Shou-Hang Bo （薄首行）
Assistant Professor
UM– SJTU Joint Institute
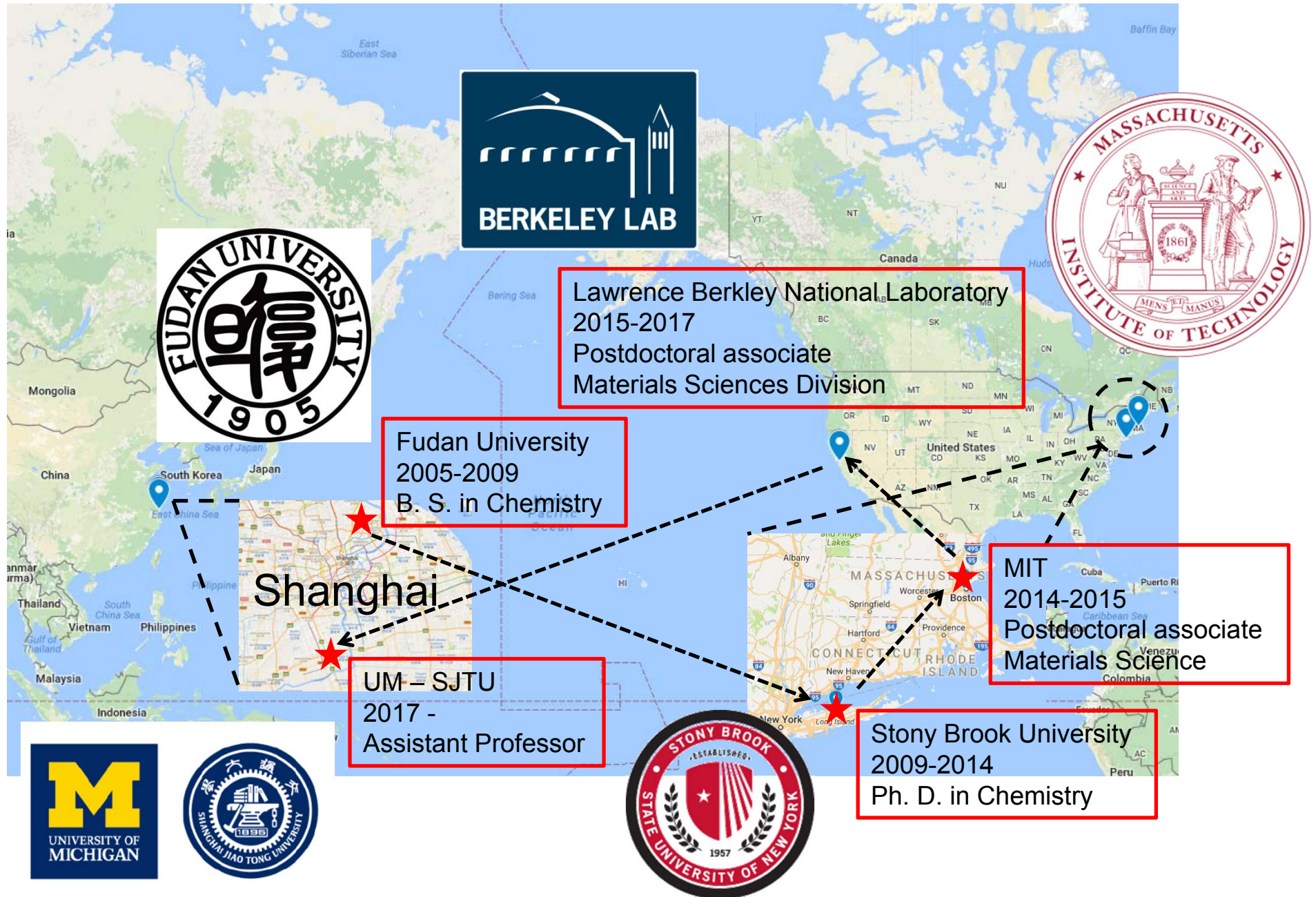
shouhang.bo@sjtu.edu.cn

Born in Xingtai, Hebei

B. S. in Chemistry, Fudan University, 2009
Ph. D. in Chemistry, Stony Brook University, 2014

Postdoctaral Fellow,
Department of Materials Science & Engineering, MIT, 2014 – 2015

