ChemE 2200 – Chemical Thermodynamics Lecture 10

Today:

The Gibbs-Helmholtz Equation.
Solid-Liquid-Gas Phase Equilibria.
The Chemical Potential, μ.

Defining Question:

For two phases,
thermal equilibrium requires equal temperatures,
physical equilibrium requires equal pressures, and
chemical equilbrium requires equal ????”

Reading for Today’s Lecture:

McQuarrie & Simon, Chapter 22.7, 23.1-23.4

Reading for Thermodynamics Lecture 11:

McQuarrie & Simon, Chapter 26.1-26.7

1st Prelim

TOMORROW, March 11, 7:30 – 9:30 p.m.

245 Olin Hall

Covers –

- Atomic Orbitals
- Molecular Orbitals
- Molecular Spectroscopy
- Electrons in Solids
- Classical Thermodynamics through 1st Law

Covers –

- Lectures through 1st half of Monday, 2/24 (Lecture T4)
- Homework through Homework 5
- Calculation Sessions through Calculation Session 5

You may use a hand-written, double-sided reference sheet.
Reference sheets will be submitted with the Prelim.
Reference sheets will be returned Wednesday, March 12.

Career Guidance

Mondays
12:20-1:10 p.m.
165 Olin

ChemE 3010 - Career Perspectives Schedule
Spring 2025

Class Date	Speaker	Class Year	Job Title/Organization
Jan. 27	**First Day of Class - Course Overview by Susan Daniel**		
Feb. 3	Brian Bauer	1986	Professor of Practice, Cornell
Feb. 10	Kathy Vaeth	1995	Senior R&D Engineering Manager, Qualitrol
Feb. 17	**No Class - February Break**		
Feb. 24	Matthew Paszek		Professor of Chemical Engineering, Cornell
Mar. 3	Karen Havenstrite	2005	Founder and CTO, Tangible Science
Mar. 10	Rob Ferris	2004	Associate Partner, McKinsey & Company
Mar. 17	Joe Mattson	PhD 2019	Senior Chemical Engineer, Corning,
Mar. 24	Taylor Milner Margaret Seeman Jess Levine	MechE '98 2020 2016	Partner/Stroud International Project Lead, Stroud International Engagement Lead, Stroud International
Mar. 31	**No Class - Spring Break**		
Apr. 7	Fazeela Rashid	2001	Growth Equity Investor, Healthbridge Innovation Fund
Apr. 14	Greg Moore	1993	Portfolio Manager at Balyasny Asset Management
Apr. 21	Kent Goklen	1983	Chemical Engineer, GlaxoSmithKline


ChemE Reunion June 2024

Recap: The Equations of Thermodynamics

energy	definition	natural variables	fundamental equation	Maxwell relation	practical equation
internal	$U = q + w$	S and V	$dU = TdS - PdV$	$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$	$dU = C_V dT + \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right]dV$
Helmholtz	$A = U - TS$	T and V	$dA = -SdT - PdV$	$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$	$dS = \frac{C_V}{T}dT + \left(\frac{\partial P}{\partial T}\right)_V dV$
enthalpy	$H = U + PV$	S and P	$dH = TdS + VdP$	$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$	$dH = C_P dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right]dP$
Gibbs	$G = H - TS$	T and P	$dG = -SdT + VdP$	$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$	$dS = \frac{C_P}{T}dT - \left(\frac{\partial V}{\partial T}\right)_P dP$

need C_P or C_V and an equation of state.

Properties of matter

$\left(\frac{\partial U}{\partial T}\right)_V = C_V$	heat capacity at constant volume
$\left(\frac{\partial H}{\partial T}\right)_P = C_P$	heat capacity at constant pressure
$\left(\frac{\partial T}{\partial P}\right)_H = \mu$	Joule-Thomson coefficient
$\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \alpha$	coefficient of thermal expansion
$-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = \kappa_T$	isothermal compressibility
$-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S = \kappa_S$	adiabatic compressibility

Some Useful Relations

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T}$$

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}$$

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

$$\left(\frac{\partial A}{\partial T}\right)_V = -S$$

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

$$\left(\frac{\partial A}{\partial V}\right)_T = -P$$

example: provides C_V dependence on V.

$$\overline{C}_P = \overline{C}_V + T\left(\frac{\partial P}{\partial T}\right)_{\overline{V}}\left(\frac{\partial \overline{V}}{\partial T}\right)_P$$

$$\boxed{\left(\frac{\partial C_V}{\partial V}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V}$$

$$\left(\frac{\partial C_P}{\partial P}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P$$

$$\left(\frac{\partial T}{\partial P}\right)_H = -\frac{1}{C_P}\left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right]$$

$$\left(\frac{\partial H}{\partial V}\right)_T = \left[T - V\left(\frac{\partial T}{\partial V}\right)_P\right]\left(\frac{\partial P}{\partial T}\right)_V$$

The Gibbs-Helmholtz Equation

(for the temperature dependence of *G*.)

Recall: The pressure dependence of *G*:

Useful Relation: $\left(\frac{\partial G}{\partial P}\right)_T = V \quad \Rightarrow \quad dG = VdP$ at constant *T*.

$$\Delta G = \int_{P_1}^{P_2} VdP$$

For an ideal gas, $\Delta G = \int_{P_1}^{P_2} \frac{nRT}{P} dP = nRT \ln \frac{P_2}{P_1}$ at constant *T*.

For the temperature dependence of *G*, one can similarly start with a *Useful Relation*:

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

But there is an easier derivation. Start with the definition of the Gibbs energy:

$$G = H - TS$$

Divide by *T*: $\frac{G}{T} = \frac{H}{T} - S$

The Gibbs-Helmholtz Equation, cont'd

$$\frac{G}{T} = \frac{H}{T} - S$$

Differentiate with respect to T at constant P:

$$\left(\frac{\partial(G/T)}{\partial T}\right)_P = \left(\frac{\partial(1/T)}{\partial T}\right)_P H + \frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_P - \left(\frac{\partial S}{\partial T}\right)_P$$

Substitute a *Property of Matter* $\left(\frac{\partial H}{\partial T}\right)_P = C_P$ and a *Useful Relation* $\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}$

$$\left(\frac{\partial(G/T)}{\partial T}\right)_P = -\frac{1}{T^2}H + \frac{1}{T}(C_P) - \frac{C_P}{T}$$

$$\boxed{\left(\frac{\partial(G/T)}{\partial T}\right)_P = -\frac{H}{T^2}}$$

The Gibbs-Helmholtz Equation (1882)

Also useful for temperature dependence of ΔG of a phase transition or chemical reaction:

$$\boxed{\left(\frac{\partial(\Delta G_{rxn}/T)}{\partial T}\right)_P = -\frac{\Delta H_{rxn}}{T^2}}$$

