CHEM 1061-003   4 MAY 2015 (Wk 15)
WEEK 15 NOTES
(BECAUSE LECTURES 2
AND 3 OF THIS WEEK WILL BE
REVIEW OF THE PRACTICE
FINAL EXAM FROM 2014, THESE
ARE THE LAST NOTES)

COPIES UP FRONT! → PICK UP THE FINAL EXAM
ANNOUNCEMENT FROM LAST WEEK

TOPICS TODAY:
FINISH CH. 12 (WILL ONLY COVER
§ 12.3, 12.4, 12.5)
1. REVIEW ON FORCES OF ATTRACTIONS
IN CMPDS (AND ATOMIC SPECIES)
2. DIPOLE-DIPOLE ATTRACTIVE FORCES
  a. NORMAL: BETWEEN POLAR MOLECULES
    WITHOUT N-H, O-H, or F-H BONDS
  b. SPECIAL: BETWEEN (USUALLY POLAR)
    MOLECULES WITH N-H, O-H, or F-H
    BONDS- "HYDROGEN BONDING"
3. WATER, A UNIQUE SOLVENT

NOTE WELL!

CHEM 1061-003   FINAL EXAM INFO
SCHEDULED FOR 10:30 AM-12:30 PM ON WEDNESDAY,
MAY 13, 2015, ROOMS ASSIGNED ACCORDING TO
THE FIRST LETTER OF YOUR SURNAME (FAMILY NAME):

A-L Smith 100
M-Z STSS 220 (NOTE: *NOT 230!!*)

TEN POINT PENALTY IF YOU TAKE EXAM IN WRONG ROOM.
NOTE: IF YOU TAKE ANOTHER INSTRUCTOR'S EXAM
WITHOUT PERMISSION, YOU WILL FAIL THE EXAM

FROM LAST FRIDAY; COPY ON HANDOUT UP-FRONT!

(2)

SURVEY OF INTERMOLECULAR FORCES OF ATTRACTION(#)

WEAKEST* (1) INDUCED DIPOLE-INDUCED DIPOLE

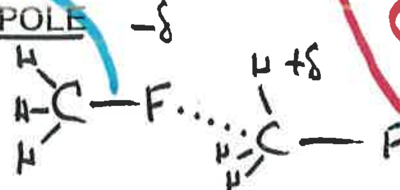
AKA: LONDON DISPERSION* OR
VAN DER WAAL'S ATTRACTIVE FORCES
(* LD FORCES)

$-\delta$ $+\delta$ $-\delta$ $+\delta$
H – H ··· H – H

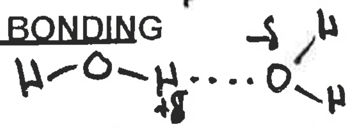
133pm

(2) DIPOLE-DIPOLE

(a) NORMAL



(b) HYDROGEN BONDING

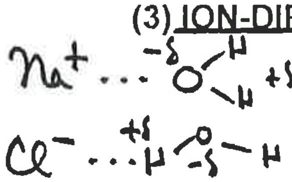


2.5 4.0
C–F
ΔEN 1.5

3.5 2.1
O–H
ΔEN 1.4

STRONGER
C···F
275pm
H·····O
125pm

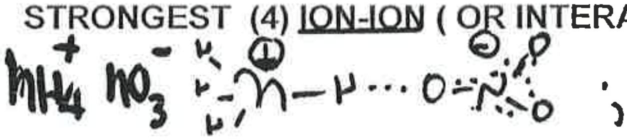
(3) ION-DIPOLE



NOTE: ATOMIC IONS ARE INCLUDED HERE. THEY ARE THE "ULTIMATE" IN POLARITY

STRONGEST (4) ION-ION (OR INTERATOMIC FOR ATOMIC IONS)

WE'VE ALREADY DISCUSSED SALTS!



; $Na^+ \cdots Cl^-$

* FOR LARGE MOLECULES, TOTAL LD FORCES OFTEN EXCEED INDIVIDUAL COVALENT BOND ENERGIES.
THIS IS WHY LARGE BIOMOLECULES, LIKE PROTEINS, OR MANY POLYMERS, LIKE POLYETHYLENE, CANNOT BE MELTED, OR VAPORIZED WITHOUT DECOMPOSITION. THE SAME IS TRUE OF MANY OTHER CMPDS WITH WEAK COVALENT BONDS AND/OR HIGH LATTICE ENERGIES.

!! ⇒ # COVALENT BONDS EXCLUDED; E.G., AN O-H BOND IN WATER.

OR A H-H BOND IN DIHYDROGEN!

ALL OF THESE NOTES ARE NOW ONLINE IN WEEK 14, PART 3

3

SURVEY OF INTERMOLECULAR FORCES OF ATTRACTION

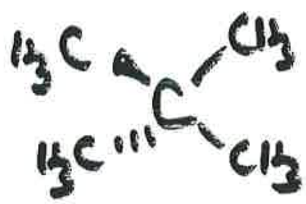
ALL FORMS OF MATTER PARTICIPATE IN LD FORCES OF ATTRACTION!