Materials Sciences Division, Lawrence Berkeley National
Laboratory, 2015 - 2017

Education and professional experiences

Research Interests

Fundamental:
Chemistry – Structure – Property Correlations in Inorganic Materials

Applied:
❑ High energy density, fast charging rechargeable batteries

❑ Theories of inorganic materials synthesis with predictive power

Office hour

Wednesdays, 3 – 5 PM, Rm 534, Longbin Building

Quiz 2

Nov. 14th, Wednesday, 8:55 AM to 9:40 AM

States of Matter (gas, liquid and solid); Thermodynamics; Physical and Chemical Equilibria

Grading

Homework Assignments	**20%**
Quizzes	**30%**
Final Exam	**50%**
Total Maximum	**100%**

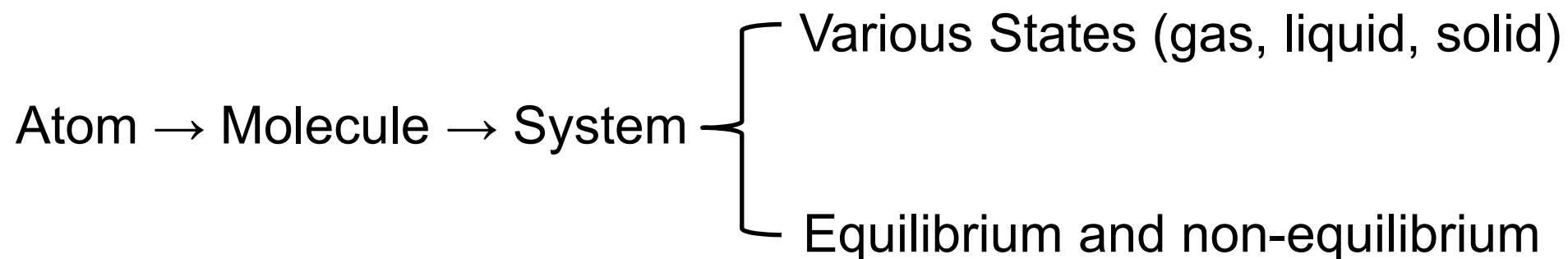Written note of one A4 paper is allowed in the tests

A, B, C, D, F

$< 60\% \rightarrow$ **F**

I reserve the right to curve the grade and I want everybody to succeed
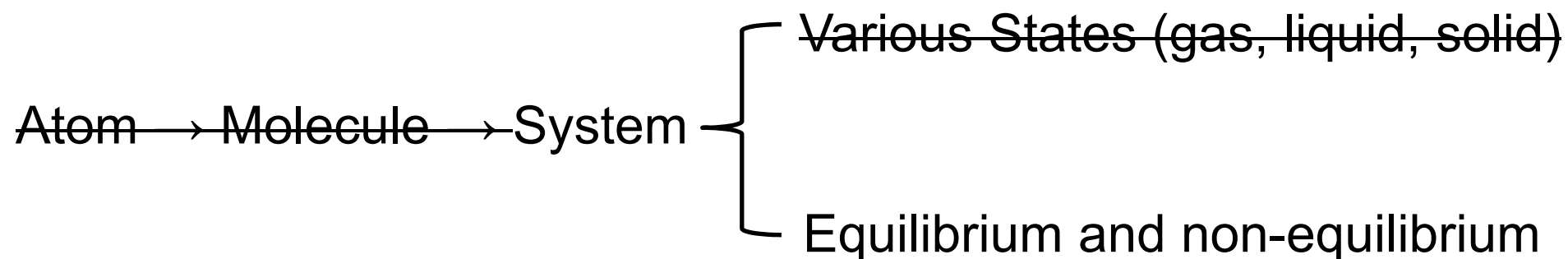
KEY QUESTIONS TO BE ADDRESSED:

1. What determine the properties of matters?

2. How to manipulate chemical reactions?

3. How science (*technology*) evolves?

Bottom-up Approach of Understanding Chemical Principles

Atom → Molecule → System
- Various States (gas, liquid, solid)
- Equilibrium and non-equilibrium

Bottom-up Approach of Understanding Chemical Principles

Atom → Molecule → System
- ~~Various States (gas, liquid, solid)~~
- Equilibrium and non-equilibrium

Path to succeed

BO	Lecture
TAs	Recitation
YOU	Reading
YOU	Homework
YOU	Quizzes
YOU	Final

Transitioning from high school to college, you are now responsible for your own education

Some math…

Tuition 50,000 RMB

~35 weeks

1,500 RMB/ week

~300 RMB/day

Every second you live is ***irreversible***

Classroom behavior

Once you are in the classroom, you must follow the rules.
Let's be professional.