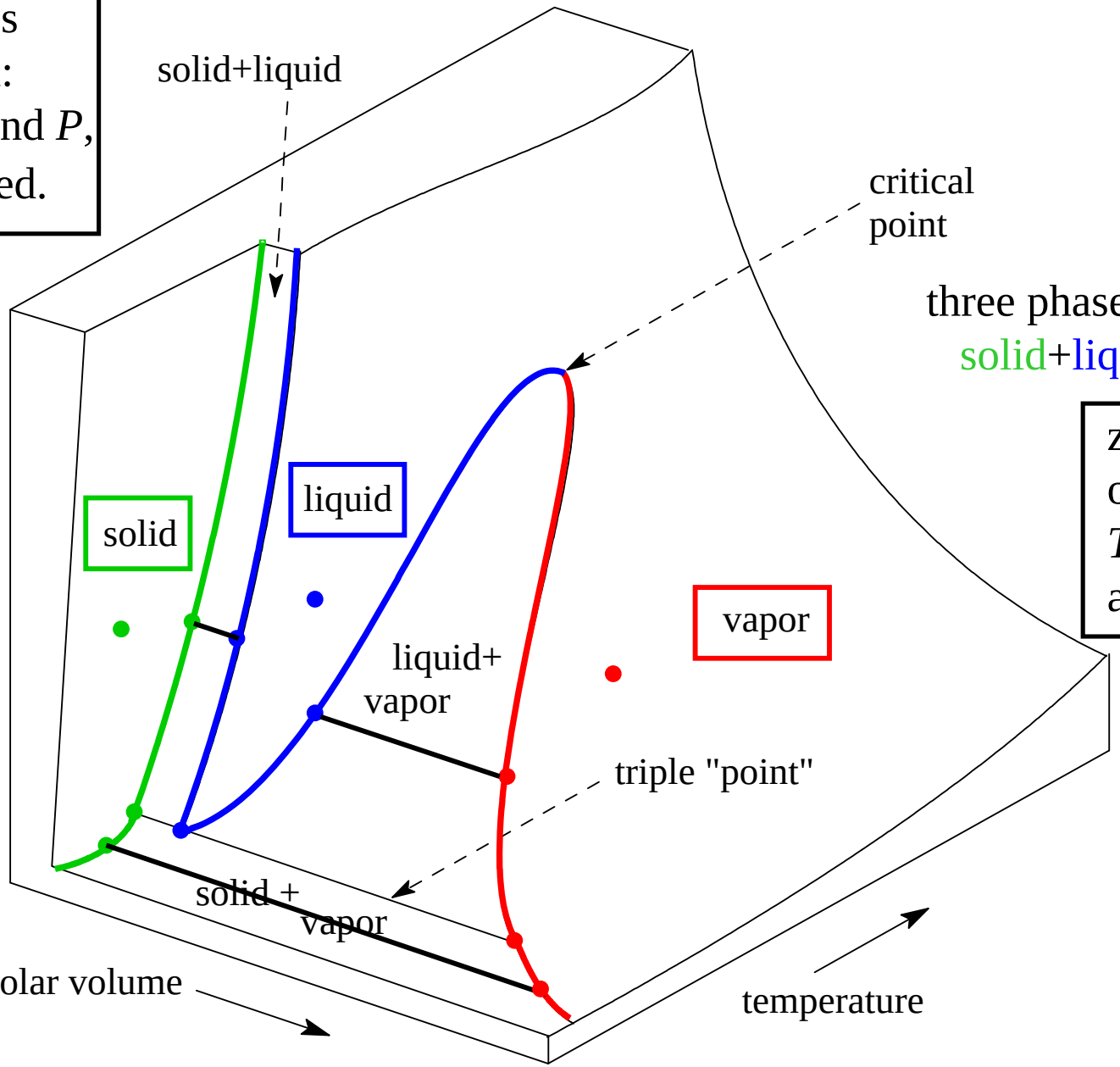
Also The Gibbs-Helmholtz Equation

A Three-Dimensional Map of a Pure Substance.