1. INDUCED DIPOLE-INDUCED DIPOLE OR LONDON DISPERSION FORCES, LD:
OR SIMPLY "DISPERSION" FORCES

a. ACOUNT FOR THE FACT THAT EVEN THE "MOST IDEAL" OF THE REAL GASES, He AND H_2, CONDENSE TO FORM LIQUIDS AT SUFFICIENTLY LOW TEMPS. NOT EXPLAINED UNTIL 1930 — FRITZ LONDON

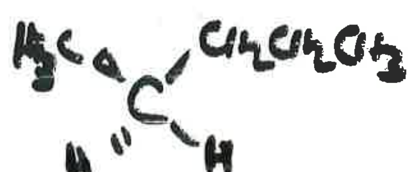
b. BECOME STRONGER AS NON POLAR MOLECULES ASSUME "LESS SPHERICAL" AND "MORE ELONGATED" STRUCTURES; I.E., LD FORCES OF ATTRACTION INCREASE AS THE TOTAL SURFACE AREA OF THE MOLECULE INCREASES-THEREBY ALLOWING MORE INTERMOLECULAR CONTACTS

EXAMPLES: CONSIDER THE BOILING PTS, @ 1 ATM P, OF THE THREE ISOMERIC PENTANES:

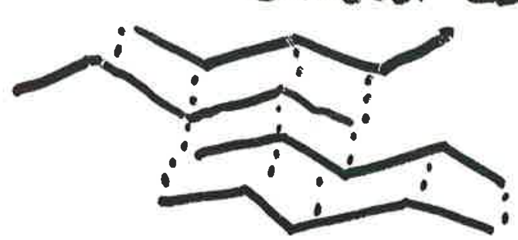


nbp +10°C
MOST "SPHERICAL"
LEAST SURFACE AREA
SMALLEST LD FORCES

nbp +28°C



nbp +35°C
MOST "ELONGATED"
BIGGEST SURFACE AREA
LARGEST LD FORCES



4

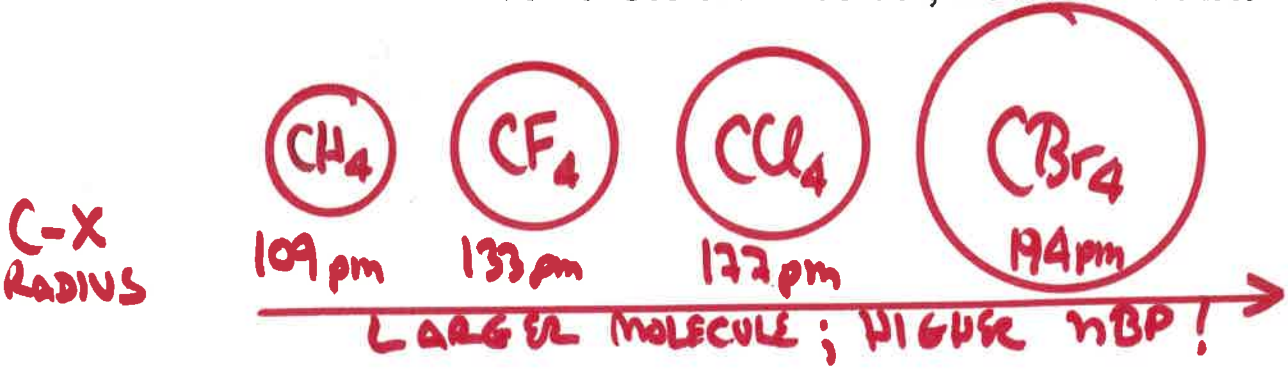
c. LONDON DISPERSION FORCES INCREASE AS MOLECULES BECOME LARGER (I.E., SURFACE CONTACTS OF MOLECULES INCREASE)

CMPDS BELOW ARE ALL NON POLAR AND ESSENTIALLY SPHERICAL IF YOU CONSIDER THEIR TIME-AVERAGED SHAPE DURING RAPID ROTATION

CX_4; X =	H	F	Cl	Br
nbp(ºC)	-161	-128	+77	+190
MM (g/mol)	16	88	154	332

EH_4; E =	C	Si	Ge	Sn
nbp(ºC)	-161	-112	-88	-52
MM	16	32	77	123

NOTE: GRAVITATIONAL FORCES OF ATTRACTION ARE USUALLY TINY (AND INSIGNIFICANT) COMPARED TO INTERMOLECULAR ATTRACTIVE FORCES. THUS, FOR EXAMPLE, THE BOILING POINT OF A SUBSTANCE ONLY DEPENDS ON PRESSURE AND IS INDEPENDENT OF GRAVITY (AT LEAST ON EARTH, MARS, MOON, ETC.) BUT LIKELY NOT WHEN GRAVITATIONAL FORCES BECOME HUGE; E.G., NEAR A NEUTRON STAR! HOWEVER, ATMOSPHERIC PRESSURE ON EARTH IS A FUNCTION OF ALTITUDE (AND HENCE GRAVITY). THUS, THE bp OF WATER AT SEA LEVEL (1.00 ATM P) IS 100 ºC BUT AT THE TOP OF MT EVEREST, ~29,000 ft, (~0.30 ATM P) IS ~ 70 ºC. BUT, AT 1 ATM P, IT IS 100 ºC ON THE MOON, MARS OR MN!