❑ No talking
❑ No food
❑ No disruptive behavior
❑ No cell phone
❑ ……

Honesty

You cannot cheat

Focus 5
Equilibrium
Physical Equilibria + Chemical Equilibria

Here

- We explore further the nature of three states of matter: solids, liquids, and gases.
- We identify how matter transforms between each of these states.
- We gain a deeper understanding of solutions, their composition, and physical properties.
- What we learn here helps us understand how to separate chemicals from each other.

One-component system

Phases and Phase Transitions

Matter exists in a single phase such as a **solid**, **liquid,** or **gas**. A **phase change** occurs when <u>converting one phase into another</u>.

Carbon has three distinct *solid phases*: diamond, graphite, and Bucky balls. **Helium** is only known to exist as a gas and liquid.

Remember (Focus 4) phase changes, <u>at constant temperature</u>, are an equilibrium process, **ΔG = 0**.

What Is Vapor Pressure?

Water vapor
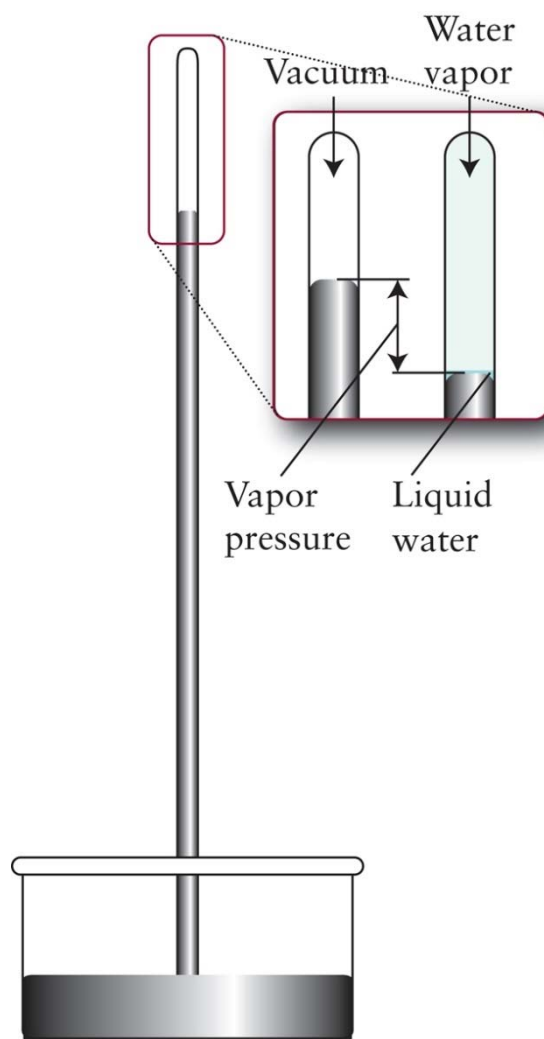
Vacuum

Vapor pressure   Liquid water

Figure 5A.1
Atkins, *Chemical Principles: The Quest for Insight*, 7e
W. H. Freeman & Company, © 2016 by P. W. Atkins, L. L. Jones, and L. E. Laverman

All of the air is evacuated from the tube.

First a tiny drop of water is added at the top:
- All of the water vaporizes.
- The water vapor exerts a force against the mercury, pushing it down.

Second, more water is added:
- However all added water continues to go into the vapor phase.

Third, still more water is added:
- This time the water added pools up on top of the mercury.
- Once water pools up, we have reached the water vapor pressure.
- The difference in height of mercury levels is the pressure of water vapor.

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Vapor Pressure: **Volatile**

A volatile substance has a vapor pressure at *ordinary temperatures*.