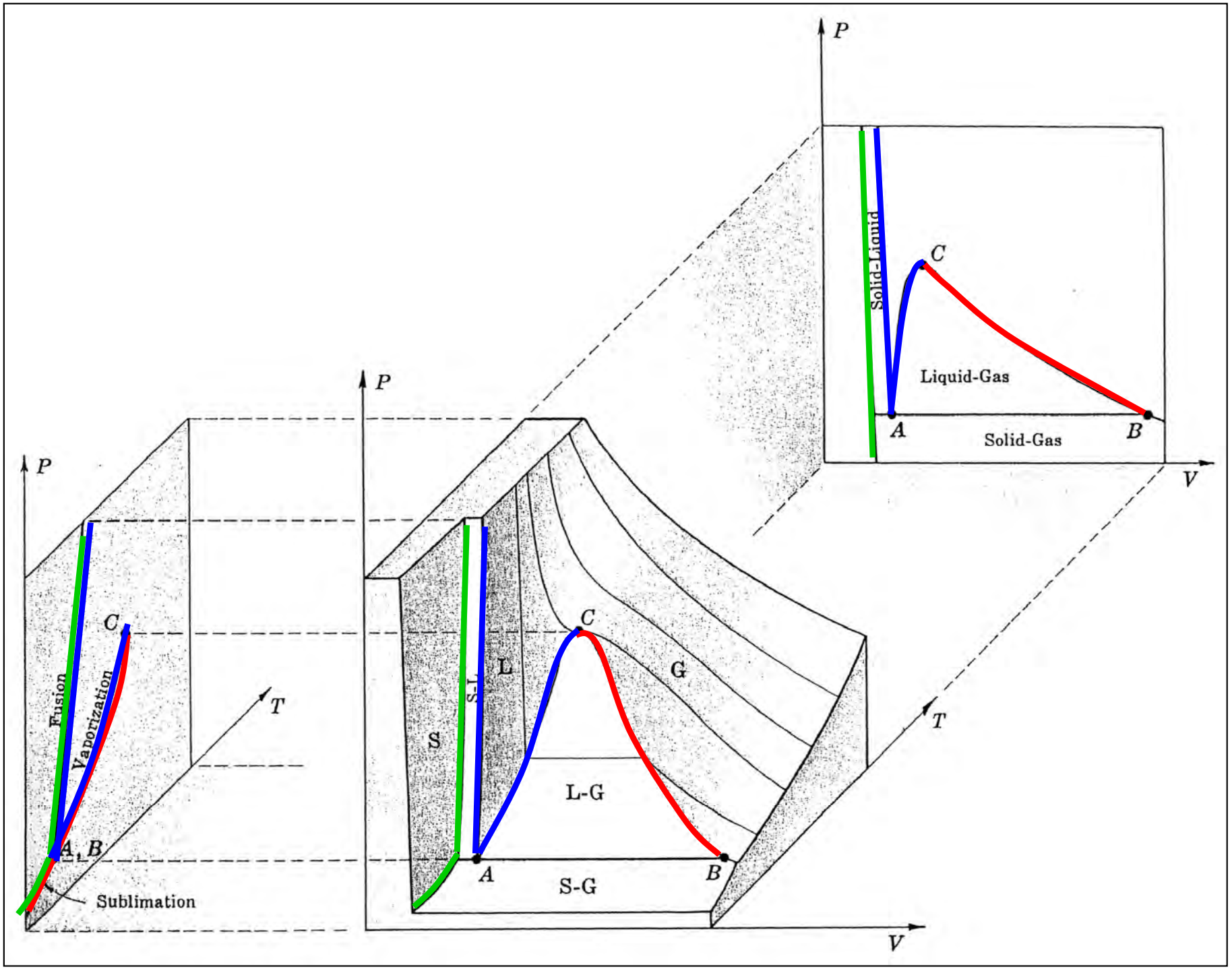
Figure 4.109, p. 300, Duncan & Reimer

one phase:
solid
liquid
vapor

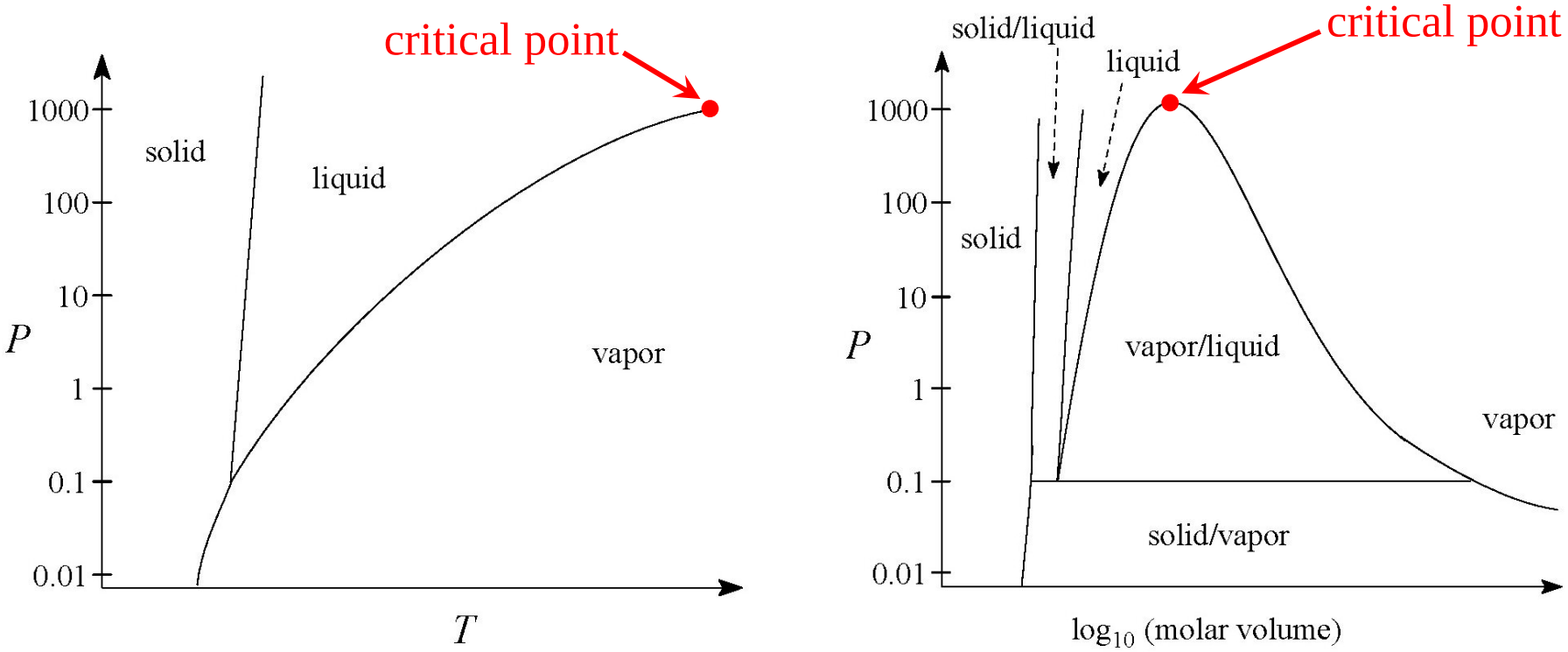
two degrees of freedom: specify T and P, $\Rightarrow$ V is fixed.



Projections of Three-Dimensional Map onto Two-Dimensional Maps



Thermodynamics of the Critical Point



Liquid and vapor are indistinguishable above the critical point.

Enthalpy of vaporization decreases with increasing temperature to zero at the critical temperature.

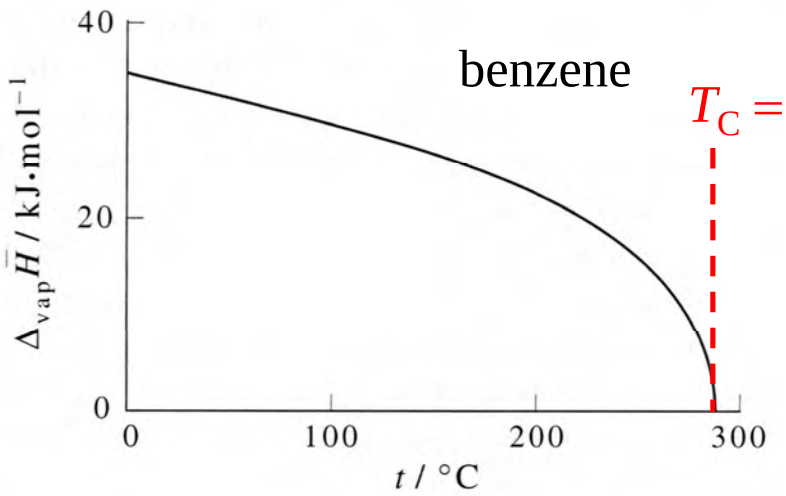
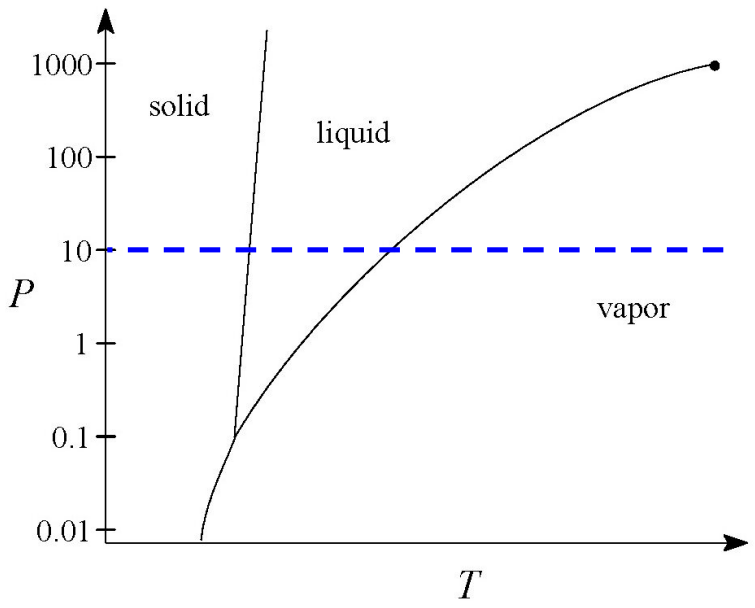
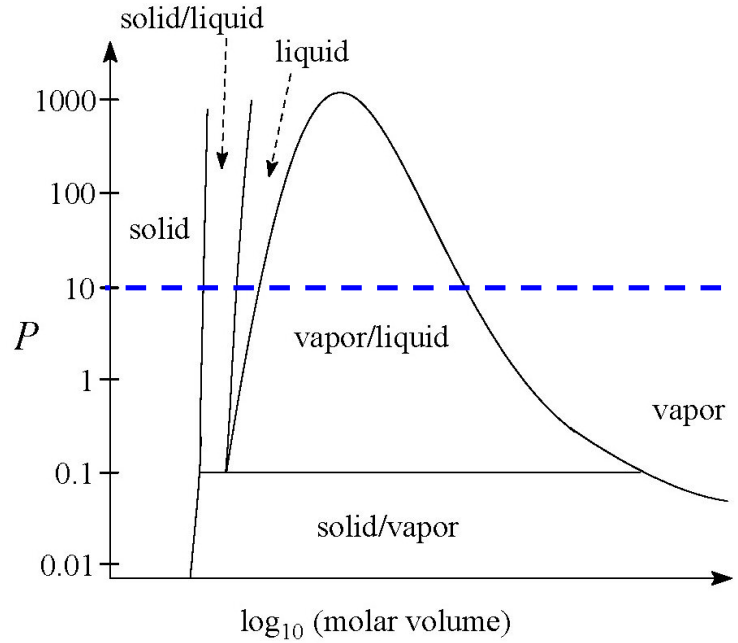
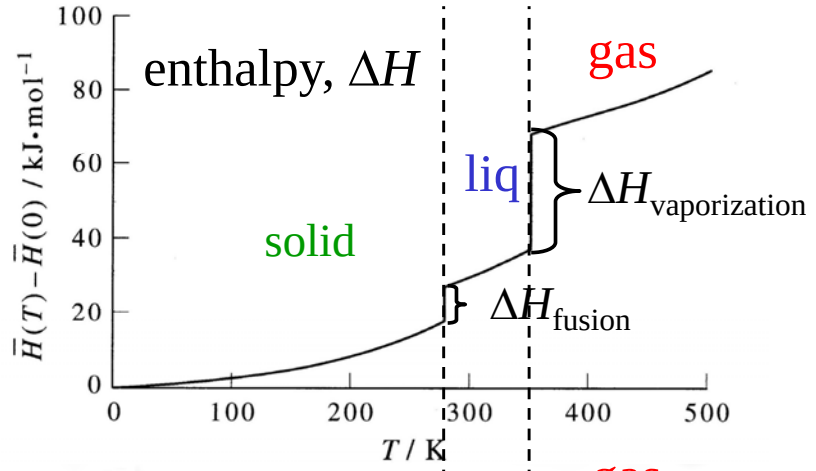


