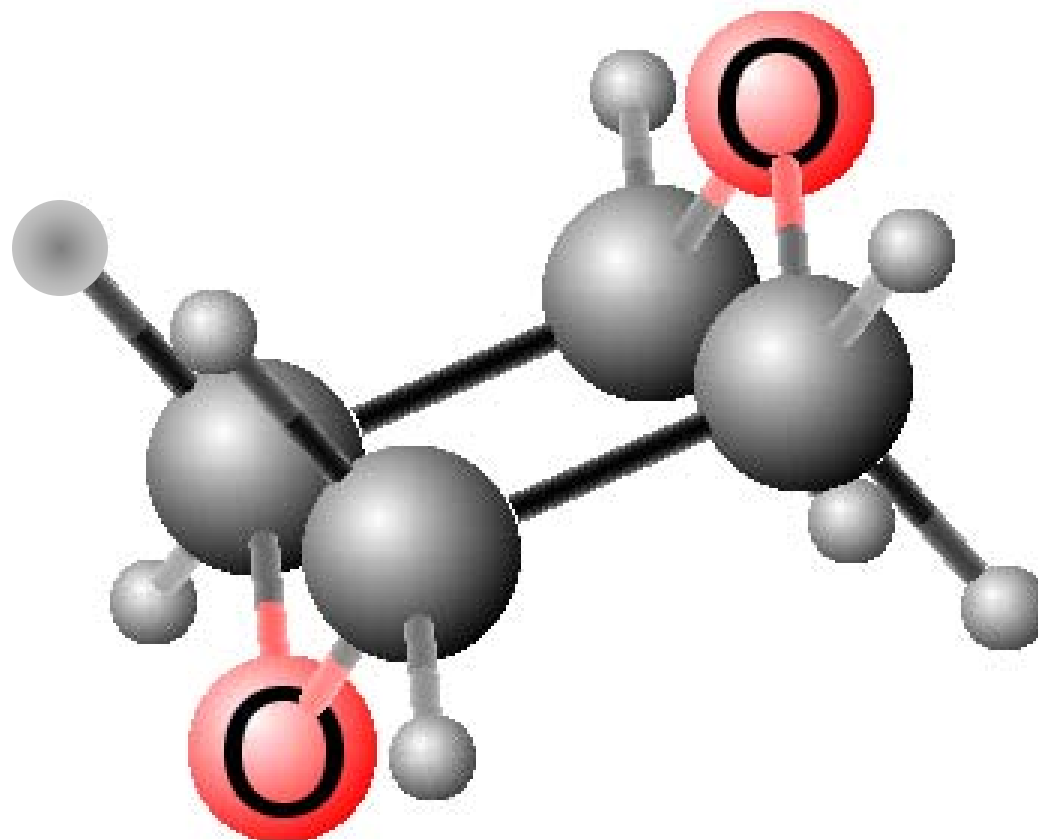


Interesting molecule of the day

WOW!

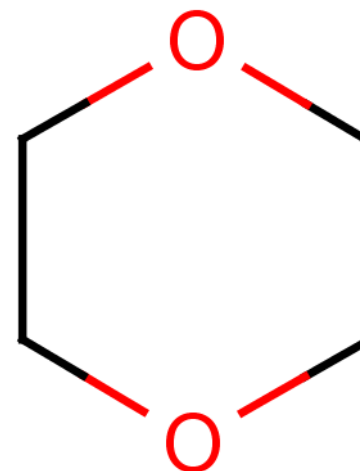
Interesting molecule of the day

- 1,4-dioxane



Interesting molecule of the day

- 1,4-dioxane
 - T_m 11.8 °C, T_b 101.5 °C
 - p_L^* 38.1 mm Hg
 - C_w^{sat} 1×10^6 mg L⁻¹
 - K_{ow} $10^{-0.27}$
 - dehydrating agent
 - polar solvent miscible with both water and most organic solvents
 - toxicity
 - inhalation by human 470 ppm
 - ingestion by rabbit 2,000 mg kg⁻¹



Interesting molecule of the day

- 1,4-dioxane and ducks
 - ~1,000 ducks died in Metro Wastewater Denver plant last winter
 - cause still undetermined
 - suspicion: loss of waterproofing
 - solvents discharged to wastewater
 - 1,4-dioxane
 - 6.1 $\mu\text{g L}^{-1}$ new state standard
 - 3,950 $\mu\text{g L}^{-1}$ allowed in Landfill discharge to wastewater
 - 15 gpm
 - 1,4-dioxane caused duck deaths?