Methanol (vapor pressure 98 Torr at 20°C) is highly volatile; mercury (1.4 mTorr) is not.

Solids also exert vapor pressures, but their vapor pressures are low because their molecules are gripped more tightly together.

When a solid vaporizes the process is called "**sublimation,**" so a solid has vapor pressure too, although usually negligibly low

Vapor Pressure: Model In a Closed System

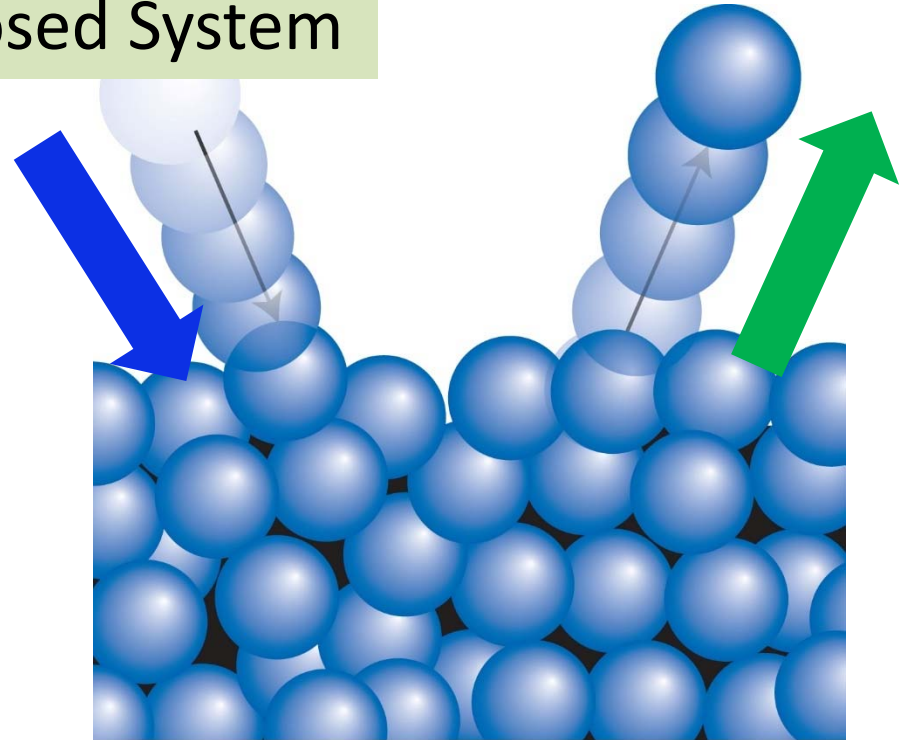Evaporation takes place at the surface because molecules are bound to fewer neighbors.

Figure 5A.2
Atkins, *Chemical Principles: The Quest for Insight*, 7e
W. H. Freeman & Company, © 2016 by P. W. Atkins, L. L. Jones, and L. E. Laverman

A **dynamic equilibrium** is when the *rate* of **escaping** matches the *rate* of **returning**. For liquid water and its vapor this is denoted:
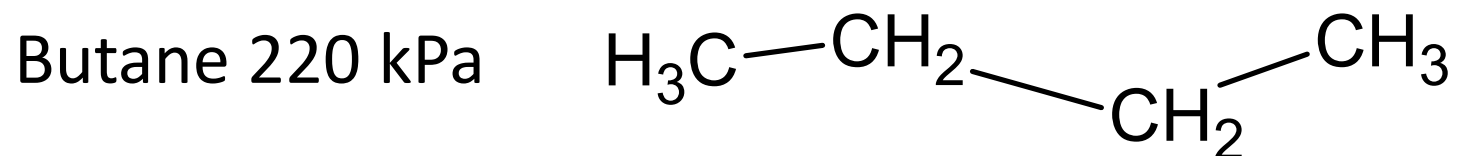
$$H_2O(l) \quad H_2O(g)$$

rate of evaporation = *rate* of condensation

Volatility and Intermolecular Forces

The strength of the intermolecular forces determines its vapor pressure.

Solids and gases aside, <u>liquids</u> with **weak intermolecular forces** have the **highest vapor pressure**.