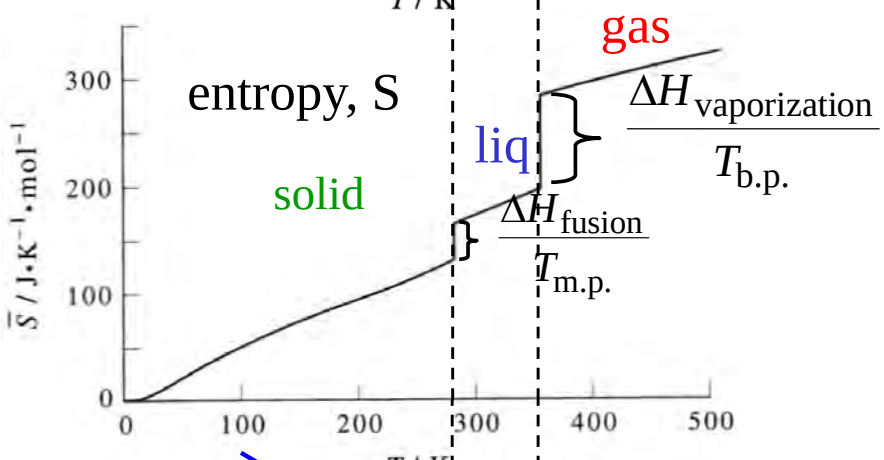
Figure 23.8 of McQuarie & Simon

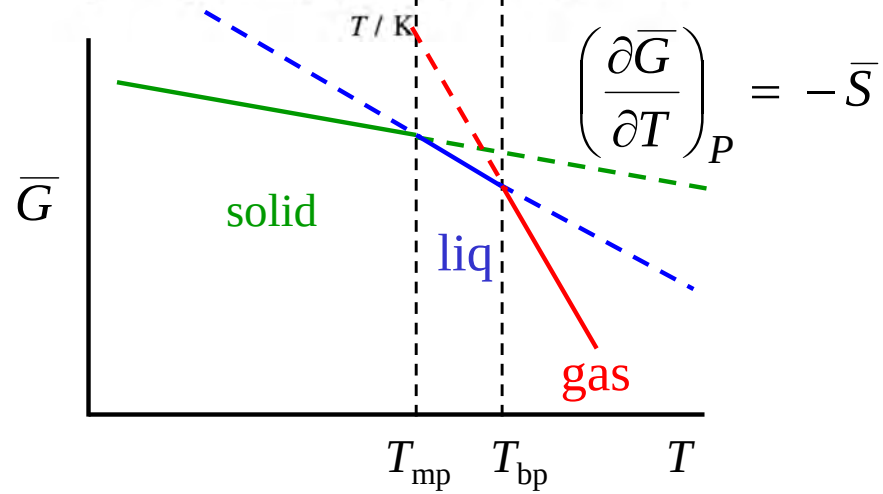
Changes in Enthalpy, Entropy, and Gibbs Energy at Constant Pressure





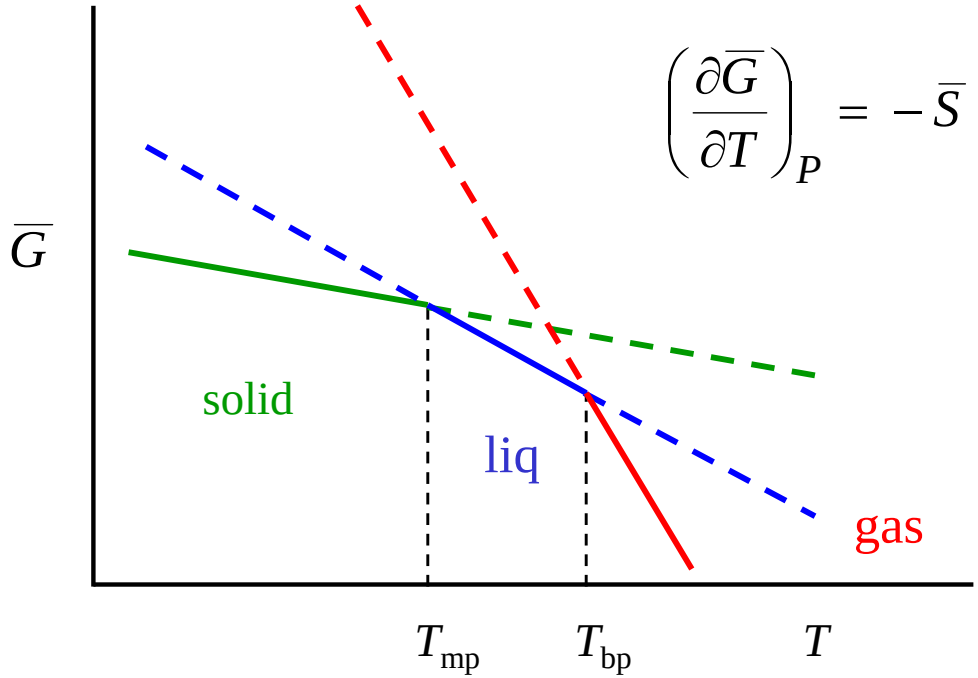






Figures 19.7, 21.2, and 23.10 from McQuarrie & Simon

Temperature Changes in Gibbs Energy at Constant Pressure



$\overline{G}_{solid} = \overline{G}_{liquid}$ at melting point

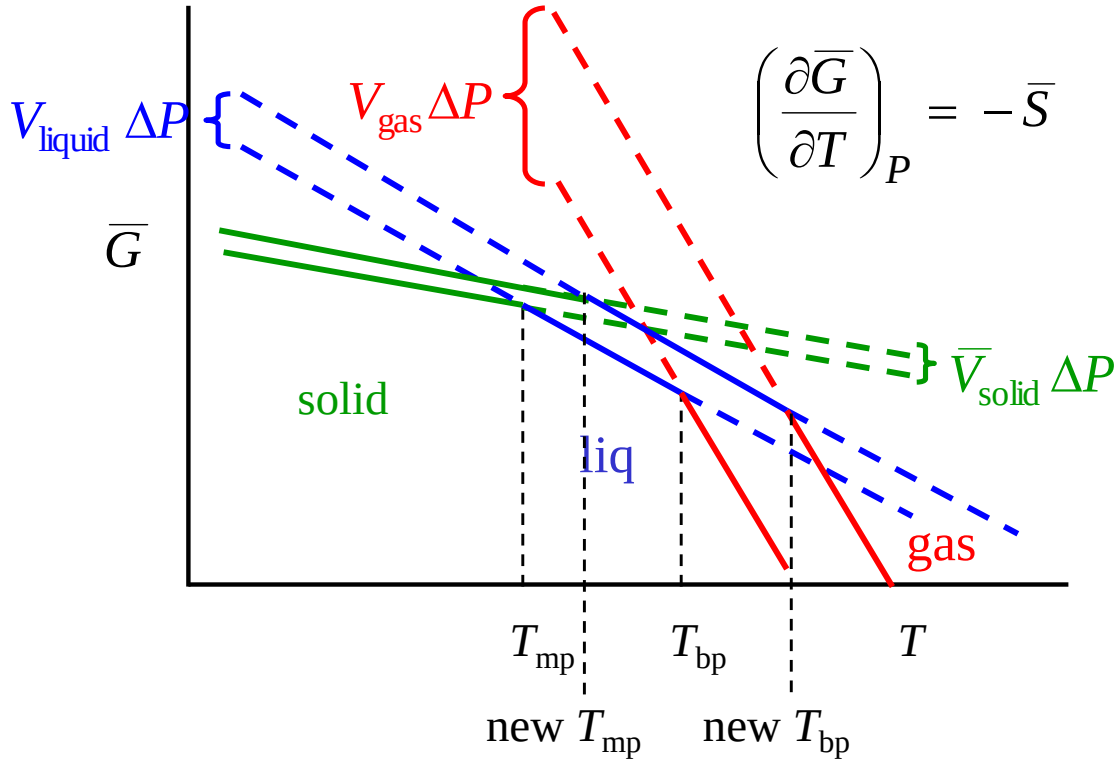
$\overline{G}_{liquid} = \overline{G}_{vapor}$ at boiling point