Interesting molecule of the day

- daily load of 1,4-dioxane from Landfill

$$(3,950 \mu\text{g L}^{-1})(15 \text{ gal min}^{-1}) \left(\frac{3.8 \text{ L}}{1 \text{ gal}} \right) \left(\frac{60 \text{ min}}{1 \text{ h}} \right) \left(\frac{24 \text{ h}}{1 \text{ d}} \right) = 3.2 \times 10^8 \mu\text{g}$$

- daily volume of wastewater treated by
 - 130,000,000 gal

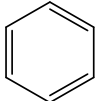
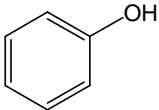
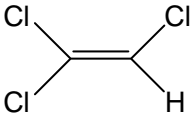
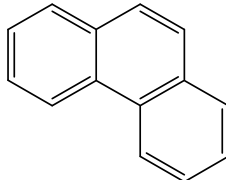
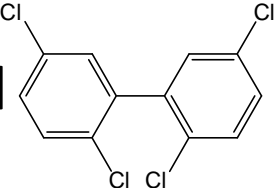
- concentration of 1,4-dioxane in wastewater

$$\left(\frac{3.2 \times 10^8 \mu\text{g d}^{-1}}{130 \times 10^6 \text{ gal d}^{-1}} \right) \left(\frac{1 \text{ gal}}{3.8 \text{ L}} \right) = 0.65 \mu\text{g L}^{-1}$$

Vapor Pressure

- A measure of the abundance of molecules in gas phase
(related to freedom!)
- p^* is the pressure of the vapor of molecules at equilibrium with the pure condensed (solid, liquid) phase
 - p_L^*
 - p_S^*
- p^* varies over **12 orders of magnitude** for compounds of interest to us.
- ENTROPY?

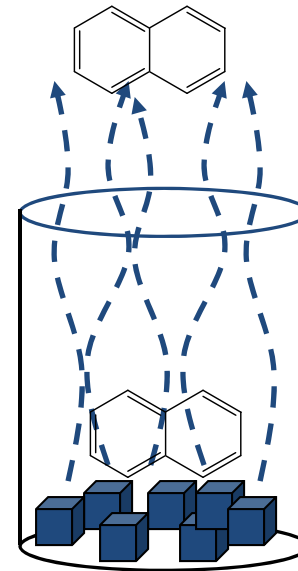
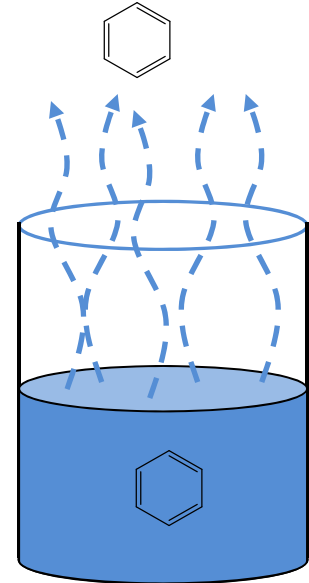
Vapor Pressure

	compound	p_L^* or p_S^* (bar)
benzene		7.9
phenol		0.00025
trichloroethene		0.098
phenanthrene		0.00000016
2,2',5,5'-tetrachlorobiphenyl		0.000000025

Vapor Pressure

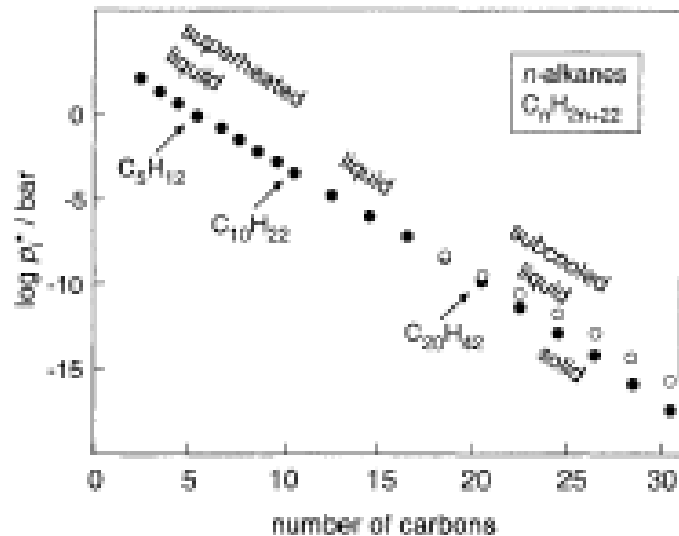
- A phase transition:
 - liquid to/from gas
 - vaporization – liquid to gas
 - condensation – gas to liquid

 - solid to/from gas
 - sublimation – solid to gas
 - condensation – gas to solid



Vapor Pressure

- Does a gas have a vapor pressure?
 - No, because vapor pressure is defined for a transition from a condensed phase (liquid, solid) to a gas phase...
 - ...but what about that Appendix C?



