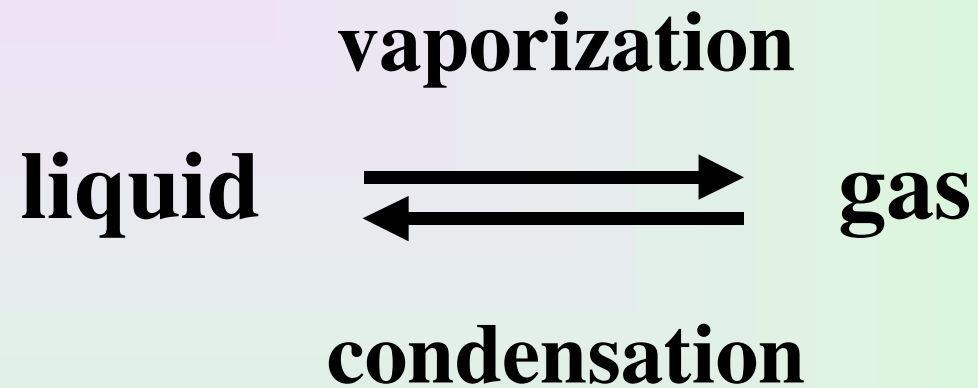
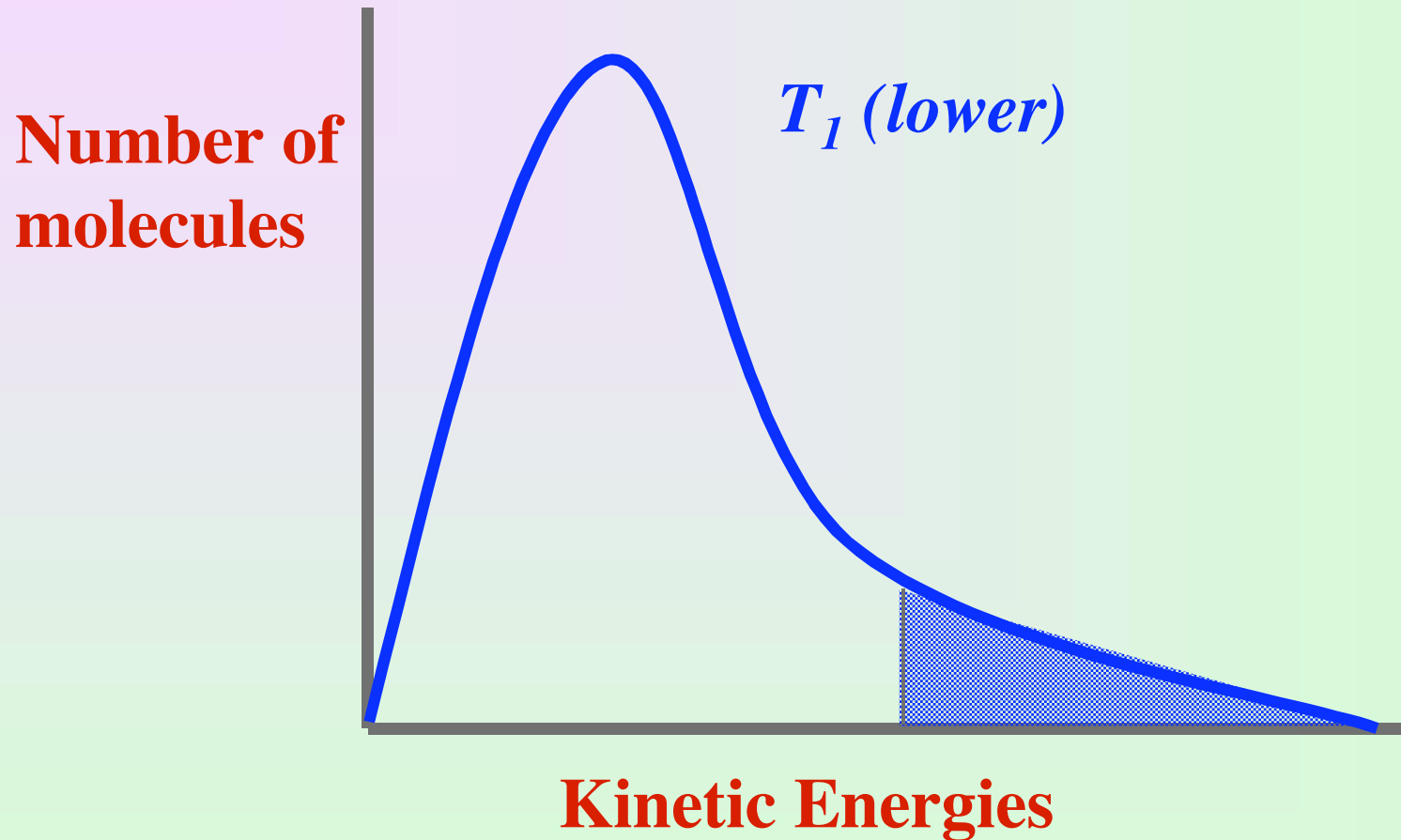