Butane 220 kPa $\quad$ H_3C-CH_2 $\quad$ CH_2 $\quad$ CH_3

<u>Liquids</u> with **strong intermolecular forces**, ones capable of **forming hydrogen bonds,** have the **lowest vapor pressure**.

Ethanol: 5.95 kPa $\quad$ H_3C-CH_2 $\quad$ OH

The Variation of Vapor Pressure with Temperature

See note

At equilibrium the molar Gibbs free energies of the liquid and vapor are the same:

$$G_{vap} = G_m(g) - G_m(l) = 0$$

Because the liquid Gibbs free energy is almost independent of pressure, we replace $G_m(l)$ with its standard value (at 1 bar),

$$G_m°(l): \quad G_m(g, P) = G_m°(g) + RT \ln P$$

to produce: $G_{vap} = \{G_m°(g) + RT \ln P\} - G_m°(l)$

Next combine the G_m terms:

The Variation of Vapor Pressure with Temperature

$\{ G_m°(g) - G_m°(l) \} + RT \ln P$

Noting that $G_m°(g) - G_m°(l) = \Delta G°_{vap}$ for a vapor and liquid:
$\Delta G°_{vap} + RT \ln P$

Solving for just $\ln P = -\dfrac{\Delta G°_{vap}}{RT}$

(Focus 4) $\Delta G°_{vap} = \Delta H°_{vap} - T\Delta S°_{vap}$ (substitute into above)

$\ln P = -\dfrac{\Delta H°_{vap}}{RT} + \dfrac{\Delta S°_{vap}}{R}$ (P and T change little, and these are state functions, so final – initial).

The Variation of Vapor Pressure with Temperature

$$\ln P_2 - \ln P_1 = \left(-\frac{\Delta H°_{vap}}{RT_2} + \frac{\Delta S°_{vap}}{R}\right) - \left(-\frac{\Delta H°_{vap}}{RT_1} + \frac{\Delta S°_{vap}}{R}\right)$$

and since entropy doesn't change much, we deduced the Clausius-Clapeyron equation.

$$\ln \frac{P_2}{P_1} = \frac{\Delta H°_{vap}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \text{ or noting the sign and } T \text{ changes}$$

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

Clausius - Clapeyron equation

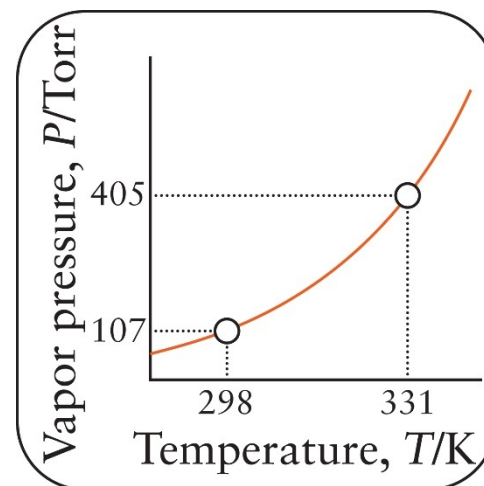$$\ln \frac{P_2}{P_1} = \frac{\Delta H°_{vap}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

Vapor pressure increases with increasing temperature because:

- $T_2 > T_1$ is positive,
- $\ln (P_2/P_1)$ is positive too because enthalpy of vaporization is positive.

$\Delta H_{vap}°$ is a measure of the intermolecular interaction strength (ion–dipole, dipole–dipole, hydrogen bonding, London forces).

Example 5A.1 Tetrachloromethane, CCl_4, which is now known to be carcinogenic, was once used as a dry-cleaning solvent. The enthalpy of vaporization of CCl_4 is 33.05 kJ·mol^{-1} and its vapor pressure at 57.8°C is 405 Torr. What is the vapor pressure of tetrachloromethane at 25.0°C?

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

Dry cleaning is NOT a dry process!