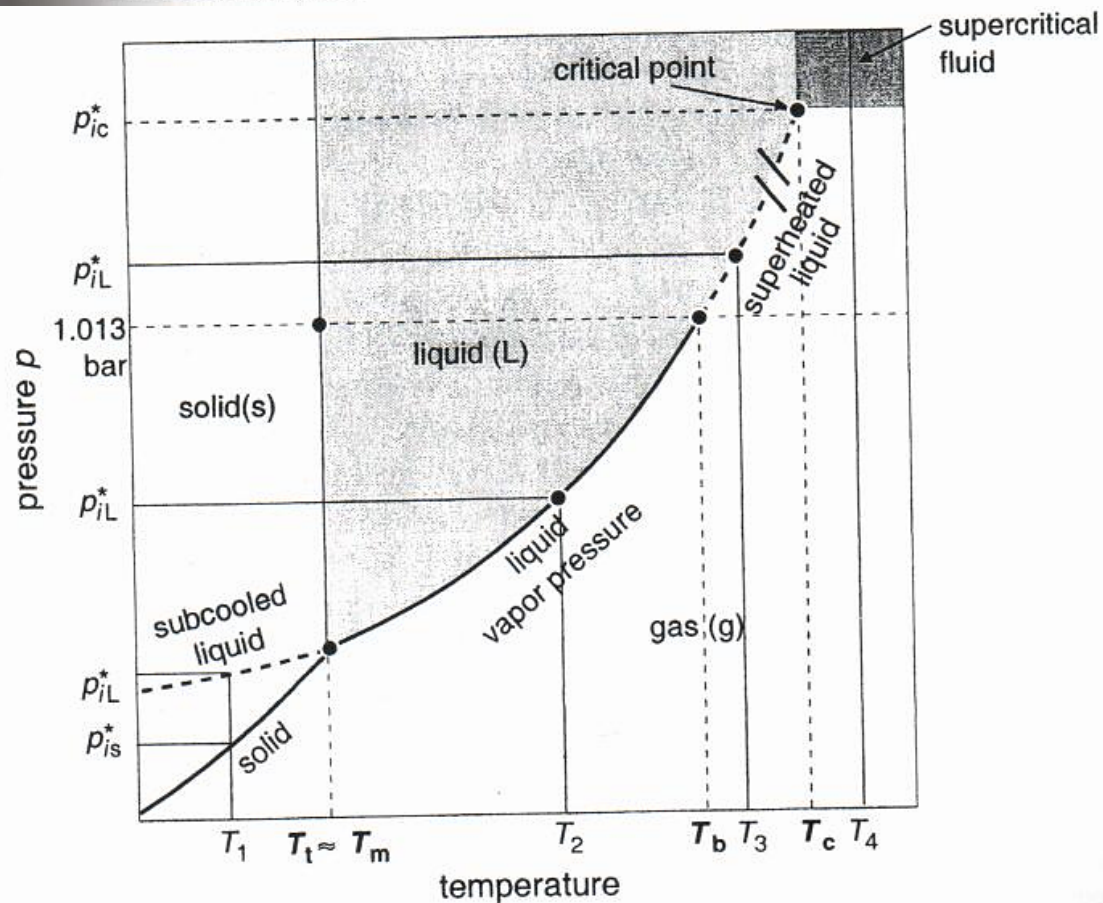
Vapor Pressure

Compound Name	Molecular Formula	M_i (g·mol ⁻¹)	ρ_i (g·cm ⁻³)	T_m (°C)	T_b (°C)	$\log p_i^*/\text{Pa}$	$-\log C_{i/w}^{\text{sat}}$	$-\log K_{i/w}$ calculated (experimental)	$\log K_{i/w}$	$pK_{i/a}$
gases										
Methane	CH ₄	16.0		-182.5	-164.0	7.45	2.82 (1bar)	-1.43	1.09	
Ethane	C ₂ H ₆	30.1		-183.3	-88.6	6.61	2.69 (1bar)	-1.30	1.81	
Propane	C ₃ H ₈	44.1		-189.7	-42.1	5.98	2.85 (1bar)	-1.46	2.36	
<i>n</i> -Butane	C ₄ H ₁₀	58.1	0.58 (L)	-138.4	-0.5	5.40	2.98 (1bar)	-1.58	2.89	
<i>n</i> -Pentane	C ₅ H ₁₂	72.2	0.63	-129.7	36.1	4.83	3.25	-1.69	3.39	
<i>n</i> -Hexane	C ₆ H ₁₄	86.2	0.66	-95.0	69.0	4.30	3.83	-1.74	4.00	
<i>n</i> -Heptane	C ₇ H ₁₆	100.2	0.68	-90.6	98.4	3.79	4.53	-1.93	4.66	
<i>n</i> -Octane	C ₈ H ₁₈	114.2	0.70	-56.8	125.7	3.26	5.20	-2.07	5.15	
<i>n</i> -Nonane	C ₉ H ₂₀	128.3	0.72	-51.0	150.8	2.76	5.77	-2.14	5.65	
<i>n</i> -Decane	C ₁₀ H ₂₂	142.3	0.73	-29.7	174.1	2.24	6.42	-2.27	6.25	
<i>n</i> -Undecane	C ₁₁ H ₂₄	156.3	0.74	-25.6	195.9	1.72				
<i>n</i> -Dodecane	C ₁₂ H ₂₆	170.3	0.75	-9.6	216.3	1.19	7.52	-2.32		
<i>n</i> -Hexadecane	C ₁₆ H ₃₄	226.4	0.77	18.2	287.0	-0.73	7.80	-0.68		
<i>n</i> -Octadecane	C ₁₈ H ₃₈	254.4	0.78	28.2	316.1	-1.78	8.08	-0.09		
“superheated” liquids										
<i>n</i> -Alkanes										
<i>Branched Alkanes</i>										