Phase Changes

Liquid-Vapor Equilibrium

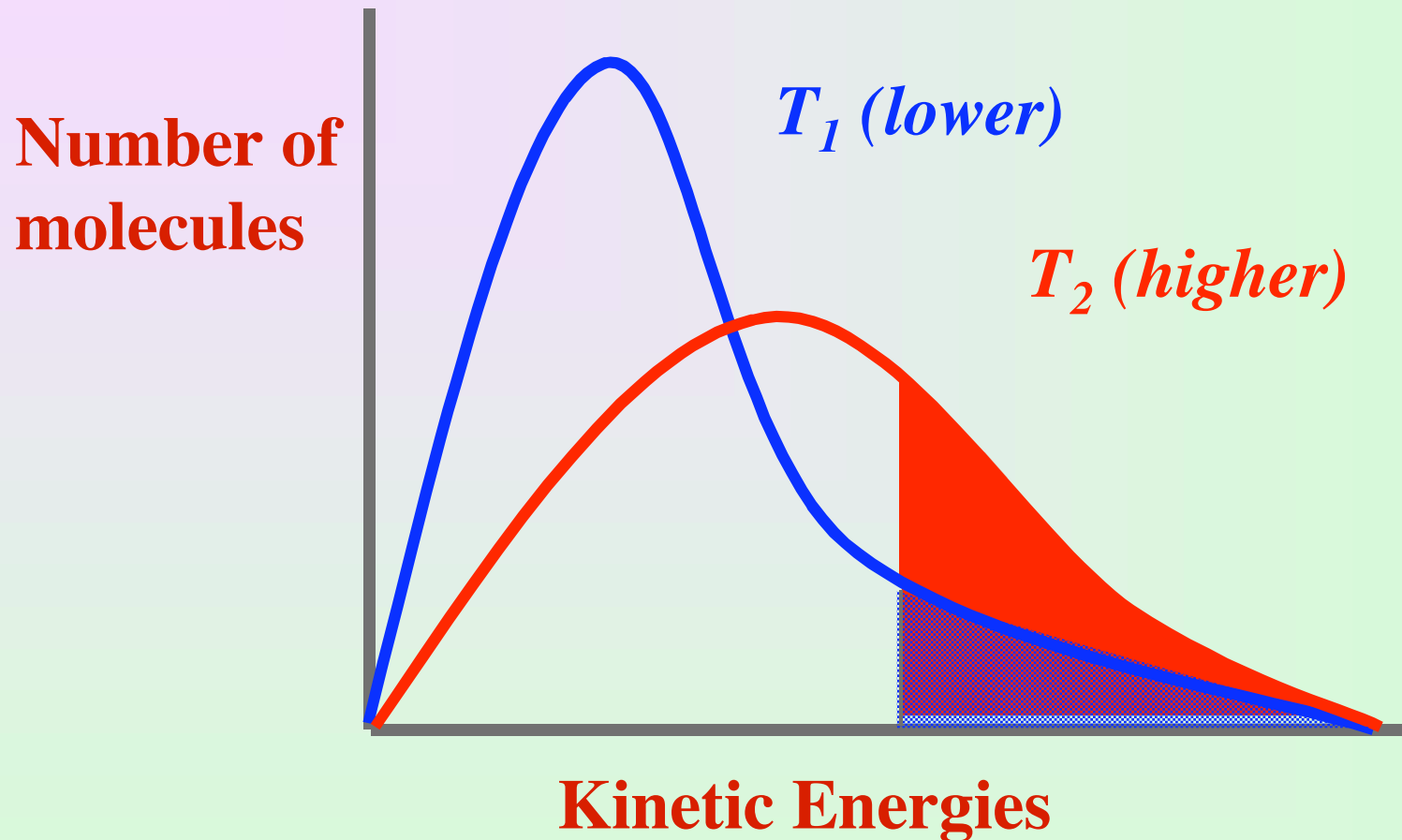


Distribution of kinetic Energies



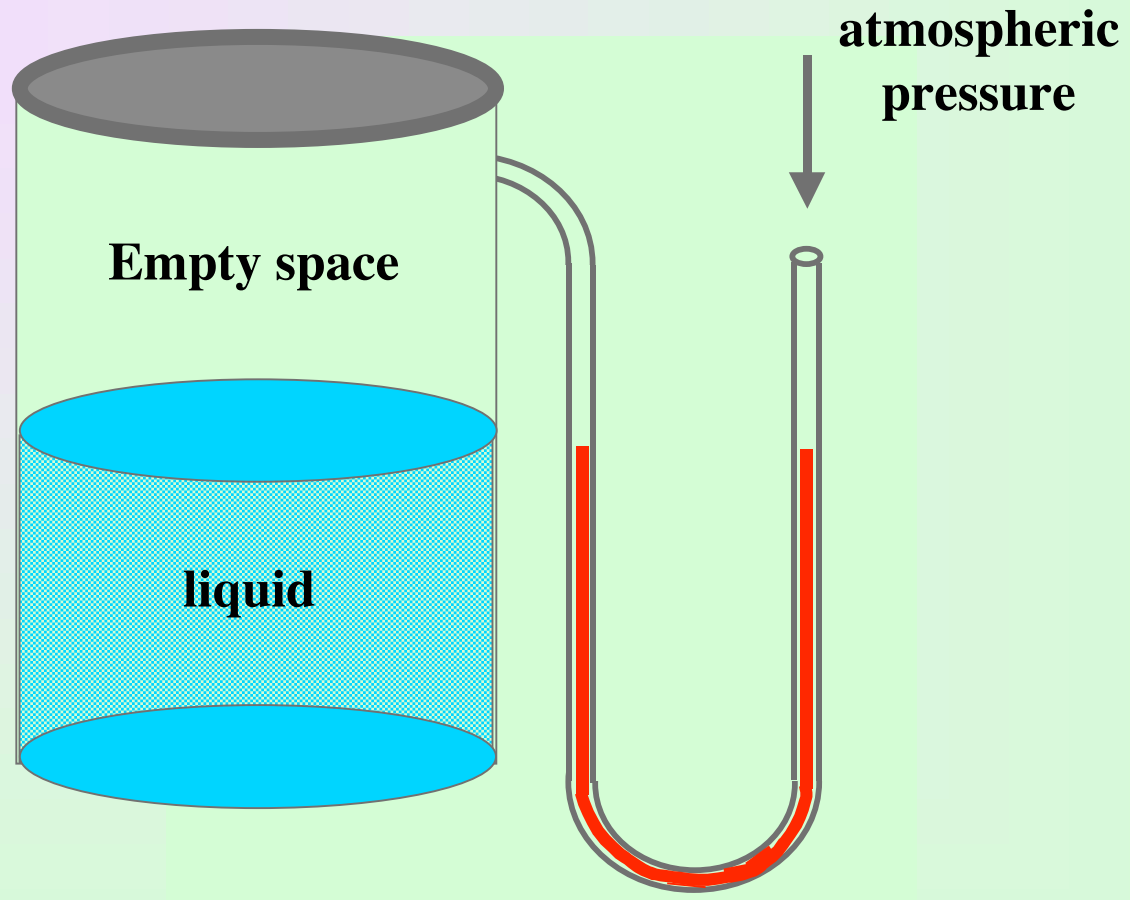
At any given temperature a certain number of molecules in a liquid possess