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

33.05 kJ·mol^{-1} corresponds to 3.305×10^4 J·mol^{-1}

$T_2 = 25.0 + 273.15$ K $= 298.2$ K

$T_1 = 57.8 + 273.15$ K $= 331.0$ K

$R = 8.3145$ J·K^{-1}·mol^{-1}

$$\ln \frac{P_2}{P_1} = \frac{3.305 \times 10^4 \text{ J·mol}^{-1}}{8.3145 \text{ J·K}^{-1}\text{·mol}^{-1}} \left(\frac{1}{331.0 \text{ K}} - \frac{1}{298.2 \text{ K}} \right)$$

$\ln \dfrac{P_2}{P_1} = -1.33$, $P_1 = 405$ Torr

$P_2 = 405$ Torr $\times\ e^{-1.33} = 107$ Torr

Water at 100°C   Gold at 2807°C

The **_normal boiling point_**, T_b, is the temperature it boils at when the atmospheric pressure is 1 atm.

At lower pressures, for instance at the summit of Mt. Everest, the pressure is about 240 Torr and water boils at only 70°C.

Example 5A.2 The vapor pressure of ethanol at 34.9°C is 13.3 kPa. Use the data in Table 4C.1 to estimate the normal boiling point of ethanol.

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

$\Delta H°_{vap}$ = 43.5 kJ·mol⁻¹ or 4.35 × 10⁴ J·mol⁻¹ → $\Delta H°_{vap} = 43.5 \text{ kJ·mol}^{-1}$ or $4.35 \times 10^4 \text{ J·mol}^{-1}$

T_2 = 34.9 + 273.15 K = 308.0 K

P_2 = 13.3 kPa

P_1 = 101.325 kPa (this corresponds to 1 atm or T_b)

R = 8.3145 J·K⁻¹·mol⁻¹ → $R = 8.3145 \text{ J·K}^{-1}\text{·mol}^{-1}$

$$\ln \frac{13.3 \text{ kPa}}{101.325 \text{ kPa}} = \frac{4.35 \times 10^4 \text{ J·mol}^{-1}}{8.3145 \text{ J·K}^{-1}\text{·mol}^{-1}} \left(\frac{1}{T_1} - \frac{1}{308.0 \text{ K}} \right)$$

$$\frac{1}{T_1} = \ln \frac{13.3 \text{ kPa}}{101.325 \text{ kPa}} \times \frac{8.3145 \text{ J·K}^{-1}\text{·mol}^{-1}}{4.35 \times 10^4 \text{ J·mol}^{-1}} + \frac{1}{308.0 \text{ K}}$$

= 350. K or 77°C (Vapor is not a prefect ideal gas.)

Freezing and Melting

Water at 0.0°C   Gold at 1064°C

Liquids solidify (freeze) when molecules do not have enough energy to wriggle past their neighbors.

The **normal freezing point**, T_f, is the temperature a liquid freezes at 1 atm.

The *melting temperature* is the same as the *freezing temperature*.

Freezing and Melting: Water Is Unusual

Most substances are more dense in the solid phase than liquid, *water being an exception*.

Water is highly unusual, at 0.0°C, density$_{liquid}$ > density$_{solid}$

Ice floats on water.

Solid water hydrogen bonds hold the molecules apart at low temperatures.

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Freezing and Melting: Water is Unusual