2-Methylpropane (isobutane)	C ₄ H ₁₀	58.1	0.56 (L)	-159.4	-11.7	5.56	3.07 (1bar)	-1.68	2.82	
2-Methylbutane (isopentane)	C ₅ H ₁₂	72.2	0.62	-159.9	27.9	4.96	3.18	-1.75		
2,2-Dimethylpropane (neopentane)	C ₅ H ₁₂	72.2	0.59 (L)	-16.6	9.5	5.24	3.34 (1bar)	-1.95	3.11	
2-Methylpentane (isohexane)	C ₆ H ₁₄	86.2	0.64	-153.8	60.1	4.45	3.80	-1.86	3.60	
2,2-Dimethylbutane (neohexane)	C ₆ H ₁₄	86.2	0.65	-99.8	49.7	4.63	3.65	-1.89	3.42	
2,2,4-Trimethylpentane (isooctane)	C ₈ H ₁₈	114.2	0.69	-107.4	99.2	3.81	4.67	-2.09		
<i>Unsaturated and Alicyclic Hydrocarbons</i>										
1,3-Butadiene	C ₄ H ₆	54.1	0.62 (L)	-108.9	-4.4	5.45	1.86	-0.47	1.99	
2-Methyl-1,3-butadiene (isoprene)	C ₅ H ₈	68.1	0.68	-146.0	34.0	4.86	2.04	-0.51	2.05	
1,4-Pentadiene	C ₅ H ₈	68.1	0.66	-148.3	26.0	5.00	2.08	-0.69		
Cyclopentene	C ₅ H ₈	68.1	0.77	-135.1	44.2	4.70	2.09	-0.40		

Table 4.1 Normal Melting Points (T_m), Normal Boiling Points (T_b), and Critical Points (T_c, p_{ic}^*) of some n-Alkanes. Note that temperatures are given in °C and not in K^a

Compound	T_m (°C)	T_b (°C)	T_c (°C)	p_{ic}^* (bar)	Location of Ambient Temperature (i.e., 25°C in Fig. 4.2 ($T_1 \dots T_4$))	Aggregate State at 25°C
Methane (CH ₄)	-182.5	-164.0	-82.6	46.04	T_4	gas
n-Butane (C ₄ H ₁₀)	-138.4	-0.5	152.0	37.84	T_3	gas
n-Decane (C ₁₀ H ₂₂)	-29.7	174.1	344.5	21.04	T_2	liquid
n-Eicosane (C ₂₀ H ₄₂)	36.8	343.0	496.0	11.60	T_1	solid

^a All data from Lide (1995).