sufficient kinetic energy to escape from the surface

Distribution of kinetic Energies



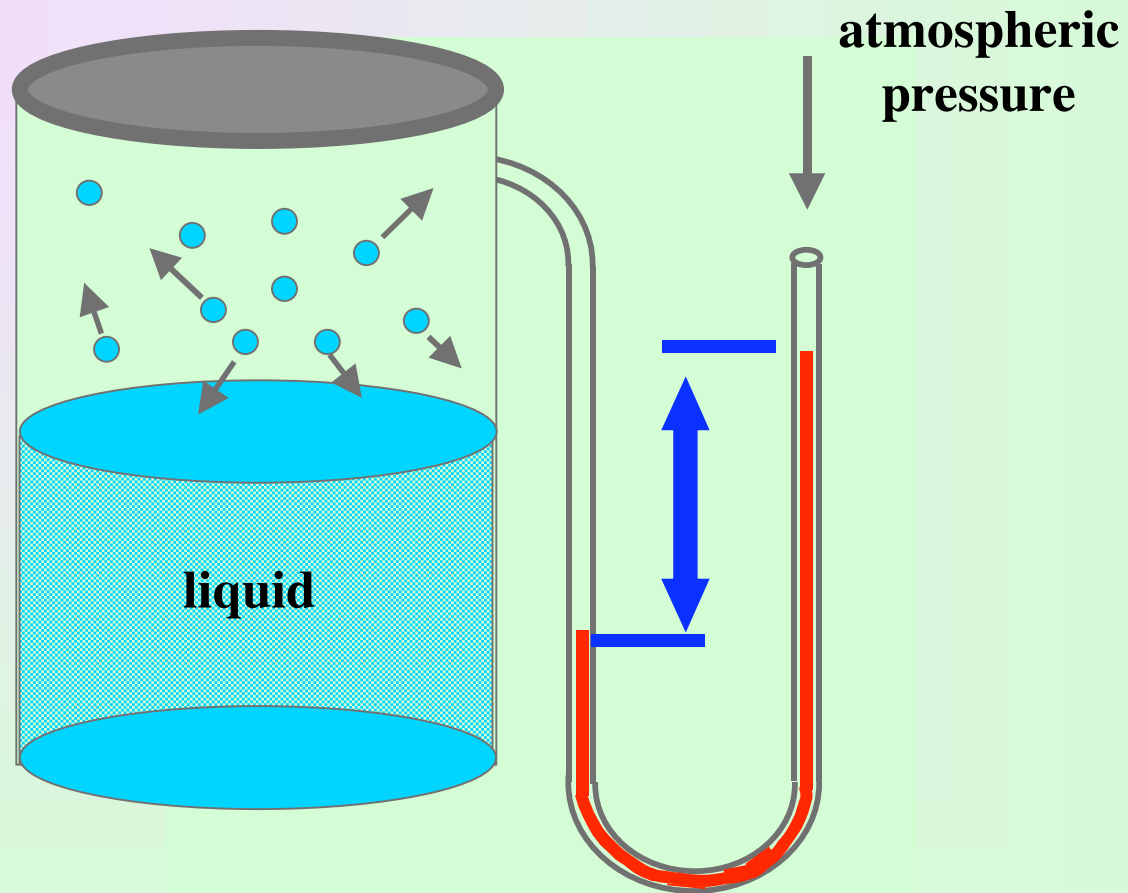
At higher temperatures more molecules in a liquid possess sufficient kinetic energy to escape from the surface

