

LECTURE NOTES FOR GENERAL CHEMISTRY © MM 2001

CHAPTER 11 STATES OF MATTER AND INTERMOLECULAR FORCES

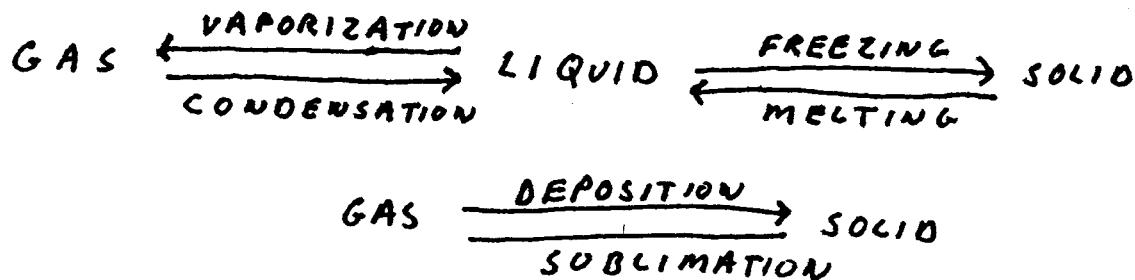
THE 3 STATES OF MATTER

GAS - FAST, ENERGETIC MOLECULES, NEARLY NO INTERMOLECULAR FORCES, NEITHER FIXED VOLUME OR SHAPE, COMPRESSIBLE

LIQUID - MOLECULES ARE CLOSE TOGETHER, INTERMOLECULAR FORCES STRONG ENOUGH TO HOLD A FIXED VOLUME, BUT WEAK ENOUGH TO ALLOW FLOW INTO ANY SHAPE

SOLID - MOLECULES IN DIRECT CONTACT, STRONG INTERMOLECULAR FORCES FIX SHAPE AND VOLUME. HARD TO COMPRESS

PHASE CHANGES

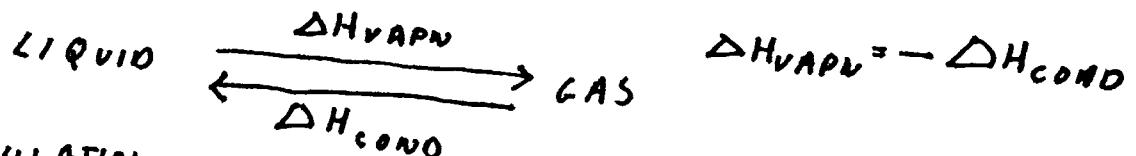


VAPORIZATION

WHEN HEATED, A LIQUID GAINS ENOUGH KINETIC ENERGY TO BOIL, OR VAPORIZIZE. ΔH_{VAPN} = HEAT OF VAPORIZATION

ΔH_{VAPN} IS DIFFERENT FOR EACH TYPE OF MOLECULE.

MOLECULES WITH STRONG INTERMOLECULAR FORCES REQUIRE MORE ENERGY TO BREAK FREE OF THE LIQUID STATE



EXAMPLE CALCULATION

HOW MANY KJ DOES IT TAKE TO BOIL(VAPORIZE) 1 L OF H_2O ?
 $\Delta H_{VAPN} = 44.0 \text{ KJ/mol}$ FOR H_2O

$$\frac{1000 \text{ g}}{18 \text{ g/mol}} = 55.5 \text{ mol H}_2\text{O} \times 44.0 \text{ kJ/mol} = 2442 \text{ kJ}$$

VAPOR PRESSURE

DEFINED AS THE PARTIAL PRESSURE OF A LIQUID'S VAPOR WHEN LIQUID AND VAPOR ARE IN EQUILIBRIUM

THE VAPOR PRESSURE OF A LIQUID IS TEMPERATURE DEPENDENT
EXAMPLE CALCULATION USING THE IDEAL GAS LAW

AT 50°C , THE VAPOR OVER A LIQUID H_2O SAMPLE CONTAINS 0.076 g H_2O PER LITER. WHAT IS THE VAPOR PRESSURE OF H_2O AT 50°C ?