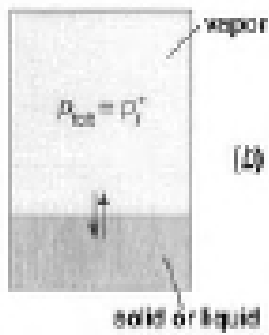


Gibbs phase rule:

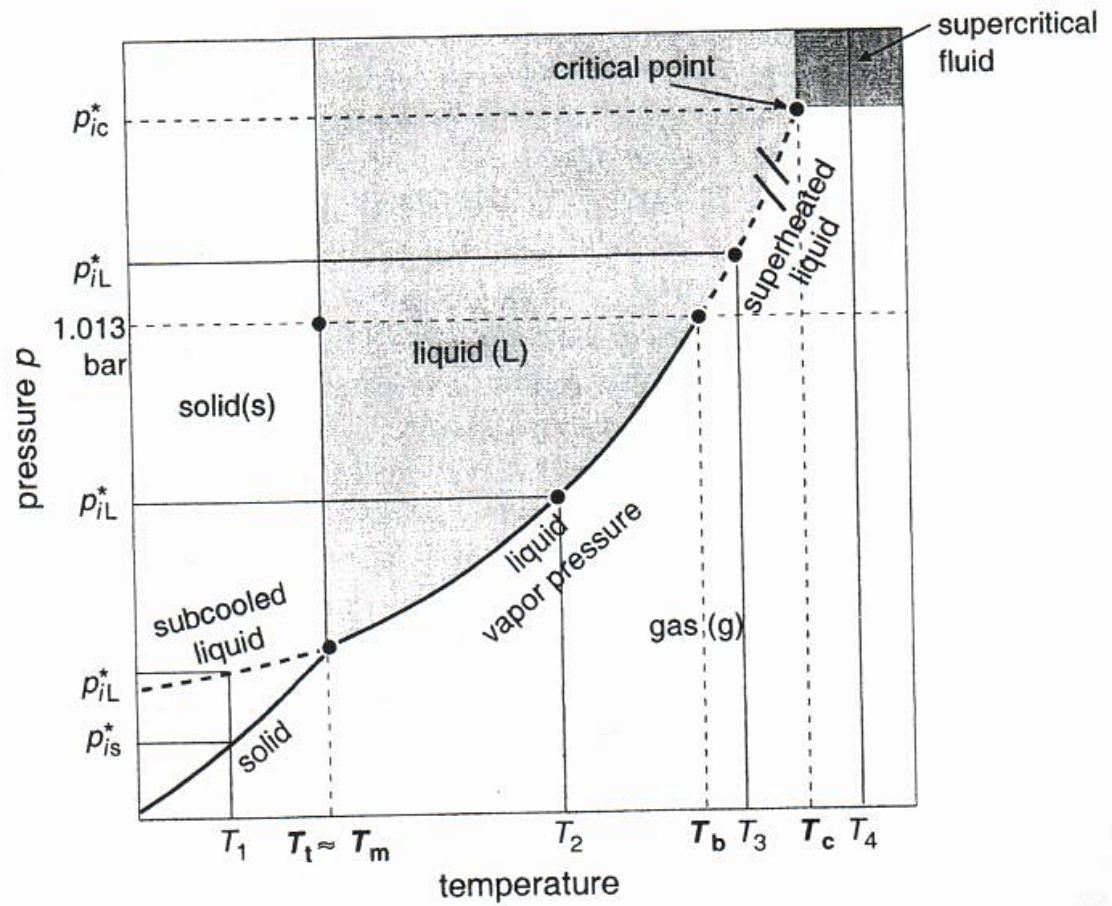
$$df = \# \text{comp} - \text{phases} + 2$$

