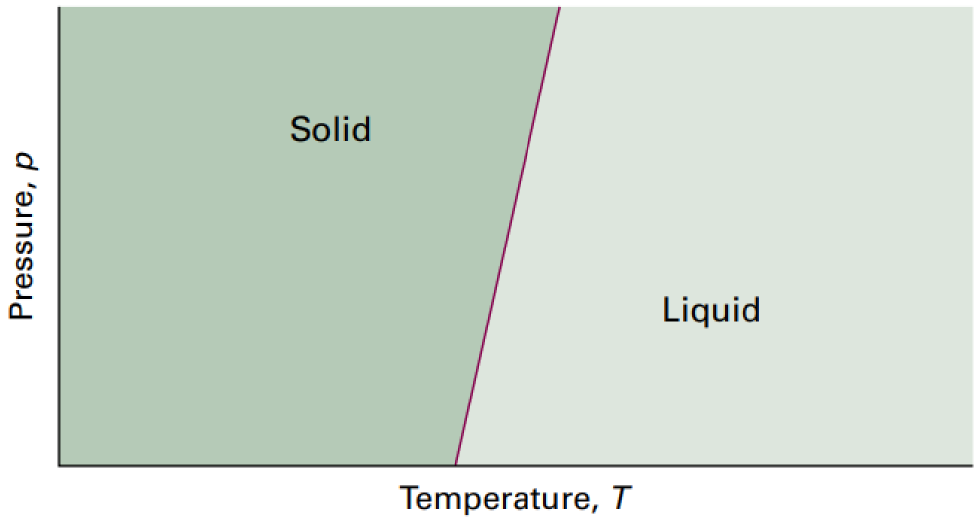

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x<<1; $\ln(1+x) = x$

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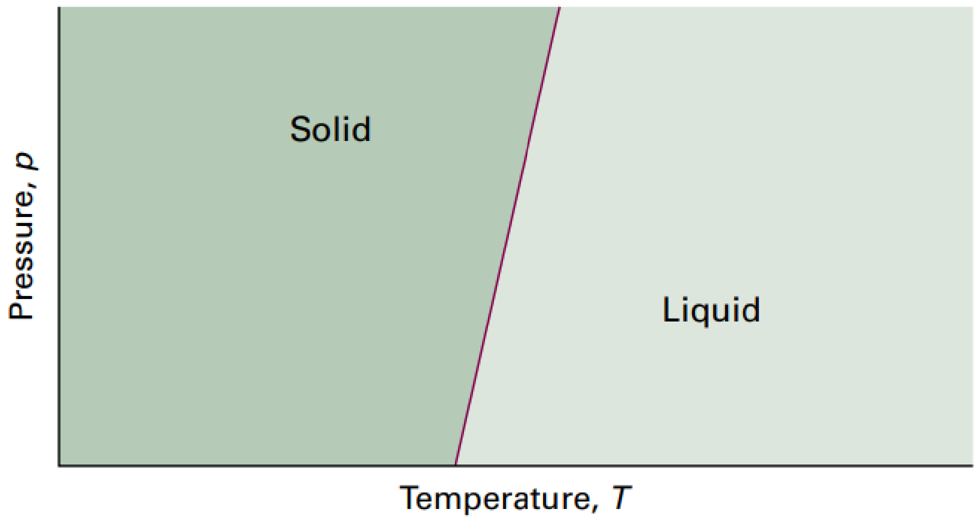

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$$\ln \frac{T}{T^*} = \ln\left(1 + \frac{T - T^*}{T^*}\right) \approx \frac{T - T^*}{T^*}$$

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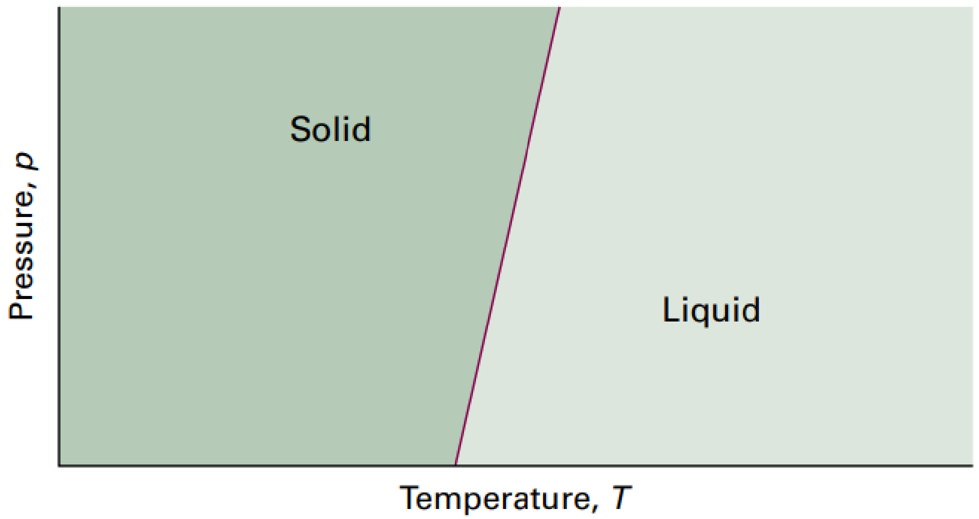