$$PV = nRT \quad P = \frac{nRT}{V}$$

$$\frac{0.076 \text{ g}}{18 \text{ g/mol}} = .0042 \text{ mol}$$

$$P = \frac{.0042 \text{ mol} \times 0.821 \frac{\text{L} \cdot \text{ATM}}{\text{mol} \cdot \text{K}} \times 348^\circ\text{K}}{1.0 \text{ L}}$$

$$P = 0.12 \text{ ATM}$$

BOILING POINT

VAPORIZATION OCCURS NOT ONLY AT THE SURFACE, BUT THROUGHOUT THE LIQUID

THE NORMAL B.P. IS WHEN THE PRESSURE = 1.0 ATM

THE CRITICAL POINT

HEATING A LIQUID IN A CLOSED CONTAINER PREVENTS BOILING BECAUSE THE PRESSURE KEEPS BUILDING

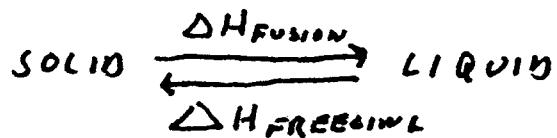
EVENTUALLY THE VAPOR DENSITY INCREASES TO THE POINT WHERE LIQUID AND VAPOR ARE INDISTINGUISHABLE

THIS IS THE CRITICAL POINT, THE CRITICAL TEMP, THE CRITICAL PRESS
ABOVE THIS POINT A SUPERCRITICAL FLUID EXISTS

PHASE CHANGES IN SOLIDS

IN A SOLID, ATOMS OR MOLECULES HAVE VIBRATIONAL ENERGY. THEY VIBRATE AROUND A FIXED POSITION.

AS TEMPERATURE INCREASES, VIBRATIONS BECOME STRONGER UNTIL THEY ARE STRONG ENOUGH TO BREAK THE INTERMOLECULAR FORCES. THIS IS MELTING, OR FUSION

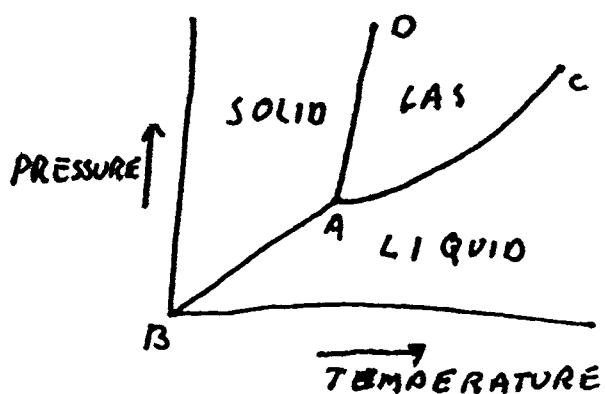


A SOLID MAY TRANSITION DIRECTLY TO A GAS. THIS IS SUBLIMATION

$$\Delta H_{\text{SUBLIM}} = \Delta H_{\text{FUSION}} + \Delta H_{\text{VAPN}} \quad (\text{BY HESSIAN})$$

THE TRIPLE POINT IS THAT POINT ON A PHASE DIAGRAM WHERE SOLID, LIQUID AND GAS CAN COEXIST.

A PHASE DIAGRAM REPRESENTS TEMPERATURE AND PRESSURE CONDITIONS AT WHICH EACH PHASE EXISTS



A IS THE TRIPLE POINT
A-O IS THE FUSION CURVE
A-B IS THE SUBLIMATION CURVE
A-C IS THE VAPOR PRESSURE CURVE
C IS THE CRITICAL POINT

INTERMOLECULAR FORCES

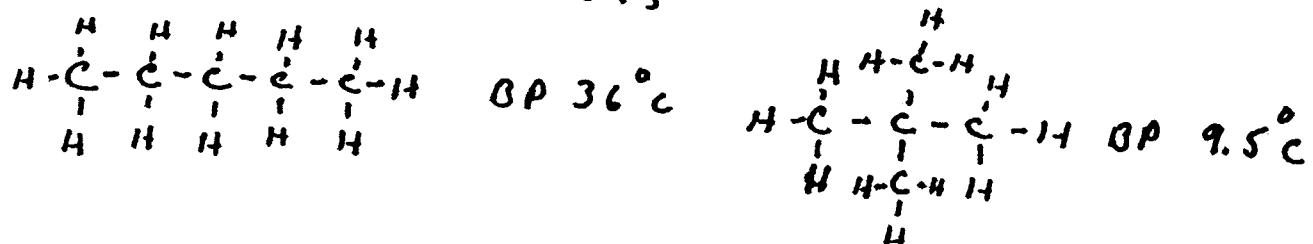
- ARE ELECTROSTATIC - THE + IS ATTRACTED TO THE -
- ARE ALL DIPOLAR - A DIPOLE HAS A + END AND A - END
- Dipoles may be very small and temporary
- or large and permanent

THE WEAKEST ATTRACTIVE FORCES ARE DISPERSION FORCES
 IF A NONPOLAR MOLECULE IS POLARIZABLE, A COLLECTION
 OF MOLECULES MAY BE HELD TOGETHER BY A CONTINUING SERIES
 OF TEMPORARY, CORRELATED, INDUCED DIPOLES