As ice melts, the hydrogen bonds collapse, allowing water molecules to pack more closely.
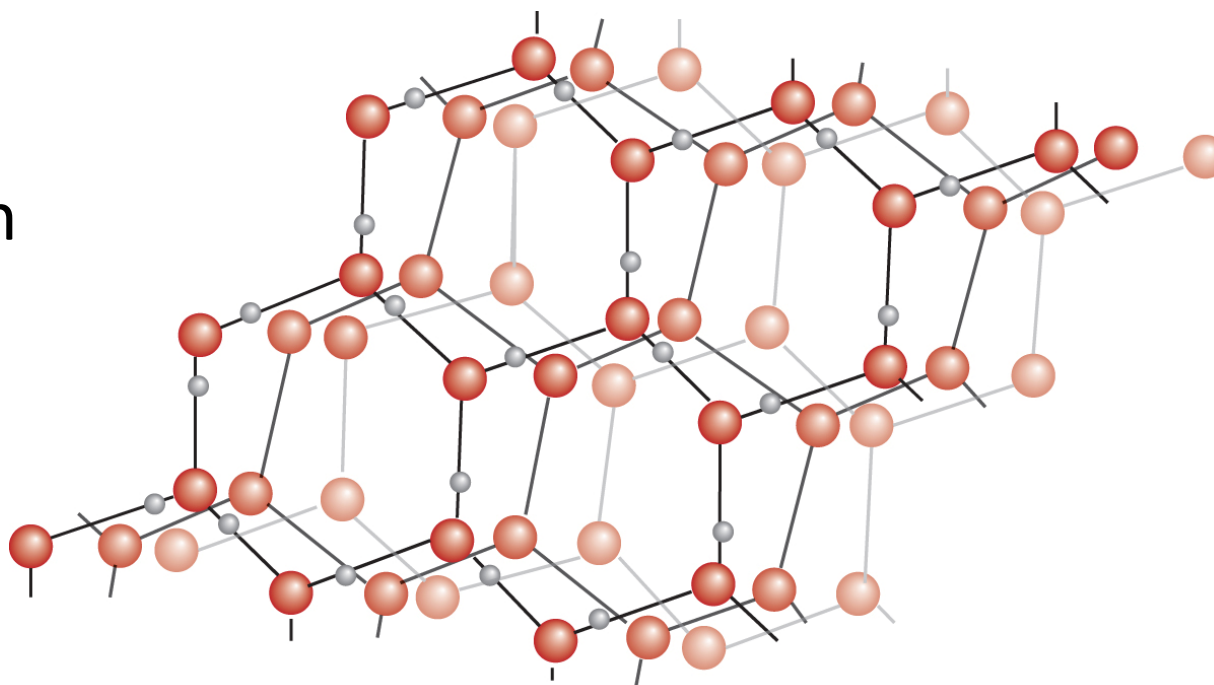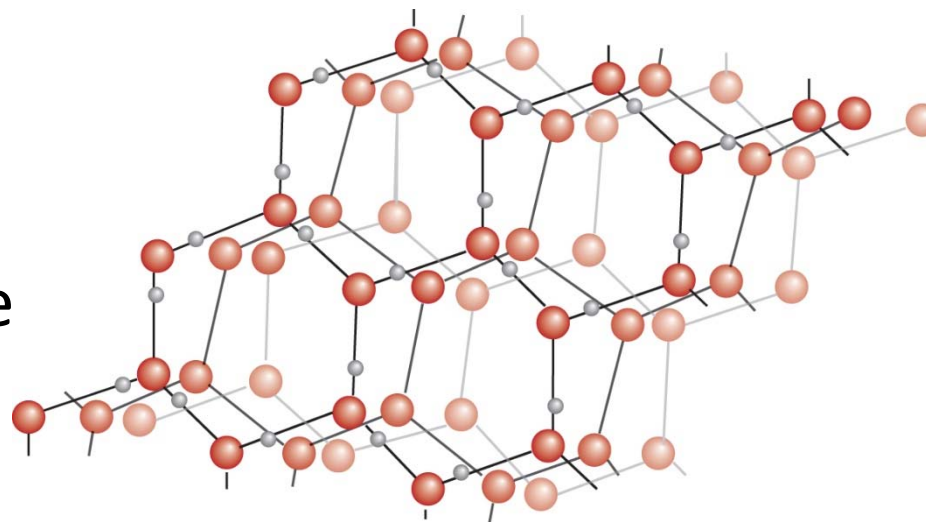

Figure 5B.1
Atkins, *Chemical Principles: The Quest for Insight*, 7e
W. H. Freeman & Company, © 2016 by P. W. Atkins, L. L. Jones, and L. E. Laverman

Why is ice slippery???
1 atm → 0 °C melting point
400 atm → -3 °C melting point
However, best skating temperature -5 °C, and -40 °C (north or south poles) staking is still possible

LETTER

2017, Nature

Role of stacking disorder in ice nucleation

Laura Lupi[1], Arpa Hudait[1], Baron Peters[2], Michael Grünwald[1], Ryan Gotchy Mullen[2], Andrew H. Nguyen[1] & Valeria Molinero[1]