$\overline{G}_{solid} < \overline{G}_{liquid} < \overline{G}_{vapor}$ below melting point

$\overline{G}_{liquid} < \overline{G}_{solid} < \overline{G}_{vapor}$ above melting point, below boiling point

$\overline{G}_{vapor} < \overline{G}_{liquid} < \overline{G}_{solid}$ above boiling point

Changes in T_{mp} and T_{bp} at Higher Pressure



From a Useful Relation: $\left(\frac{\partial \bar{G}}{\partial P}\right)_T = \bar{V}$

Because $\bar{V} > 0$, $\bar{G}$ increases with pressure, and $\bar{V}_{solid} < \bar{V}_{liquid} < \bar{V}_{gas}$

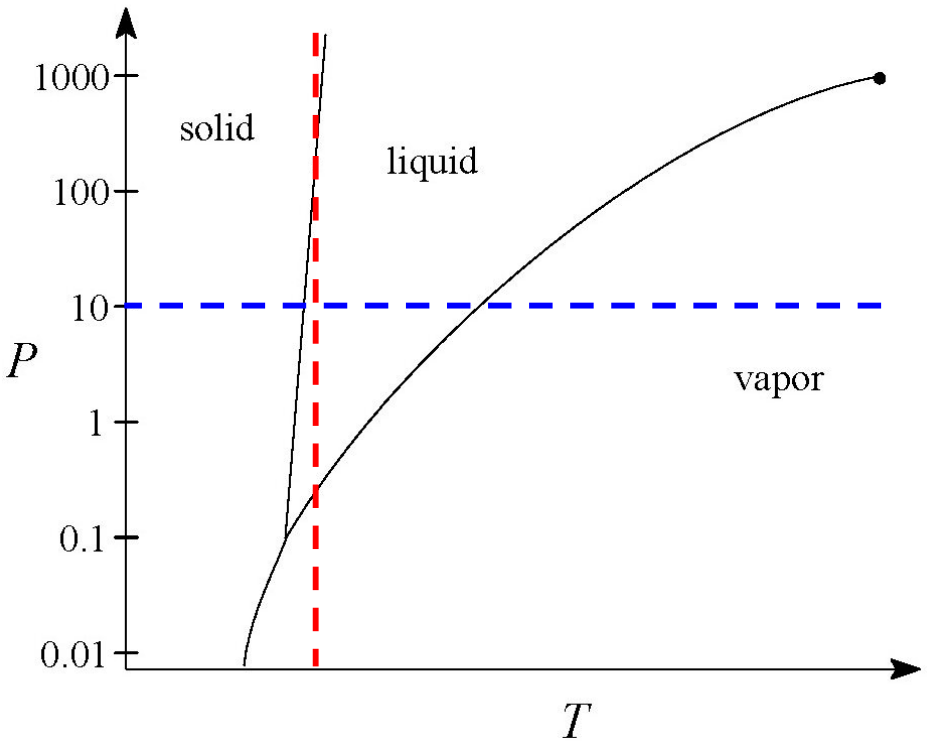
How does the melting point of ice change with increasing pressure?

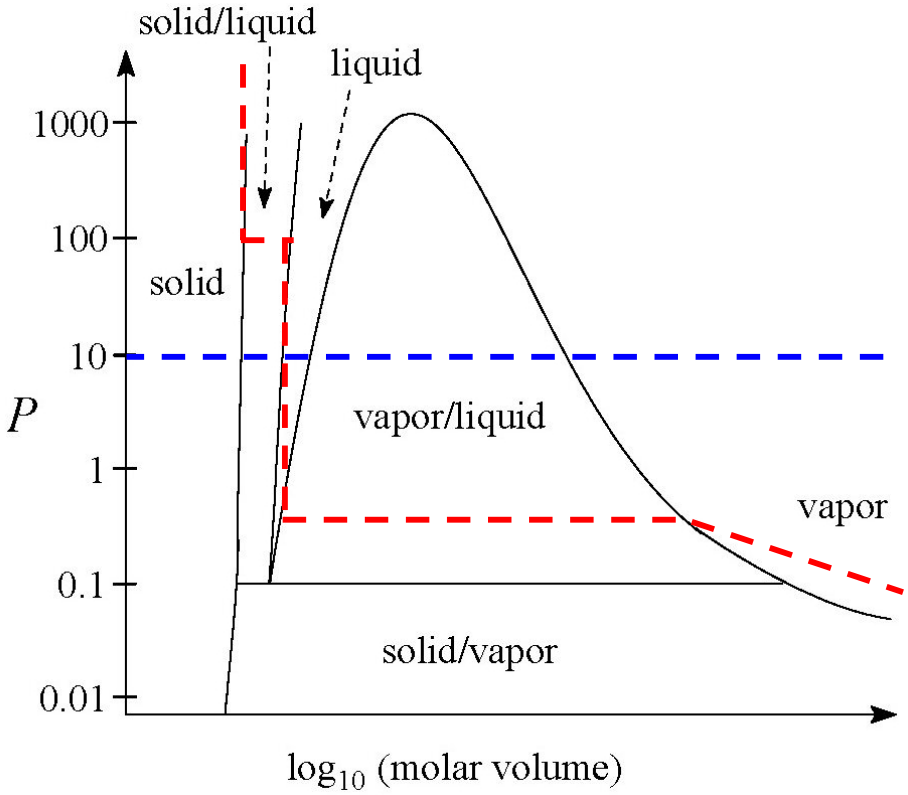
$\bar{V}_{ice} > \bar{V}_{water}$ so the melting point *decreases* a higher pressure.

Ice Skating!

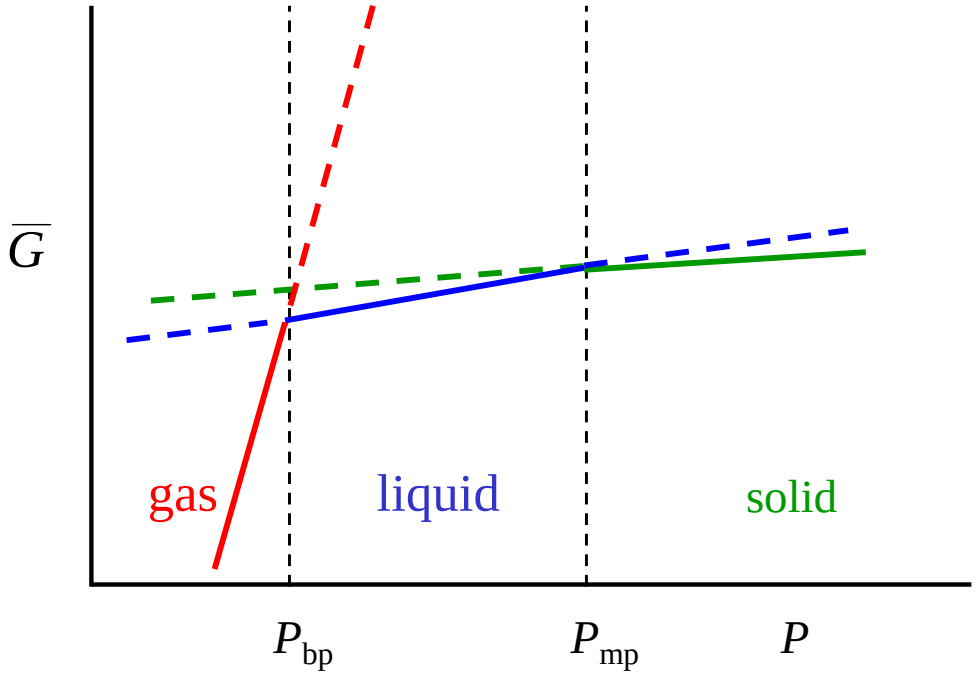
See McQuarrie & Simon Figure 23.6.