Vapor Pressure



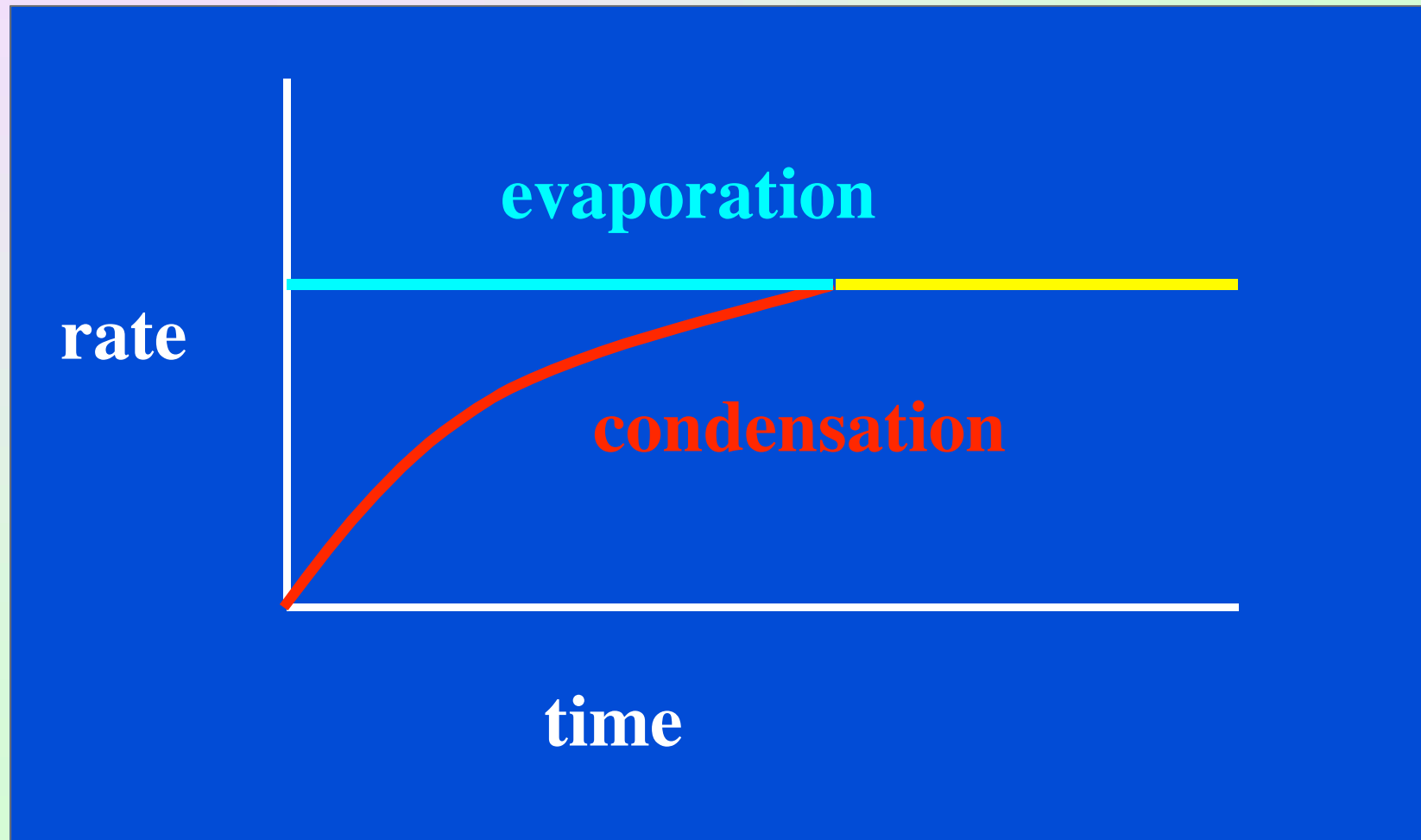
before evaporation

$$P_{\text{v.p.}} = P_{\text{atm}} + h_{\text{Hg}}$$



at equilibrium

At equilibrium the rates of evaporation and condensation are equal.