LD FORCES OF ATTRACTION

d. CAN BECOME HUGE FOR MOLECULES OF HIGH MOLECULAR MASS

FOR EXAMPLE:

	CH_4	*n*-$C_{10}H_{22}$	*n*-$C_{20}H_{42}$	*n*-$C_{40}H_{82}$
nbp(°C)	-161	+174	+340	DEC(*)
MM	16	142	282	562

(*)TOTAL LD FORCES ARE SO LARGE THAT C-C BONDS OF $C_{40}H_{82}$ BREAK BEFORE ENOUGH HEAT CAN BE ADDED TO BOIL THIS MOLECULE AT 1 ATM. P!

MANY HYDROCARBONS AND OTHER MOLECULES OF HIGH MOLECULAR MASSES MUST BE DISTILLED AT REDUCED PRESSURES (P << 1 ATM), WHERE BOILING POINTS ARE LOWER, TO PREVENT THERMAL DECOMPOSITION

! ⇒ MANY SUBSTANCES HAVE SUCH HIGH MOLECULAR MASSES (POLYMERS AND MANY BIOMOLECULES) THAT THEY CANNOT BE DISTILLED UNDER ANY CONDITIONS. THUS, ON HEATING THEY DECOMPOSE! THIS IS ALSO TRUE OF MANY SALTS, WHICH ARE EFFECTIVELY "IONIC POLYMERS"

2. DIPOLE-PIPOLE ATTRACTIVE FORCES.
BOTH NON POLAR AND POLAR MOLECULES ARE ATTRACTED TO ONE-ANOTHER BY LONDON DISPERSION FORCES, BUT IN ADDITION, POLAR MOLECULES CAN PARTICIPATE IN OFTEN STRONGER DIPOLE-DIPOLE FORCES OF ATTRACTION.
THUS, IF NON POLAR AND POLAR MOLECULES HAVE ABOUT THE SAME SHAPE AND MOLECULAR MASS (SO LD FORCES ARE ABOUT THE SAME), POLAR MOLECULES WILL INVARIABLY HAVE HIGHER BP's AT 1 ATM P; E.G.,

	SiH_4	PH_3	SH_2
	non-polar	weakly-polar	polar
ΔEN	0.3	0.1	0.4
nbp (°C)	-112	-88	-60
MM (g/mol)	32	34	34

DIPOLE-DIPOLE ATTRACTIVE FORCES IN PH_3

DIPOLE-DIPOLE:
VERY WEAK IN PH_3;
MIGHT CONTRIBUTE ~3% TO OVERALL INTERMOLECULAR INTERACTION.

DIPOLE-DIPOLE ATTRACTIVE FORCES INCREASE AS THE DIPOLE MOMENTS OR POLARITIES OF MOLECULES BECOME LARGER. EXAMPLES (WHEREIN LD FORCES ARE KEPT ABOUT THE SAME IN THE FOLLOWING PAIRS OF MOLECULES):

(i) $CH_3-C\equiv C-H$ ← WEAKLY POLAR — $CH_3-C\equiv N:$ ← HIGHLY POLAR

	$CH_3-C\equiv C-H$	$CH_3-C\equiv N:$
nbp	−23°C	+81°C
mp	−103°C	−48°C
μ =	0.78	3.92

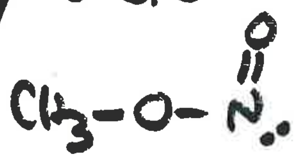
(ii)

BENZENE, C_6H_6

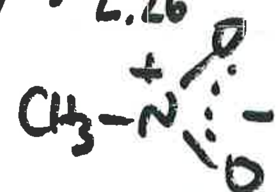
PYRIDINE, C_5H_5N

	BENZENE	PYRIDINE
nbp	+80°C	+115°C
mp	+5.5°C	−42°C
μ =	0.0	2.26

(iii)



nbp −12°C



+101°C

"INTERNAL SALT" LIKE AMINO ACIDS

COMPARISON OF NORMAL BOILING POINTS OF ALKANES, AMMONIA, WATER, ALCOHOLS, AMINES, ETHERS (OF ABOUT THE SAME SIZE, SHAPE, AND MM TO MAINTAIN APPROX. CONSTANT LD FORCES)

	CH_4	NH_3	OH_2	FH
ΔEN	0.4	0.9	1.4	1.9
MM= (g/mol)	16	17	18	20
nbp (ºC)	-161	-33	+100	+20

DRAMATIC INCREASE IN NBP

WHY SO LOW COMPARED TO H_2O?

	$CH_3CH_2CH_3$	CH_3OCH_3	CH_3NHCH_3	$CH_3CH_2NH_2$	CH_3CH_2OH
MM	44	46	45	45	46
nbp	-42	-25	+7	+17	+78

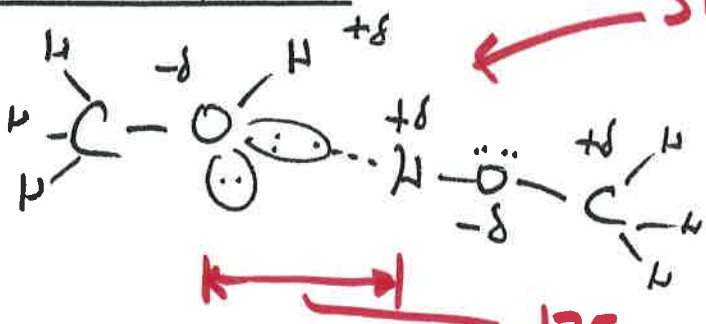
CONCLUSION: HF and MOLECULES CONTAINING N-H AND O-H BONDS HAVE ABNORMALLY HIGH BOILING POINTS. THESE ARE DUE TO HYDROGEN BONDING, AN ESPECIALLY STRONG DIPOLE-DIPOLE INTERACTION, WHICH IS A PURELY COULOMBIC OR ELECTROSTATIC FORCE OF ATTRACTION.