Changes in Gibbs Energy at Constant Temperature





Pressure Changes in Gibbs Energy at Constant Temperature



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

$\overline{G}_{solid} = \overline{G}_{liquid}$ at melting pressure

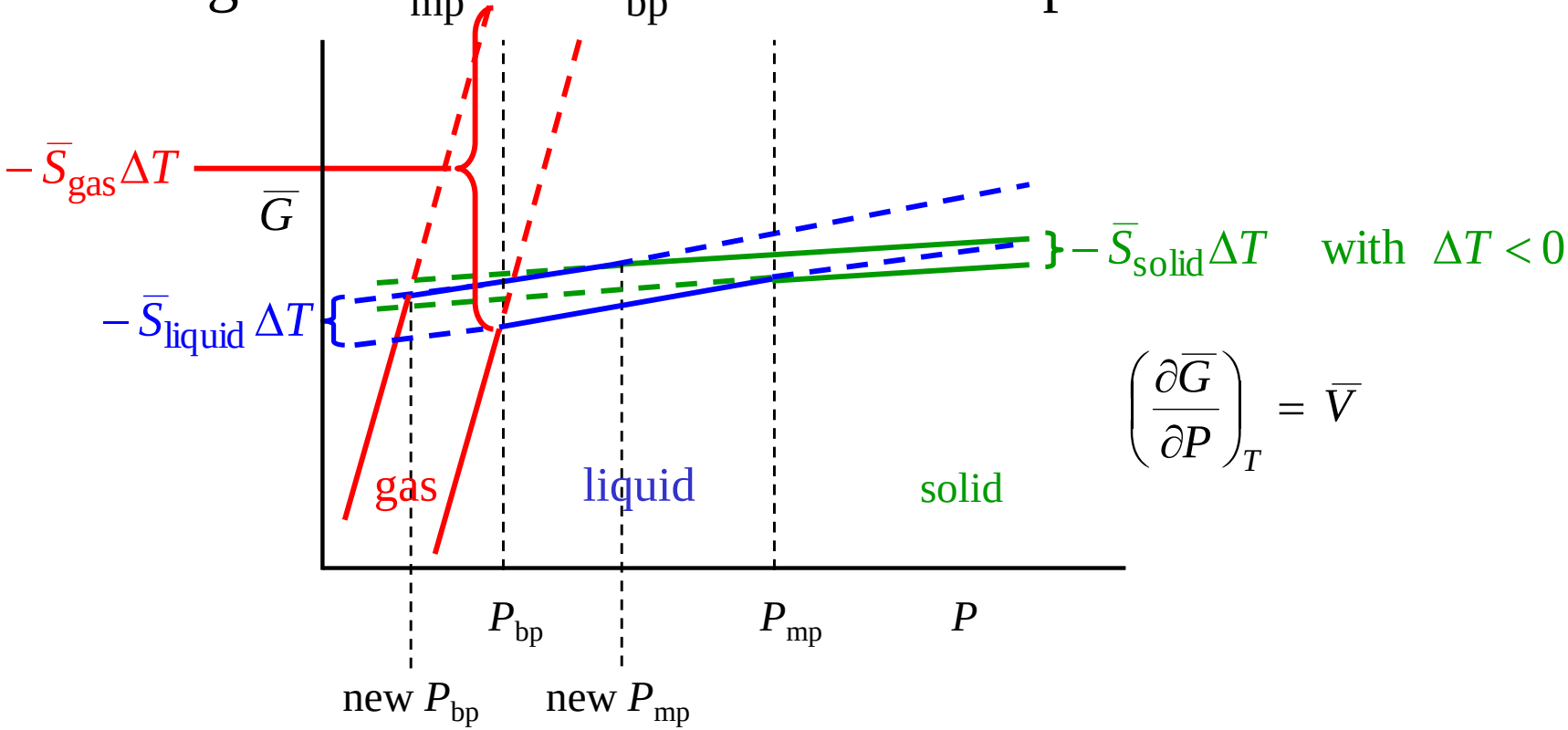
$\overline{G}_{liquid} = \overline{G}_{vapor}$ at boiling pressure

$\overline{G}_{solid} < \overline{G}_{liquid} < \overline{G}_{vapor}$ at pressures above melting pressure

$\overline{G}_{liquid} < \overline{G}_{solid} < \overline{G}_{vapor}$ below melting pressure, above boiling pressure

$\overline{G}_{vapor} < \overline{G}_{liquid} < \overline{G}_{solid}$ at pressures below boiling pressure

Changes in T_{mp} and T_{bp} at Lower Temperature

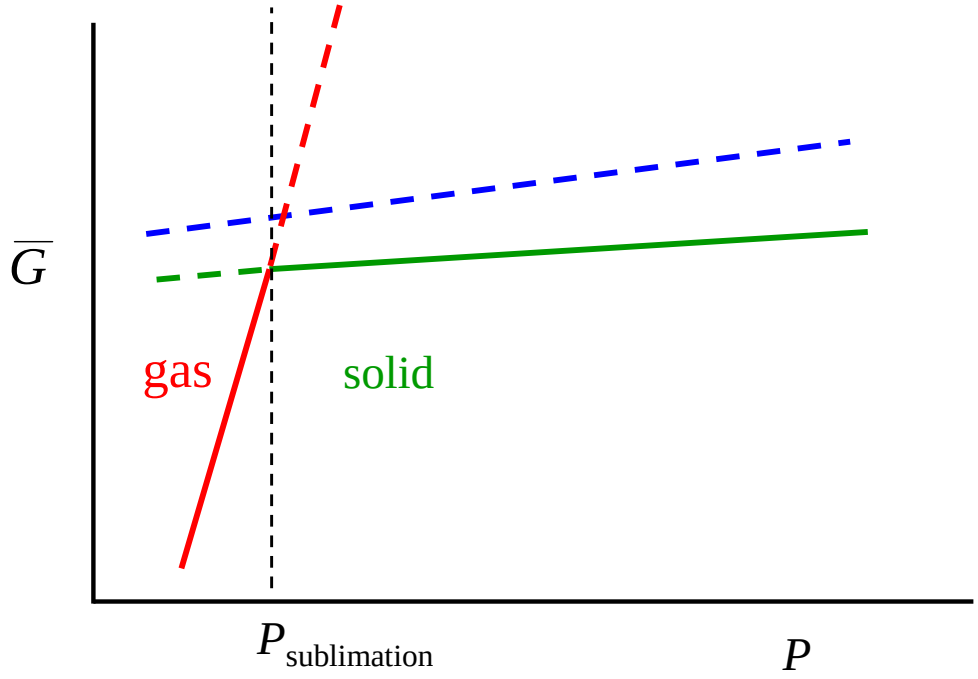


From a Useful Relation: $\left(\frac{\partial \bar{G}}{\partial T}\right)_P = -\bar{S}$

Because $-\bar{S} < 0$, $\bar{G}$ increases with decreasing temperature, and $\bar{S}_{solid} < \bar{S}_{liquid} < \bar{S}_{gas}$

Changes in T_{mp} and T_{bp} at Lower Temperature, cont'd

Consider a constant-temperature path below the triple point.