Condensation and Evaporation

evaporation and condensation are dynamic processes

evaporation and condensation occur simultaneously

the rate of evaporation depends on the temperature and the surface area

the rate of condensation increases as the number of molecules in the gas phase increases

a system is at equilibrium when the rates of the forward and reverse processes are equal

Vapor Pressure

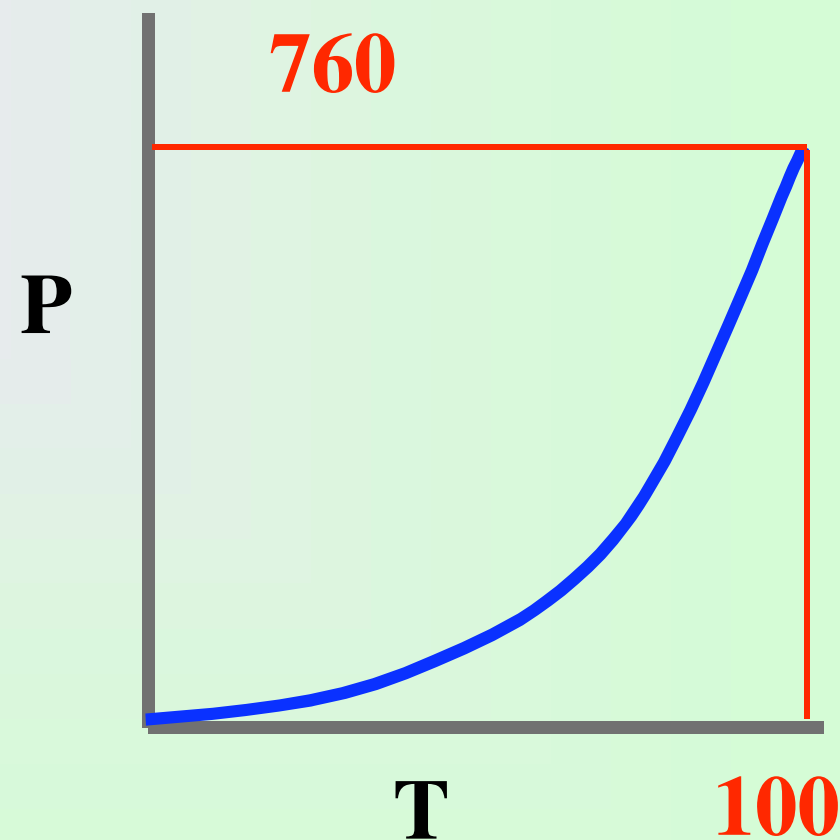
pressure of the vapor, when vapor and liquid are in equilibrium with one another