SHOW ICE CRYSTAL: 3D INTERACTIONS OF H_2O MOLECULES

REQUIREMENTS FOR HYDROGEN BONDING OR H-BONDING

a. MOLECULE MUST CONTAIN A VERY POLAR E-H BOND, WHERE ELEMENT E IS USUALLY N, O, or F, THE MOST ELECTRONEGATIVE ATOMS.

b. MOLECULE MUST CONTAIN N, O, or F ATOMS HAVING ONE OR MORE LONE PAIRS. E.G., METHANOL, CH_3OH



STRONGEST DIPOLE-DIPOLE INTERACTION IN CH_3OH.

175 pm

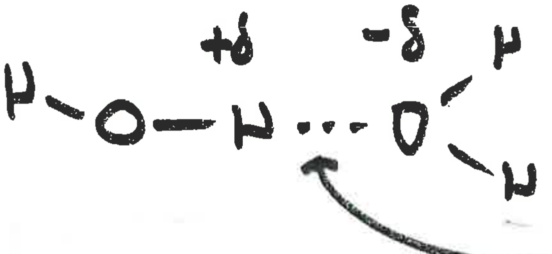
FEATURES OF H-BONDING:

a. COVALENTLY BOUND HYDROGEN IS VERY SMALL, HAS NO LONE PAIRS TO PREVENT CLOSE APPROACH OF N, O, or F

b. N, O, and F ARE VERY ELECTRONEGATIVE AND SMALL, SO THEY CAN CLOSELY APPROACH A RATHER POSITIVE H TO GIVE A QUITE STRONG DIPOLE-DIPOLE ATTRACTIVE FORCE. IT IS TOTAL BLISS!!!

HOW STRONG?

H−O 463 KJ/mol
H−H 432 KJ/mol



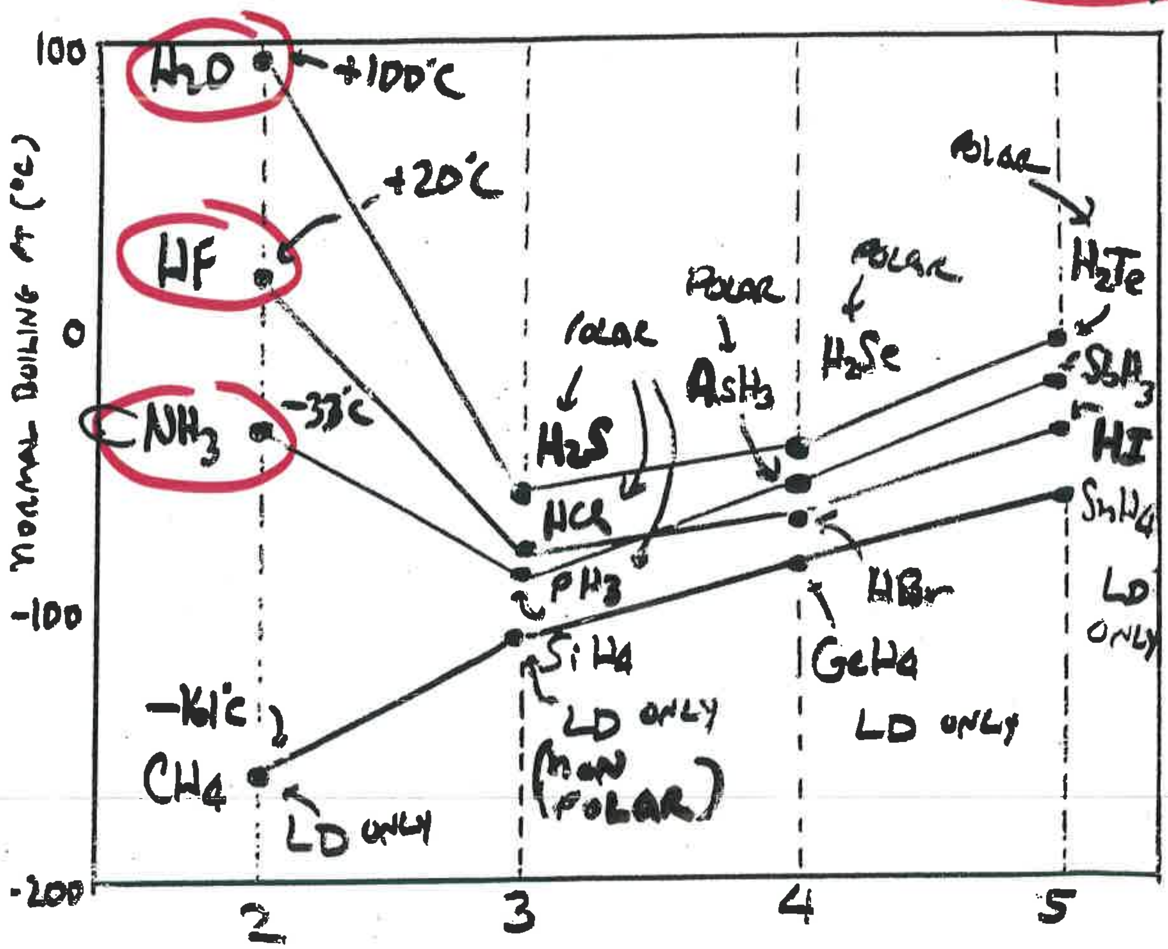
~5 KJ/mol

TINY COMPARED TO COVALENT BONDS... BUT...