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$$p=p^*+\frac{\Delta_{fus}H}{\Delta_{fus}V}\ln\frac{T}{T^*}$$

$$p\approx p^*+\frac{\Delta_{fus}H}{T^*\Delta_{fus}V}(T-T^*)$$

melting temperature is T* when the pressure is p*
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For the solid-liquid boundary

Liquid-vapor boundary

$$\boxed{\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta_{\mathrm{trs}} S}{\Delta_{\mathrm{trs}} V}}$$

Liquid-vapor boundary

$$\boxed{\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta_{\mathrm{trs}} S}{\Delta_{\mathrm{trs}} V}}$$

for the liquid–vapour boundary

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta_{\mathrm{vap}} H}{T \Delta_{\mathrm{vap}} V}$$

Liquid-vapor boundary

$$\boxed{\frac{dp}{dT} = \frac{\Delta_{trs}S}{\Delta_{trs}V}}$$

for the liquid–vapour boundary

$$\frac{dp}{dT} = \frac{\Delta_{vap}H}{T\Delta_{vap}V}$$

$$\Delta_{vap}V \approx V_m(g)$$

Liquid-vapor boundary

$$\boxed{\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta_{\mathrm{trs}}S}{\Delta_{\mathrm{trs}}V}}$$

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$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta_{\mathrm{vap}}H}{T\Delta_{\mathrm{vap}}V}$$

$$\Delta_{\mathrm{vap}}V \approx V_{\mathrm{m}}(\mathrm{g}) = RT/p.$$

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$$\frac{\mathrm{d}p}{\mathrm{d}T}=\frac{\Delta_{\mathrm{vap}}H}{T(RT/p)}$$

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$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta_{\mathrm{vap}}H}{T(RT/p)} = \frac{p\Delta_{\mathrm{vap}}H}{RT^2}$$

By using $\mathrm{d}x/x = \mathrm{d}\ln x$,

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By using $\mathrm{d}x/x = \mathrm{d}\ln x$,

$$\boxed{\frac{\mathrm{d}\ln p}{\mathrm{d}T} = \frac{\Delta_{\mathrm{vap}} H}{RT^2}}$$

Clausius–Clapeyron equation

Liquid-vapor boundary

$$\boxed{\frac{dp}{dT} = \frac{\Delta_{trs}S}{\Delta_{trs}V}}$$

for the liquid–vapour boundary

$$\frac{dp}{dT} = \frac{\Delta_{vap}H}{T\Delta_{vap}V}$$

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$$\frac{dp}{dT} = \frac{\Delta_{vap}H}{T(RT/p)} = \frac{p\Delta_{vap}H}{RT^2}$$

By using $dx/x = d\ln x$,

$$\boxed{\frac{d\ln p}{dT} = \frac{\Delta_{vap}H}{RT^2}}$$

Clausius–Clapeyron equation

If it is also assumed that the enthalpy of vaporization is independent of temperature,

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Clausius–Clapeyron equation

If it is also assumed that the enthalpy of vaporization is independent of temperature,

$$\int_{\ln p^*}^{\ln p} d\ln p = \frac{\Delta_{vap}H}{R}\int_{T^*}^{T}\frac{dT}{T^2}$$

p* is the vapor pressure when the temperature is T*

p the vapor pressure when the temperature is T

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Clausius–Clapeyron equation

If it is also assumed that the enthalpy of vaporization is independent of temperature,

$$\int_{\ln p^*}^{\ln p} d\ln p = \frac{\Delta_{vap}H}{R}\int_{T^*}^{T}\frac{dT}{T^2}$$

$$\ln\frac{p}{p^*} = -\frac{\Delta_{vap}H}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)$$

Liquid-vapor boundary

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for the liquid–vapour boundary

$$\frac{dp}{dT} = \frac{\Delta_{vap}H}{T\Delta_{vap}V}$$

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If it is also assumed that the enthalpy of vaporization is independent of temperature,

$$\int_{\ln p^*}^{\ln p} d\ln p = \frac{\Delta_{vap}H}{R}\int_{T^*}^{T}\frac{dT}{T^2}$$

$$\ln\frac{p}{p^*} = -\frac{\Delta_{vap}H}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)$$

$$p = p^* e^{-\chi} \qquad \chi = \frac{\Delta_{vap}H}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)$$