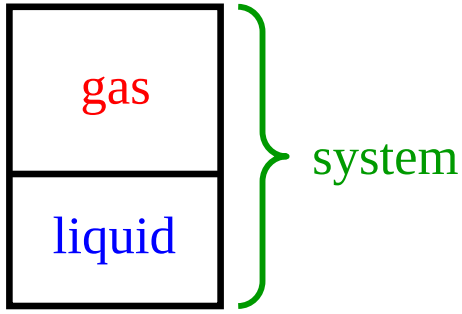


Draw a plot of ΔG vs T at constant P for a pressure below the triple point pressure.

The Chemical Potential, μ

Consider a pure substance with two phases present.

$$G_{\text{system}} = G_{\text{gas}} + G_{\text{liquid}}$$



Imagine an infinitesimal change: *dn* moles of liquid → *dn* moles of gas

$$dn_{\text{liquid}} = -dn_{\text{gas}} \quad \text{(closed system)}$$

How does G_{system} change?

$$dG_{\text{system}} = \left(\frac{\partial G_{\text{gas}}}{\partial n_{\text{gas}}}\right)_{P,T} dn_{\text{gas}} + \left(\frac{\partial G_{\text{liquid}}}{\partial n_{\text{liquid}}}\right)_{P,T} dn_{\text{liquid}}$$

Substitute $dn_{\text{liquid}} = -dn_{\text{gas}}$

$$dG_{\text{system}} = \left[\left(\frac{\partial G_{\text{gas}}}{\partial n_{\text{gas}}}\right)_{P,T} - \left(\frac{\partial G_{\text{liquid}}}{\partial n_{\text{liquid}}}\right)_{P,T}\right] dn_{\text{gas}}$$

Define the chemical potential $\equiv \mu_{\text{gas}} = \left(\frac{\partial G_{\text{gas}}}{\partial n_{\text{gas}}}\right)_{P,T}$; $\mu_{\text{liquid}} = \left(\frac{\partial G_{\text{liquid}}}{\partial n_{\text{liquid}}}\right)_{P,T}$

$$dG_{\text{system}} = (\mu_{\text{gas}} - \mu_{\text{liquid}})dn_{\text{gas}}$$

The Chemical Potential and Chemical Equilibrium

$$dG_{\text{system}} = (\mu_{\text{gas}} - \mu_{\text{liquid}})dn_{\text{gas}}$$

For chemical equilibrium, $dG = 0 \quad \Rightarrow \quad \mu_{\text{gas}} = \mu_{\text{liquid}}$

If not at equilibrium, change n_{gas} (and n_{liquid})

For thermal equilibrium, $dG = 0 \quad \Rightarrow \quad T_{\text{gas}} = T_{\text{liquid}}$

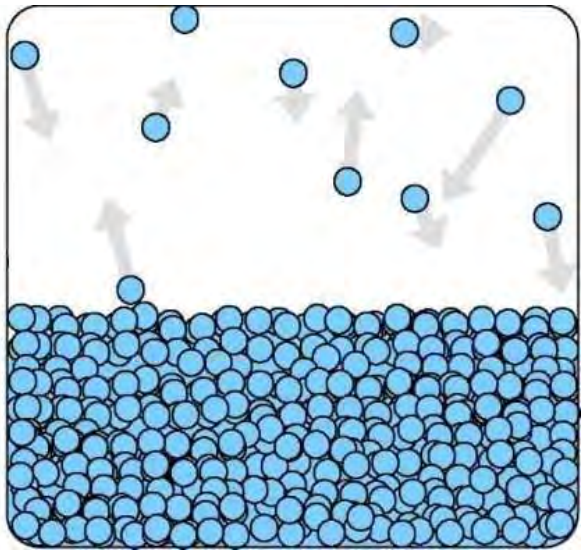
If not at equilibrium, change S_{gas} (and S_{liquid}) $\qquad dS = \dfrac{q_{\text{rev}}}{T}$

For physical equilibrium, $dG = 0 \quad \Rightarrow \quad P_{\text{gas}} = P_{\text{liquid}}$

If not at equilibrium, change V_{gas} (and V_{liquid})

Molecular Basis for Infinitesimal Mass Transfer

Consider a molecule transfering to the gas phase from the liquid phase.



Does dG_{system} decrease?

If 'yes' – molecule stays in the gas phase.

If 'no' – molecule returns to the liquid phase.

Assume dG_{system} is negative when a molecule moves to the gas phase.

$$dG_{system} = (\mu_{gas} - \mu_{liquid})dn_{gas}$$

For $dG_{system} < 0$ and $dn_{gas} > 0$, we conclude $(\mu_{gas} - \mu_{liquid}) < 0$.

The liquid has a higher chemical potential.

Molecule moves from high chemical potential to low chemical potential.

The Chemical Potential is the Molar Gibbs Energy

The Gibbs Energy, *G*, is an extensive property.

G is proportional to the system size.

$$G \propto n$$

$$G = n\mu$$

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

Maxwell Relations and Useful Equations extend to Chemical Potential.

$$\left(\frac{\partial \mu}{\partial P}\right)_T = \left(\frac{\partial \overline{G}}{\partial P}\right)_T = \overline{V} \qquad \left(\frac{\partial \mu}{\partial T}\right)_P = \left(\frac{\partial \overline{G}}{\partial T}\right)_P = -\overline{S}$$

The Clapeyron Equation

At equilibrium, $\mu_{gas} = \mu_{liquid}$

$$\bar{G}_{gas} = \bar{G}_{liquid}$$

$$\bar{V}_{gas}dP - \bar{S}_{gas}dT = \bar{V}_{liquid}dP - \bar{S}_{liquid}dT$$

$$(\bar{V}_{gas} - \bar{V}_{liquid})dP = (\bar{S}_{gas} - \bar{S}_{liquid})dT$$

$$\frac{dP}{dT} = \frac{\bar{S}_{gas} - \bar{S}_{liquid}}{\bar{V}_{gas} - \bar{V}_{liquid}}$$