FIG 12.15, P.433; 6th of TEXT
P.470, 7th

INFLUENCE OF HYDROGEN BONDING ON THE NORMAL BP's OF SIMPLE HYDROGEN CMPDS OF THE CARBON, NITROGEN, OXYGEN, AND FLUORINE FAMILIES OF ELEMENTS

ONLY EH_4 MOLECULES ARE NON POLAR



ROW OF PERIODIC TABLE

OF THESE MOLECULES,

ONLY NH_3, H_2O, AND HF PARTICIPATE IN HYDROGEN BONDING IN THE LIQUID PHASE. ALL OTHERS ARE ONLY ASSOCIATED BY DIPOLE-DIPOLE AND/OR LD ATTRACTIVE FORCES

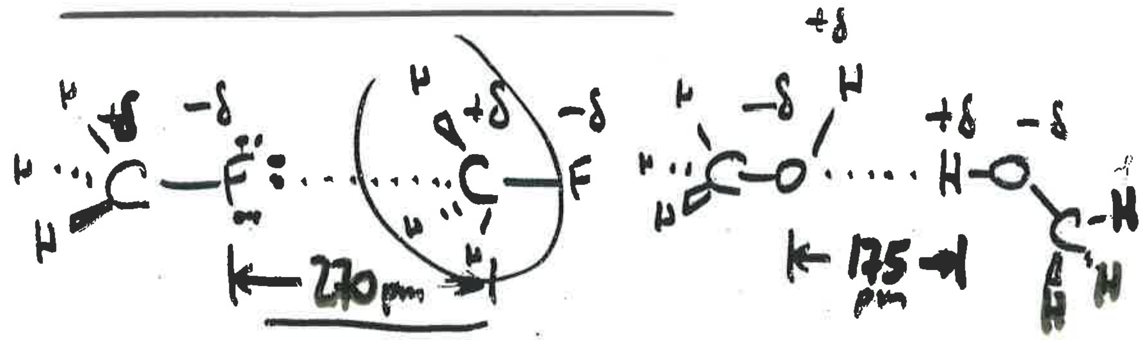
IMPORTANT GUIDELINE ON H-BONDING: THE CLOSEST INTERMOLECULAR CONTACTS POSSIBLE FOR HYDROGEN AND N, O, or F ARE MUCH SHORTER THAN THOSE OF ATOMS IN OTHER POLAR BONDS: FOR EXAMPLE: COMPARISON OF THE DIPOLE-DIPOLE ATTRACTIVE FORCES IN METHYL FLUORIDE, CH_3F, VS CH_3OH. (ESPECIALLY INTERESTING SINCE CH_3F HAS THE HIGHER DIPOLE MOMENT, μ, OF THE TWO MOLECULES!)

	CH_3F	CH_3OH
nbp(°C)	-78	+65
MM(g/mol)	34	32
μ (Debye)	1.85	1.70

Δ(NBP): 143 C°

WE SAY THAT METHYL ALCOHOL IS A MUCH MORE STRONGLY ASSOCIATED LIQUID THAN METHYL FLUORIDE BECAUSE ITS INTERMOLECULAR FORCES OF ATTRACTION ARE MUCH STRONGER, LEADING TO THE SIGNIFICANTLY HIGHER BOILING POINT. WHY ARE THEY STRONGER?

INTERMOLECULAR FORCES OF ATTRACTION IN CH_3F VS CH_3OH THE MOST POLAR BOND IS PRESENT IN CH_3F, WHERE THE C-F BOND IS MORE POLAR (ΔEN = 1.5) THAN EITHER THE O-H (ΔEN = 1.4) OR the C-O BOND (ΔEN = 1.0) IN CH_3OH. BUT THE SHORTEST POSSIBLE INTERMOLECULAR C•••F CONTACT IN CH_3F IS MUCH LONGER THAN THE RELATED O•••H CONTACT IN CH_3OH.



$$E \propto \frac{Q_1 Q_2}{d}$$

d = INTERMOLECULAR F-C or O-H DISTANCES

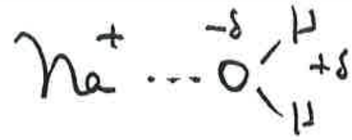
THE BOTTOM LINE IS THAT CH_3OH "WINS OUT" OVER CH_3F BECAUSE "d" IS MUCH SMALLER FOR CH_3OH. THIS EXAMPLE EMPHASIZES WHY H- BONDING IS UNIQUE AMONG DIPOLE-DIPOLE INTERACTIONS, OWING TO THE VERY SMALL SIZE OF ATOMIC HYDROGEN WHEN BOUND TO NON-METALS.