Liquid-vapor boundary

$$\boxed{\frac{dp}{dT} = \frac{\Delta_{trs}S}{\Delta_{trs}V}}$$

for the liquid–vapour boundary

$$\frac{dp}{dT} = \frac{\Delta_{vap}H}{T\Delta_{vap}V}$$

$$\Delta_{vap}V \approx V_m(g) = RT/p.$$

$$\frac{dp}{dT} = \frac{\Delta_{vap}H}{T(RT/p)} = \frac{p\Delta_{vap}H}{RT^2}$$

By using $dx/x = d\ln x$, $$\boxed{\frac{d\ln p}{dT} = \frac{\Delta_{vap}H}{RT^2}}$$

Clausius–Clapeyron equation

If it is also assumed that the enthalpy of vaporization is independent of temperature,

$$\int_{\ln p^*}^{\ln p} d\ln p = \frac{\Delta_{vap}H}{R}\int_{T^*}^{T}\frac{dT}{T^2}$$

$$\ln\frac{p}{p^*} = -\frac{\Delta_{vap}H}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)$$

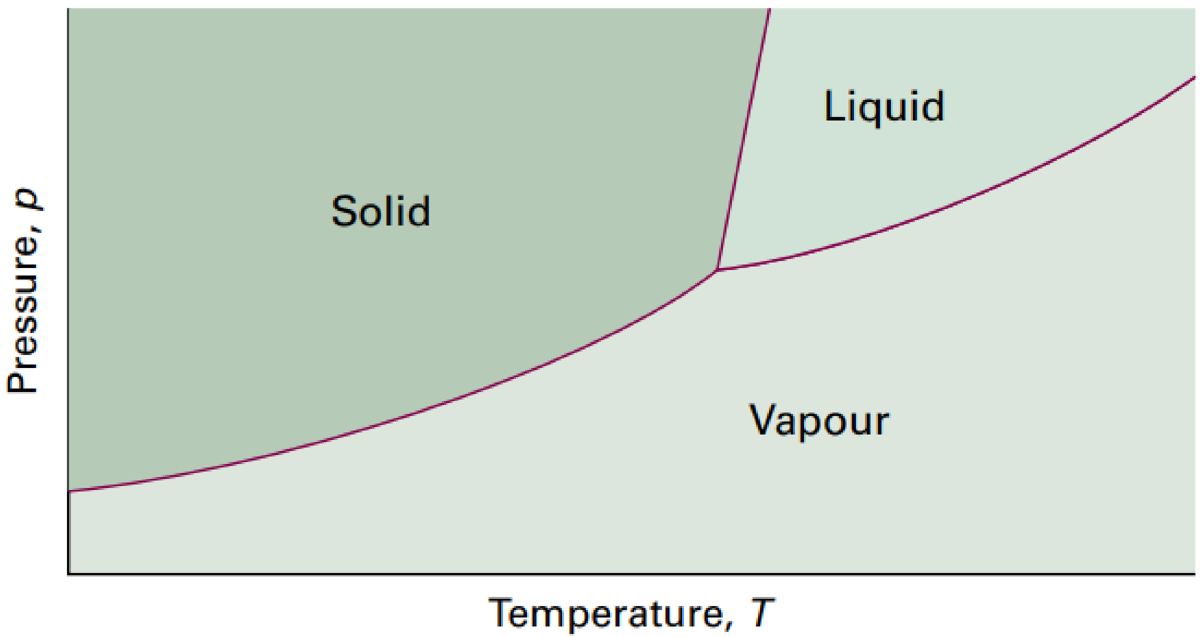
$$p = p^* e^{-\chi} \qquad \chi = \frac{\Delta_{vap}H}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)$$

p* is the vapor pressure when the temperature is T*
p the vapor pressure when the temperature is T

Solid-vapor boundary

$$\frac{dp}{dT} = \frac{\Delta_{sub}H}{T\Delta_{sub}V}$$

$$p \approx p^* + \frac{\Delta_{sub}H}{T^* V_m(g)}(T - T^*)$$



CHEM3520 - Spring 2023

Focus 1: Properties of gases

Focus 2: The First Law

Focus 3: The Second and Third Laws

Focus 4: Physical transformation of pure substances

Focus 5: Simple mixtures

Focus 6: Chemical equilibrium

Focus 16: Molecules in motion

Focus 17: Chemical kinetics

Focus 18: Reaction dynamics

Focus 19: Processes at solid surfaces