The freezing of water affects the processes that determine Earth's climate. Therefore, accurate weather and climate forecasts hinge on good predictions of ice nucleation rates[1]. Such rate predictions are based on extrapolations using classical nucleation theory[1,2], which assumes that the structure of nanometre-sized ice crystallites corresponds to that of hexagonal ice, the thermodynamically stable form of bulk ice. However, simulations with various water models find that ice nucleated and grown under atmospheric temperatures is at all sizes stacking-disordered, consisting of random sequences of cubic and hexagonal ice layers[3-8]. This implies that stacking-disordered ice crystallites either are more stable than hexagonal ice

nucleation at 230 K to evaluate and rank 26 variables (Extended Data Table 2) as candidate coordinates for describing the transformation from liquid to ice, and find that measures of size and energy of the ice nucleus rank consistently better than crystallite shape and cubicity. Histograms of committor probability (the fraction of trajectories that commit to the crystalline state)[21] are used to evaluate the quality of reaction coordinates and reveal that—as assumed by CNT—the size of the ice nucleus, which is measured with neighbour-correlated bond-order parameters[22] that identify cubic and hexagonal ice[3,23], is an effectively perfect ice nucleation coordinate (Fig. 1a). The overlap between the exact and computed committor distributions indicates that varia-

Phase diagram

Phase Diagrams: CO$_2$

A phase diagram is a map showing phases at different <u>pressures</u> and <u>temperatures</u>.

The region marked "**solid**" is the solid phase of ice. Other regions are marked "**liquid**" and "**vapor**."

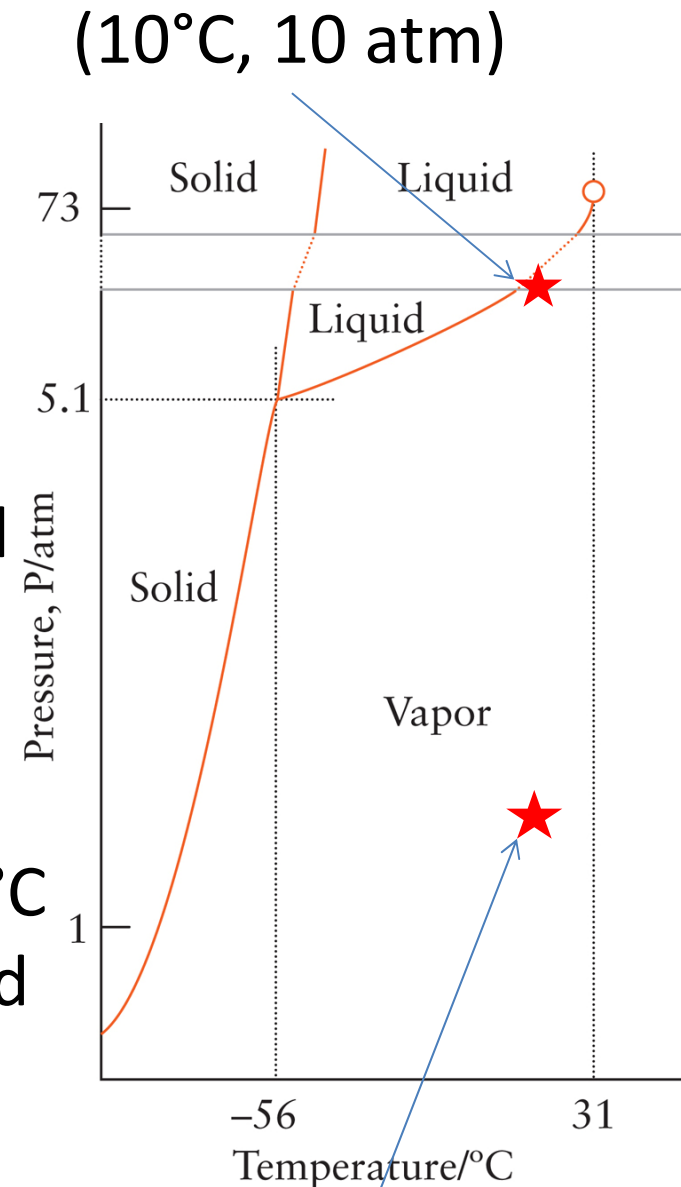This shows that carbon dioxide at 10°C and 2 atm will be a gas. At 10 atm and 10°C, CO$_2$ will condense to a liquid.

(10°C, 10 atm)

Solid   Liquid

73

Liquid

5.1

Solid

Pressure, P/atm

Vapor

1

−56   31

Temperature/°C

(10°C, 2 atm)