ON HANDOUT!

FINAL TOPIC: WATER, A UNIQUE SOLVENT

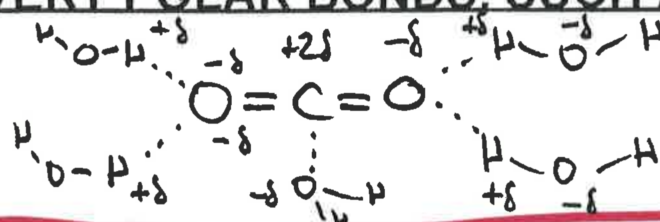
THE SMALL SIZE OF H_2O AND HIGHLY POLAR CHARACTER OF O–H BONDS ARE IMPORTANT HERE!

1. WATER IS UNUSUALLY EFFECTIVE IN DISSOLVING BOTH IONIC AND NON IONIC SUBSTANCES (ESPECIALLY ORGANIC MOLECULES CONTAINING N AND O ATOMS OR BETTER, NH OR OH GROUPS) DUE TO ITS ABILITY TO SOLVATE BOTH CATIONS, E.G.,



AND ANIONS, E.G.,

AND NEUTRAL MOLECULES CONTAINING VERY POLAR BONDS, SUCH AS CO_2

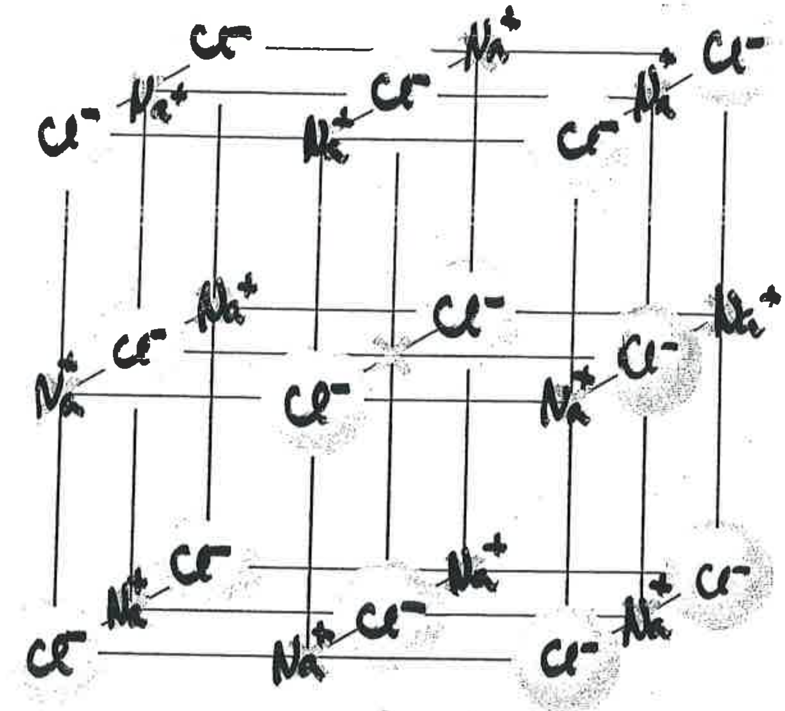


DOUBLE-EDGED SWORD: RELATIVELY PURE WATER IS A PRECIOUS COMMODITY BECAUSE IT DISSOLVES PRACTICALLY EVERYTHING TO SOME DEGREE-EVEN TOXIC MERCURY METAL HAS A SMALL SOLUBILITY IN WATER, 56 μg/L at 25°C (from Merck Index, 12th ed, 1996, p. 5953)

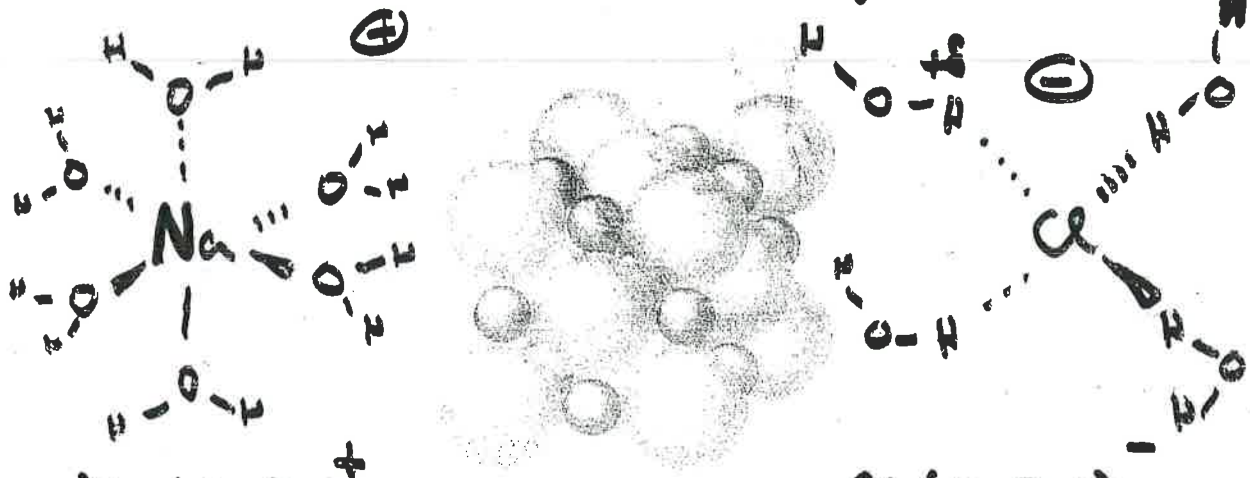
DISSOLVING OF SODIUM CHLORIDE IN WATER, A REVERSIBLE CHEMICAL REXN!