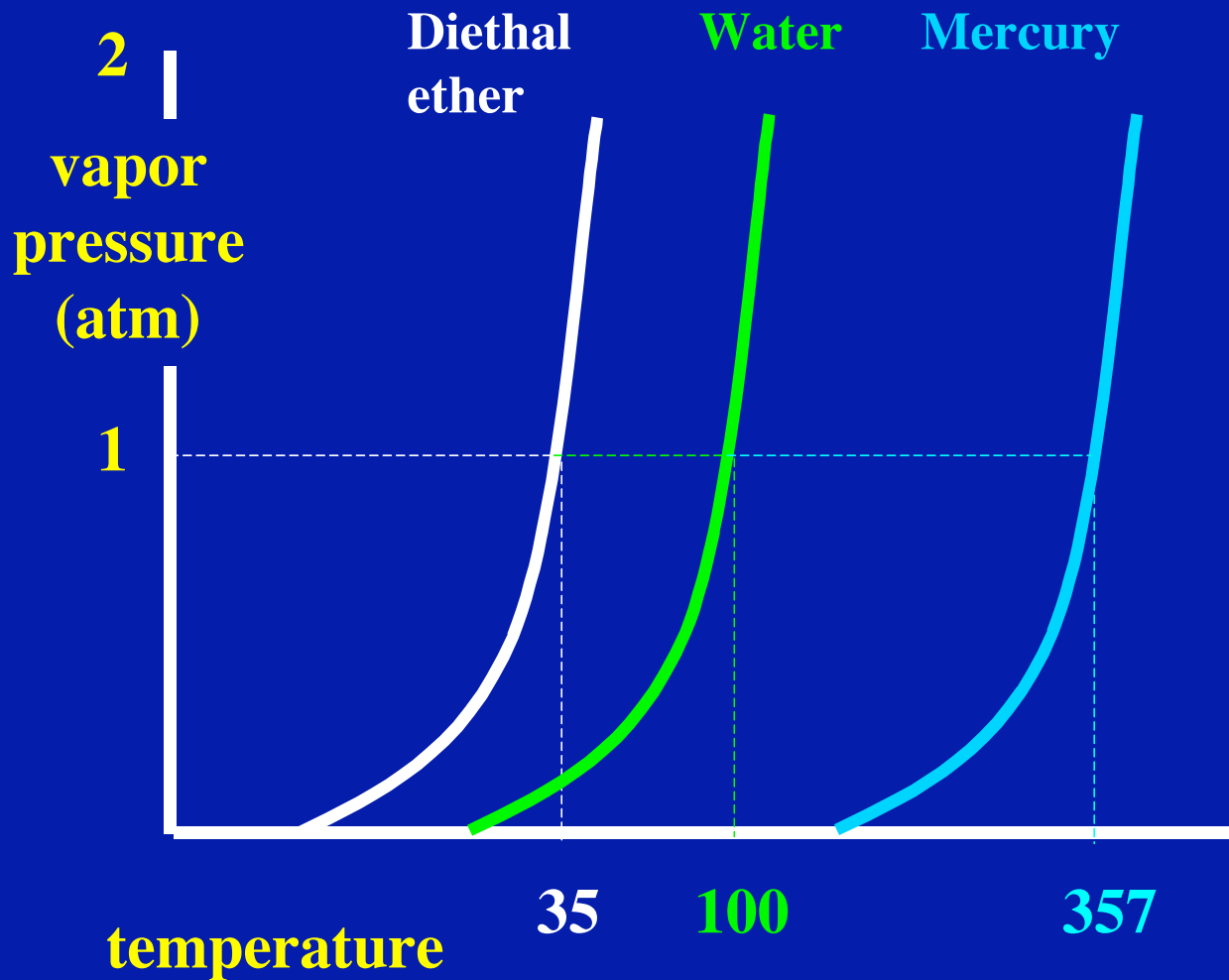
vapor pressure is a characteristic property of a particular substance

Increases with temperature

Vapor Pressure of Water

T (C°)	P (torr)
0.0	4.579
10.0	9.209
20.0	17.535
25.0	23.756
30.0	31.824
40.0	55.324
60.0	149.4
70.0	233.7
90.0	525.8

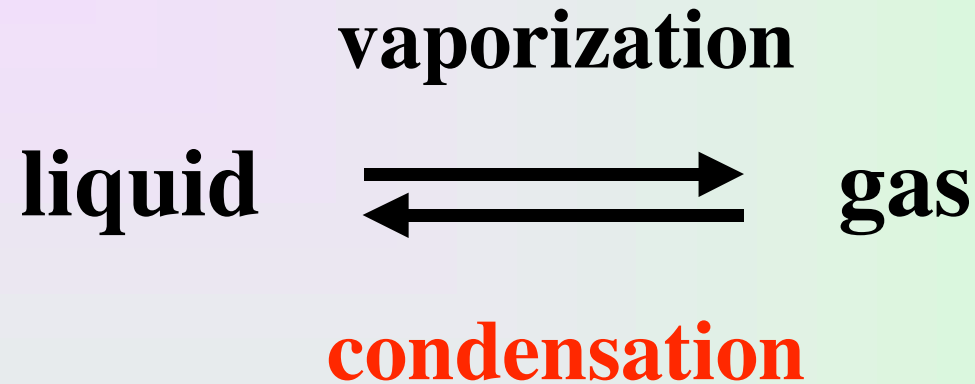




The increase in vapor pressure with temperature for three liquids at 1 atm pressure are shown on the horizontal axis.