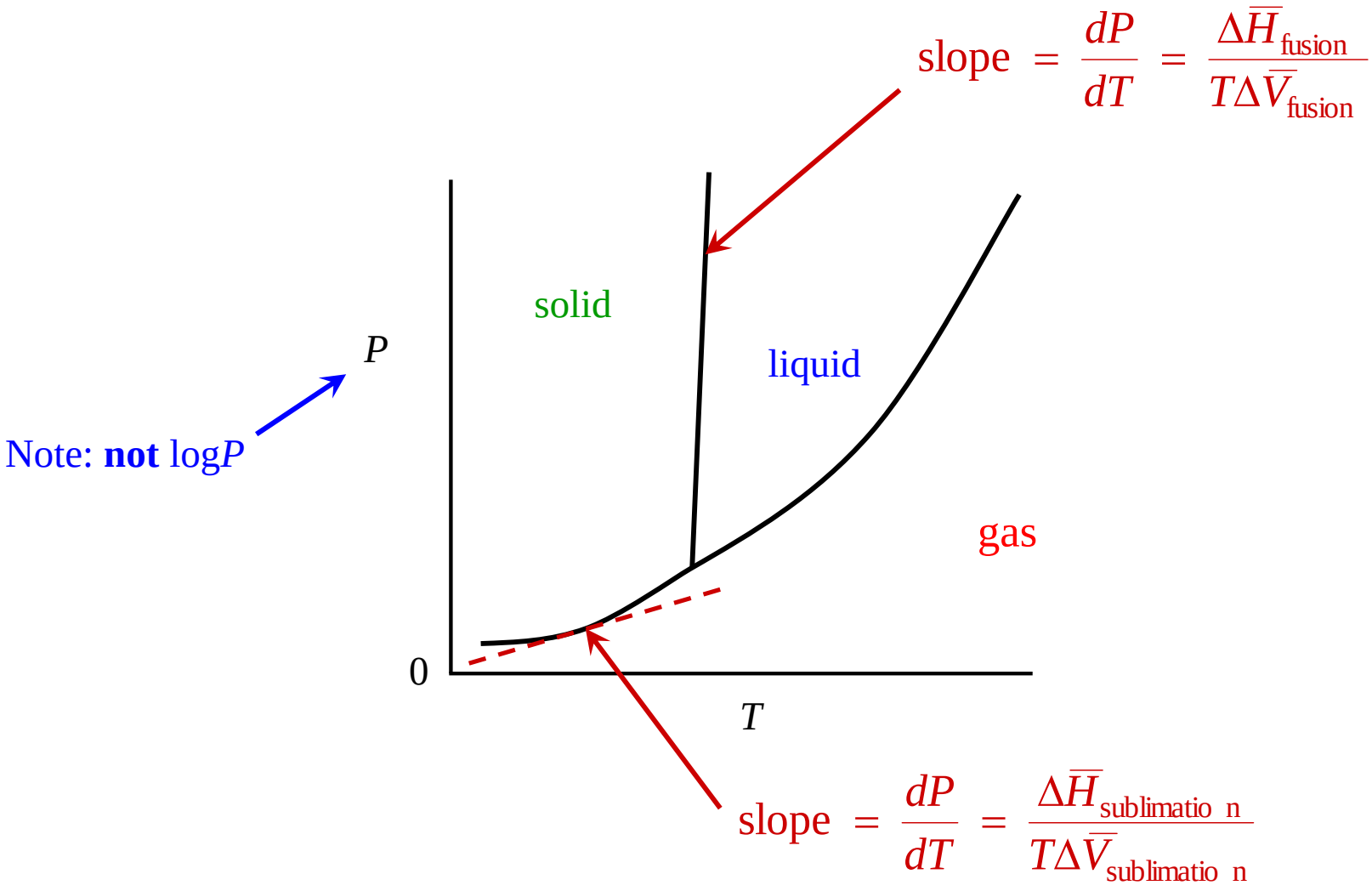
Recall $\Delta\bar{S}_{transition} = \dfrac{\Delta\bar{H}_{transition}}{T}$

$$\boxed{\frac{dP}{dT} = \frac{\Delta\bar{H}_{transition}}{T\Delta\bar{V}_{transition}}}$$

The Clapeyron Equation (1834)

The Clapeyron Equation, cont'd

$$\frac{dP}{dT} = \frac{\Delta\overline{H}_{\text{transition}}}{T\Delta\overline{V}_{\text{transition}}}$$



The Clausius–Clapeyron Equation

Consider the Clapeyron equation for liquid-gas transitions:

$$\frac{dP}{dT} = \frac{\Delta\bar{H}_{\text{vaporization}}}{T(\bar{V}_{\text{gas}} - \bar{V}_{\text{liquid}})}$$

Assume we are far below the critical point, such that $\bar{V}_{\text{gas}} \gg \bar{V}_{\text{liquid}} \Rightarrow \bar{V}_{\text{gas}} - \bar{V}_{\text{liquid}} \approx \bar{V}_{\text{gas}}$

$$\frac{dP}{dT} = \frac{\Delta\bar{H}_{\text{vaporization}}}{T\bar{V}_{\text{gas}}}$$

Assume the gas is ideal: $\bar{V}_{\text{gas}} = \frac{RT}{P}$

$$\frac{dP}{dT} = \frac{\Delta\bar{H}_{\text{vaporization}}}{T\left(\frac{RT}{P}\right)}$$

$$\frac{1}{P}\frac{dP}{dT} = \frac{\Delta\bar{H}_{\text{vaporization}}}{T^2}$$

note: $d(\ln P) = \frac{1}{P}\frac{dP}{dT}$

$$\boxed{\frac{d(\ln P)}{dT} = \frac{\Delta\bar{H}_{\text{vaporization}}}{RT^2}}$$

The Clausius–Clapeyron Equation (1850)

Applying the Clausius–Clapeyron Equation

$$\frac{d(\ln P)}{dT} = \frac{\Delta\overline{H}_{\text{vaporization}}}{RT^2}$$

separate ‘n’ integrate:

$$\int_{\ln P_1}^{\ln P_2} d(\ln P) = \int_{T_1}^{T_2} \frac{\Delta\overline{H}_{\text{vaporization}}}{RT^2}\,dT$$

assume $\Delta\overline{H}_{\text{vaporizati on}}$ is constant

$$\ln P_2 - \ln P_1 = -\frac{\Delta\overline{H}_{\text{vaporization}}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Use to calculate the change in vapor pressure with change in temperature.

Also valid for vapor pressure above a solid. *Why*?

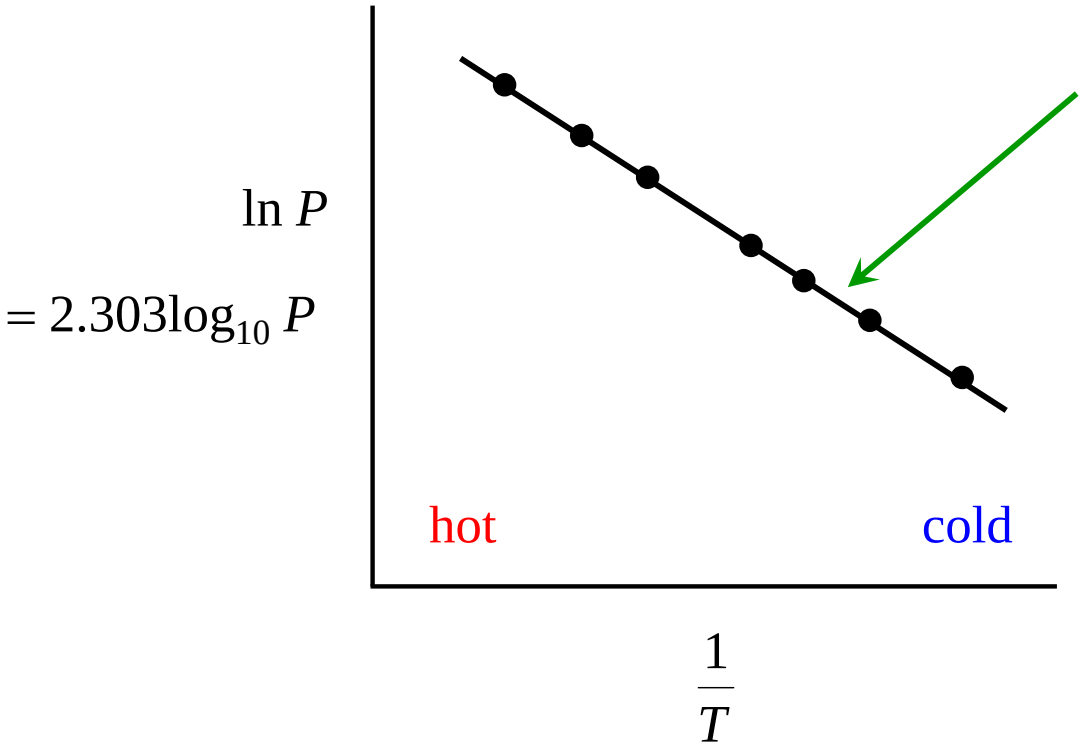
$$\ln P_2 - \ln P_1 = -\frac{\Delta\overline{H}_{\text{sublimation}}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Applying the Clausius–Clapeyron Equation, cont'd

$$\frac{d(\ln P)}{dT} = \frac{\Delta\overline{H}_{\text{vaporization}}}{RT^2}$$

separate 'n' take indefinite integrals:

$$\ln P = -\frac{\Delta\overline{H}_{\text{vaporization}}}{R}\left(\frac{1}{T}\right) + \text{constant}$$



$$\text{slope} = -\frac{\Delta\overline{H}_{\text{vaporizati on}}}{R}$$

If the line is straight, the heat of vaporization is constant.