(SIMILAR DIAGRAM IN TEXT, FIG. 4.2, P. 136) 6th

P. 140 7th



$NaCl_{(s)} + \text{excess } H_2O \longrightarrow Na^+(aq) + Cl^-(aq)$



$Na(OH_2)_6^+$ (b) $Cl(H\text{-}O\text{-}H)_x^-$

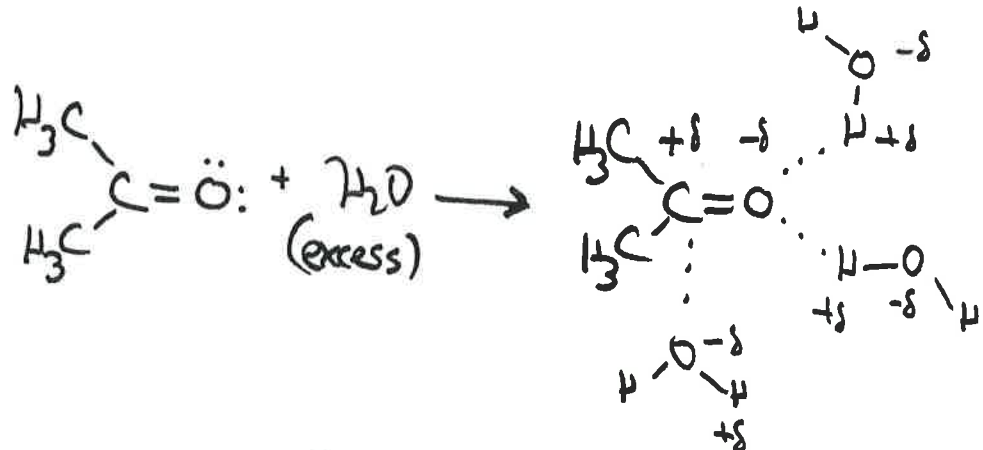
Figure 10.35
Cubic closest packing in NaCl

Steven S. Zumdahl, *Chemistry,* Third Edition, © 1993 by D. C. Heath and Company

x may be 4, but is not well defined

FOR NEUTRAL ORGANIC MOLECULES TO HAVE GOOD SOLUBILITY IN WATER THEY MUST CONTAIN NITROGEN OR OXYGEN ATOMS SINCE FUNCTIONAL GROUPS CONTAINING THESE ATOMS CAN FORM HYDROGEN BONDS TO WATER.

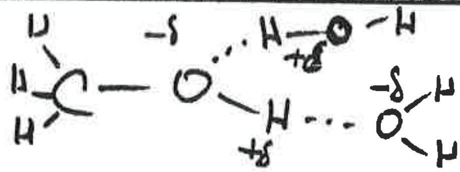
FOR EXAMPLE, ACETONE, WHICH IS TOTALLY MISCIBLE (OR SOLUBLE IN ALL PROPORTIONS) WITH WATER.



REVERSIBLE HYDRATION OF ACETONE

ACETONE CANNOT ~~FROM~~ FORM HYDROGEN BONDS TO ITSELF, BUT IT CAN EFFECTIVELY "BREAK INTO THE H-BONDED NETWORK OF WATER" BY FORMING H-BONDS TO WATER.

THESE FUNCTIONAL GROUPS ARE CALLED "HYDROPHILIC" (WATER-LOVING) BECAUSE THEY HAVE OXYGEN OR NITROGEN ATOMS WHICH CAN FORM H-BONDS WITH WATER. ALCOHOLS, AMINES, CARBOXYLIC ACIDS AND OTHER CMPDS WITH O-H OR N-H BONDS ARE EVEN MORE HYDROPHILIC (AND MORE SOLUBLE IN WATER) BECAUSE THEY CAN BOTH DONATE AND ACCEPT H-BONDS, E.G.,



HYDROPHILIC OR "WATER-LOVING" ORGANIC MOLECULES

R-OH	ALCOHOLS
R-O-R	ETHERS ← MANY ETHERS ARE ONLY PARTIALLY MISCIBLE WITH H_2O
R-C(O)H	ALDEHYDES
R-C(O)R	KETONES
R-C(O)OH	CARBOXYLIC ACIDS
R-C(O)OR'	ESTERS
R-C(O)NR'$_2$	AMIDES
R-NH$_2$	
R-NHR'	AMINES
R-NR'$_2$	
R-NH$_3$(+)	AMMONIUM IONS (MORE SOLUBLE THAN AMINES IN H_2O)
R-NO$_2$	NITRO CMPDS
R-CN	NITRILES