Heat of Vaporization and Boiling Point

Equilibrium and Vapor Pressure



Molar heat of a vaporization = ΔH_{vap}

Related to the strength of intermolecular forces

Molar heat of a condensation = $-\Delta H_{\text{vap}}$
exothermic

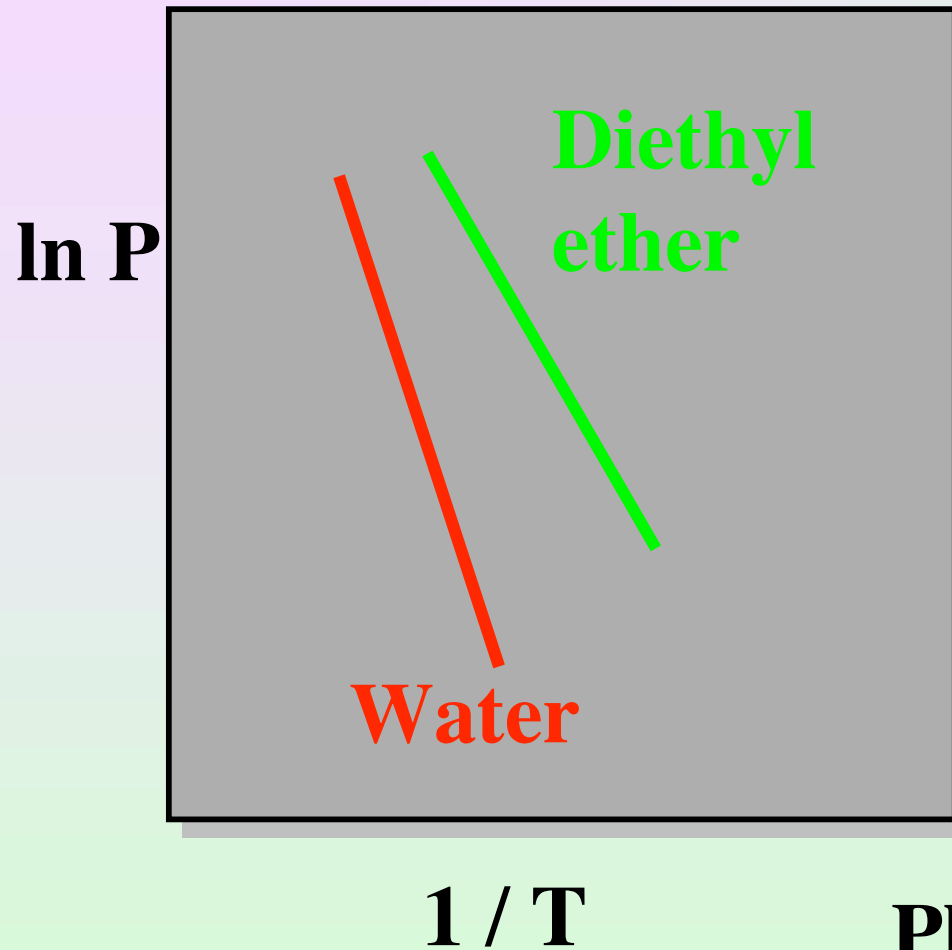
Clausius-Clapeyron Equation

$$\ln P = - \frac{\Delta H_{\text{vap}}}{RT} + C$$

rearrange to give equation of straight line

$$\ln P = - \frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T} \right) + C$$

a plot of $\ln P$ versus $1/T$ gives a straight line
with a slope of $-\Delta H_{\text{vap}}/R$



$$\text{Slope} = - \frac{\Delta H_{\text{vap}}}{R}$$

**Plots of ln P verses 1 / T
for water and diethyl
ether.**

Alternative form of Clausius-Clapeyron Equation

$$\ln P = - \frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T} \right) + C$$

$$\ln \left(\frac{P_1}{P_2} \right) = \frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

Example

the vapor pressure of ethyl ether is 401 mmHg at 18°C. Calculate its vapor pressure at 32.0 °C ($\Delta H_{\text{vap}} = 26.0 \text{ kJ/mol}$)

$$\ln \left(\frac{P_1}{P_2} \right) = \frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad P_2 = 656.7 \text{ mmHg}$$

$$\ln \left(\frac{401 \text{ mmHg}}{P_2} \right) = \frac{26000 \text{ J/mol}}{8.314 \text{ J/Kmol}} \left(\frac{1}{305 \text{ K}} - \frac{1}{291 \text{ K}} \right)$$

Molar heats of vaporization for selected liquids

substance		B.Pt. °C	ΔH_{vap} kJ/mol
Argon	Ar	- 186	6.3
Methane	CH ₄	- 164	9.2
Diethyl ether	CH ₃ CH ₂ OCH ₂ CH ₃	34.6	26.0
Ethanol	CH ₃ CH ₂ OH	78.3	39.3
Benzene	C ₆ H ₆	80.1	31.0
Water	H ₂ O	100	40.79
Mercury	Hg	357	59.0

Definition of Boiling Point

temperature at which vapor pressure of a substance equals external pressure

***normal boiling point:* boiling point when the external pressure equals 1 atmosphere**

Critical Temperature and Pressure

Critical Points

critical temperature: temperature above which gas cannot be liquefied no matter how great the applied pressure (is the highest temperature at which a substance can exist as a liquid)

critical pressure: the minimum pressure required to bring about liquefaction at the critical temperature

Critical Pressures and Temperatures for selected compounds

substance		T_c (°C)	P_c (atm)
Argon	Ar	- 186	6.3
Methane	CH₄	- 83.0	45.6
Carbon dioxide	CO₂	31.0	73.0
Ethanol	CH₃CH₂OH	243	63
Benzene	C₆H₆	288.9	47.9
Water	H₂O	374.4	219.5
Mercury	Mg	1462	1036