THE GREATER THE POLARIZABILITY, THE STRONGER THE FORCES

| | | | | |
|---------------------|---------------|--------------|---------------|-------------------------------|
| F_2 | Cl_2 | Br_2 | I_2 | I IS LARGE AND POLARIZABLE |
| B.P. $-188^\circ C$ | $-34^\circ C$ | $59^\circ C$ | $184^\circ C$ | |

MOLECULAR SHAPE ALSO MATTERS

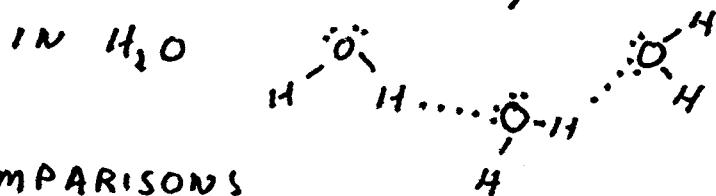


POLAR MOLECULES HAVE PERMANENT DIPOLES
 THIS RESULTS IN STRONGER DIPOLAR ATTRACTIONS

| | N_2 | NO | O_2 |
|----------------|-------|------|-------|
| DIPOLE MOMENT | 0 | 0.15 | 0 |
| BP $^{\circ}K$ | 77 | 121 | 90 |

HYDROGEN BONDS - THE STRONGEST OF DIPOLAR ATTRACTIONS

ONLY WITH $O-H$, $N-H$



COMPARISONS

STRONG INTERMOLECULAR
ATTRACTIOnS

LEADS TO HIGH BOILING POINTS

- COMPARING NONPOLAR SUBSTANCES USE MOLAR MASS AND SHAPE
- COMPARING POLAR SUBSTANCES - MORE POLAR = MORE ATTRACTIVE FORCE
- IN GENERAL, FOR SIMILAR MOLAR MASSES, POLAR MEANS HIGHER B.P. THAN NON POLAR
- HYDROGEN BONDING - HIGHEST B.P. IF ALL ($O-H$ OR $N-H$)

SOLID STRUCTURE

NETWORK COVALENT SOLIDS

THE ALLOTROPIES OF CARBON - DIAMOND, GRAPHITE, BUCKYBALLS AND NANOTUBES

THE STRUCTURE OF CRYSTALS

A REGULAR ARRAY OF IONS HELD TOGETHER BY ELECTROSTATIC ATTRACTIONS

THE ATTRACTIVE FORCE BETWEEN A CATION AND AN ANION INCREASES AS THE CHARGES INCREASE AND AS THE IONIC RADII DECREASE. LATTICE ENERGIES INCREASE ACCORDINGLY

COMPARE MgO , $NaCl$, $NiBr_2$

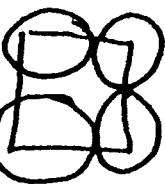
UNIT CELLS - THE SMALLEST REPEATING UNIT IN A CRYSTAL



SIMPLE CUBIC
EIGHT ATOMS
AT THE CORNERS
OF A CUBE

52.4%
FULL

1 ATOM TOTAL



BODY-CENTERED
ADD 1 ATOM
IN THE CENTER
OF THE CUBE

68% FULL

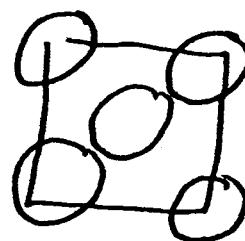
2 ATOMS TOTAL

FACE CENTERED
EACH FACE
HAS AN ATOM

74% FULL

ONLY IN THE SIMPLE CUBIC DO CORNER ATOMS TOUCH

IN BCC
CONTACT
ALONG
A BODY
DIAGONAL



IN FCC
CONTACT
ALONG A
FACE DIAGONAL

IONIC STRUCTURES

DEPEND ON THE RATIO OF RADII R_c/R_a

R_c/R_a FROM 0.225 TO 0.414 \rightarrow TETRAHEDRAL
0.414 TO 0.732 \rightarrow OCTAHEDRAL
 $> 0.732 \rightarrow$ CUBIC

CHAPTER 11

SKILLS

HEATS OF VAPORIZATION

PROBLEMS

EX 1.1, 27, 29

WORK WITH VAPORIZATION,
IDEAL GAS LAW

EX 11.3, 37, 39

DO CALCULATIONS AT PHASE
CHANGES

EXERCISE 11.5, 47
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USE PHASE DIAGRAMS

EX 11.5, 53

INTER MOLECULAR FORCES,
CRYSTAL STRUCTURES

EX 11.6, EX 11.7
59, 61, 63

NOT COVERED

SURFACE TENSION

EX 11.8, EX 11.9
73, 75