HYDROCARBON GROUPS ARE CLASSIC "HYDROPHOBIC" UNITS (WATER HATING OR FEAR OF WATER) SINCE THEY ARE UNABLE TO PARTICIPATE IN HYDROGEN BONDING. THE C-C AND C-H GROUPS ARE SO WEAKLY OR NON POLAR THAT THEY CANNOT "BREAK INTO THE H-BONDED NETWORK OF WATER". ALSO, ORGANIC HALIDES, EVEN ORGANIC FLUORIDES, CANNOT FORM EFFECTIVE H-BONDS WITH WATER. AS A RESULT, THE FOLLOWING MOLECULES (AND SIMILAR SPECIES) ARE POORLY SOLUBLE IN WATER:

pentane ;

toluene ;

CH_2Cl_2
dichloromethane

$-(CH_2-CHCl)_n-$
PVC
"POLYVINYLCHLORIDE"

CCl_4
carbon tetrachloride

PRESENCE OF LARGE (OR LONG) HYDROPHOBIC GROUPS BOUND TO HYDROPHILIC UNITS REDUCES THE SOLUBILITY OF ORGANIC MOLECULES IN WATER

EXAMPLES	SOLUB. IN WATER
ALCOHOLS	
CH_3OH, C_2H_5OH, C_3H_7OH	fully miscible
$CH_3CH_2CH_2CH_2OH$	limited
RC(O)OH (CARBOXYLIC ACIDS)	
R = CH_3, C_2H_5, C_3H_7	fully miscible
$CH_3CH_2CH_2CH_2C(O)OH$	limited

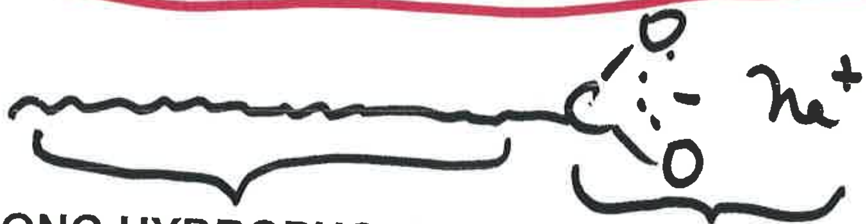
C_4H_9 (the $CH_3CH_2CH_2CH_2$ part); $\downarrow$ Na^+OH^-

$Na(+)\ C_4H_9CO_2(-)$	very soluble (forms micelles)

SODIUM SALT OF A LONG CHAIN CARBOXYLATE ION "SOAP"

HYDROPHILIC AND HYDROPHOBIC GROUPS IN WATER SOLUBLE "GLOBULAR" PROTEINS PLAY AN IMPORTANT ROLE IN DETERMINING THE 3D STRUCTURE AND PROPERTIES OF THESE IMPORTANT BIOMOLECULES

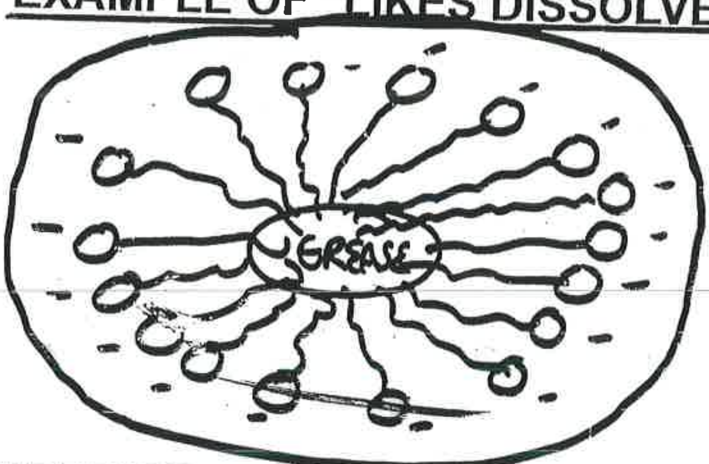
INTERESTING CHARACTERISTIC OF AQUEOUS SOLUTIONS OF SOAP: FORMATION OF MICELLES:



LONG HYDROPHOBIC HYDROCARBON CHAIN DISSOLVES IN NON- OR WEAKLY POLAR ORGANIC SOLVENTS

HYDROPHILIC Na^+ CARBOXYLATE DISSOLVES IN WATER AND OTHER QUITE POLAR SOLVENTS

MICELLE FORMATION (AKIN TO A WATER SOLUBLE GLOBULAR PROTEIN). NICE EXAMPLE OF "LIKES DISSOLVE LIKES"



SOAP MICELLE

INTERIOR NON POLAR HYDROCARBON CHAINS "DISSOLVE" EACH OTHER (AND TRAP GREASE)

DEMO FINALE: "THE GROWLING GUMMY BEAR"

{IN THIS DEMO, MR. GUMMY BEAR WILL GIVE HIS ALL FOR SCIENCE!}

THE REACTION SHOWS THE GREAT REACTIVITY OF POTASSIUM CHLORATE, $KClO_3$, A COMMON INGREDIENT IN FIREWORKS.
GUMMY BEAR: MAINLY A MIX OF GLUCOSE/FRUCTOSE, $C_6H_{12}O_6$
THE $KClO_3$ MUST BE MELTED, mp ~368°C, TO INITIATE THE REXN

$$4\,KClO_3 + C_6H_{12}O_6 \rightarrow 6\,CO_2 + 4\,KCl + 6\,H_2O$$