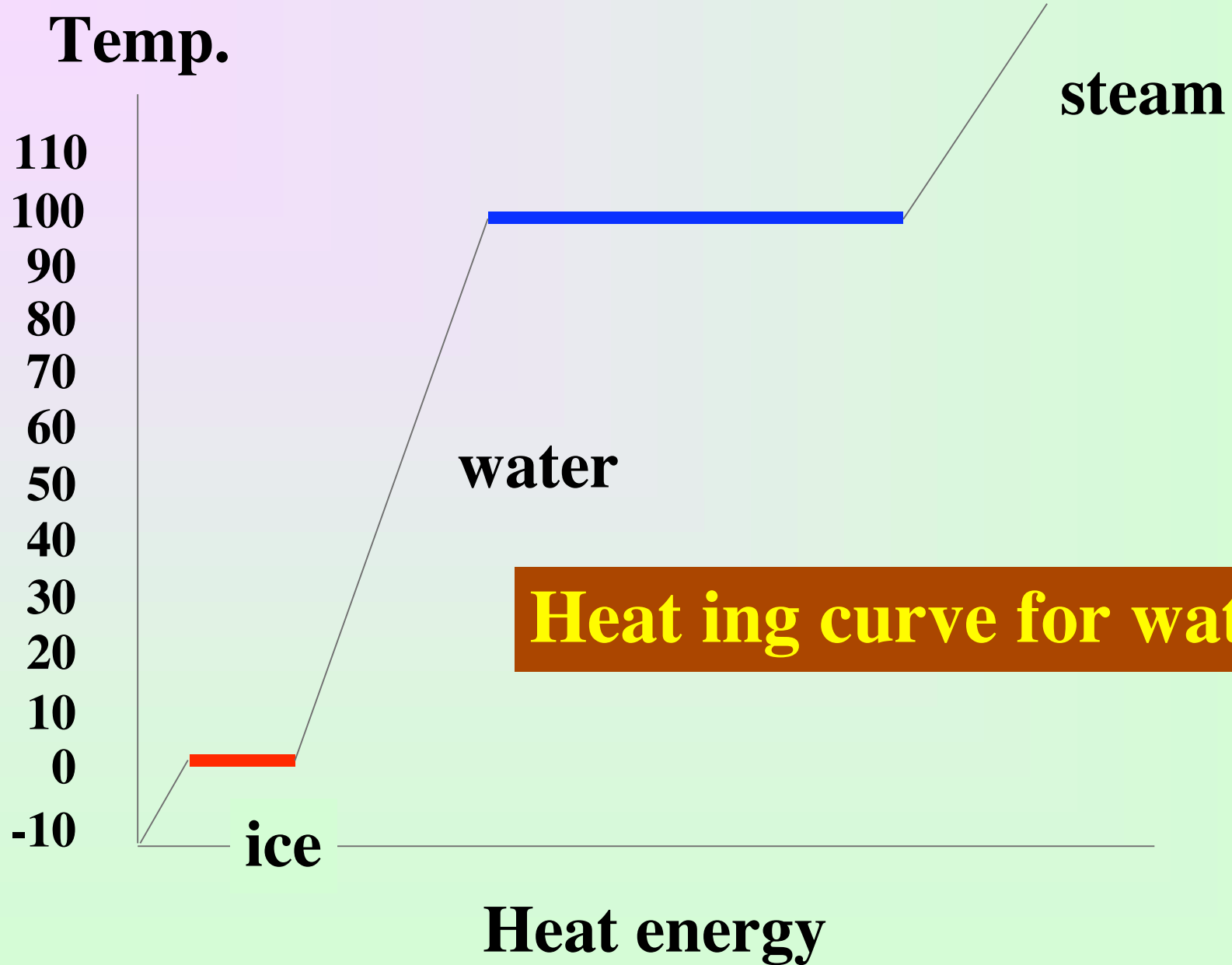
Liquid-Solid Equilibrium

Liquid-Solid Equilibrium

melting point

temperature at which solid and liquid phases coexist in equilibrium

***normal melting point:* melting point at a pressure of 1 atmosphere**



Molar heats of fusion for selected liquids

substance		M.Pt. °C	ΔH_{fusion} kJ/mol
Argon	Ar	- 190	1.3
Methane	CH ₄	- 183	0.84
Diethyl ether	CH ₃ CH ₂ OCH ₂ CH ₃	- 116.2	6.90
Ethanol	CH ₃ CH ₂ OH	- 117.3	7.61
Benzene	C ₆ H ₆	5.5	10.9
Water	H ₂ O	0	6.01
Mercury	Hg	- 39	23.4

Molar heats of vaporization and fusion for selected liquids

substance		ΔH_{vap} kJ/mol	ΔH_{fusion} kJ/mol
Argon	Ar	6.3	1.3
Methane	CH ₄	9.2	0.84
Diethyl ether	CH ₃ CH ₂ OCH ₂ CH ₃	26.0	6.90
Ethanol	CH ₃ CH ₂ OH	39.3	7.61
Benzene	C ₆ H ₆	31.0	10.9
Water	H ₂ O	40.79	6.01
Mercury	Mg	59.0	23.4

Solid-Vapor Equilibrium

Solid - Vapor Equilibrium



The process in which molecules go directly from the solid into the vapor phase is called **sublimation**.

Changes of State