Single chemical liquid/gas

P proportional to T only



Most environmental pollutants are LIQUIDS OR SOLIDS



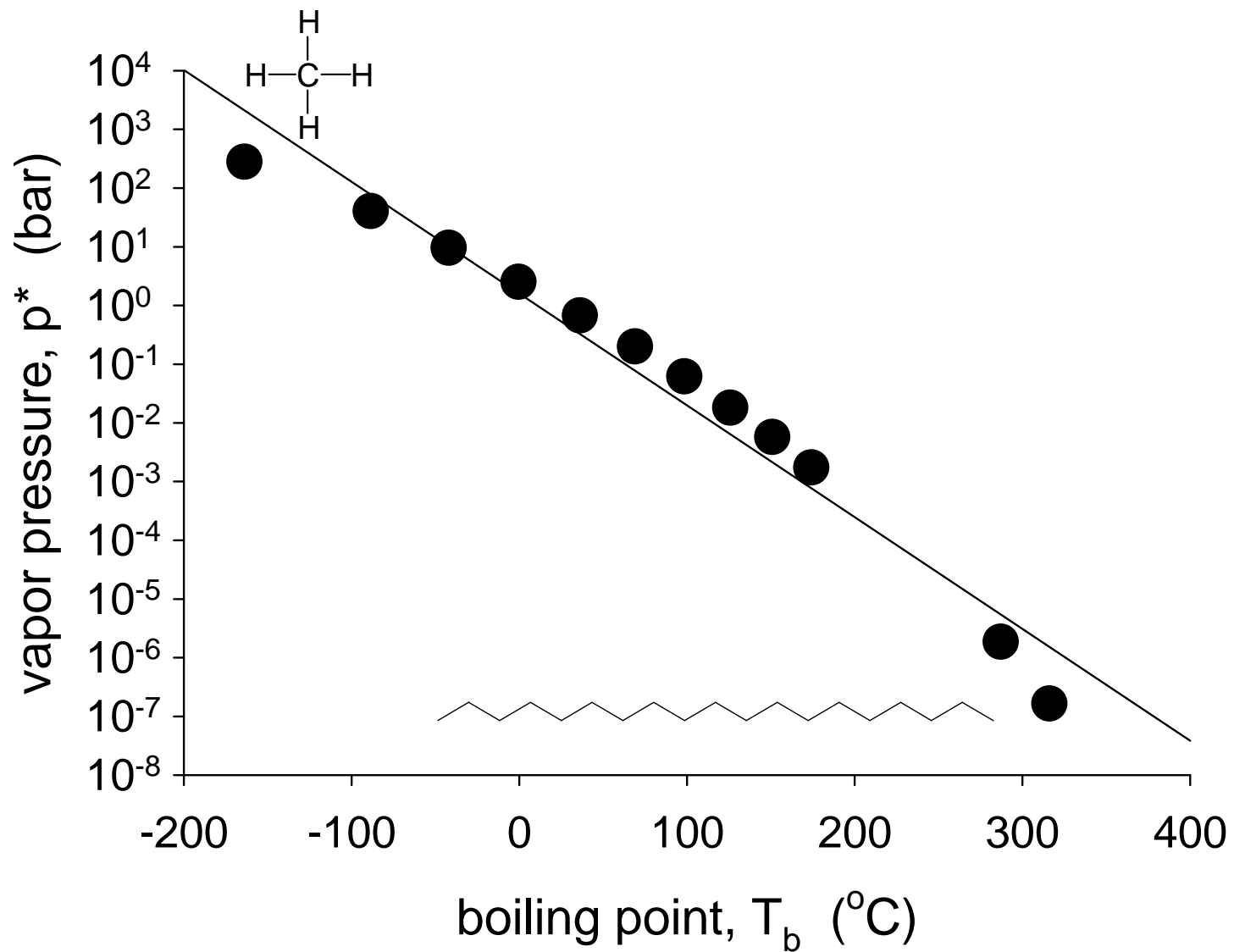
Vapor Pressure

$$\Delta_{\text{vap},\text{sub}}G = \Delta_{\text{vap},\text{sub}}H - T\Delta_{\text{vap},\text{sub}}S$$

alkane	T_b (°C)	$\log p^*$ (bar)	$\Delta_{\text{vap},\text{sub}}G$ (kJ mol ⁻¹)
methane	-164.0	2.45	-17.0
ethane	-88.6	1.61	-9.1
propane	-42.1	0.98	-5.5
butane	-0.5	0.40	-2.1
pentane	36.1	-0.17	1.4
hexane	69.0	-0.70	2.6
heptane	98.4	-1.21	5.5
octane	125.7	-1.74	8.2
nonane	150.8	-2.24	10.7
decane	174.1	-2.76	12.5
hexadecane	287.0	-5.73	25.2
octadecane	316.1	-6.78	78.5

($\Delta_{\text{vap},\text{sub}}G$ were estimated using potentially inconsistent data)

Vapor Pressure



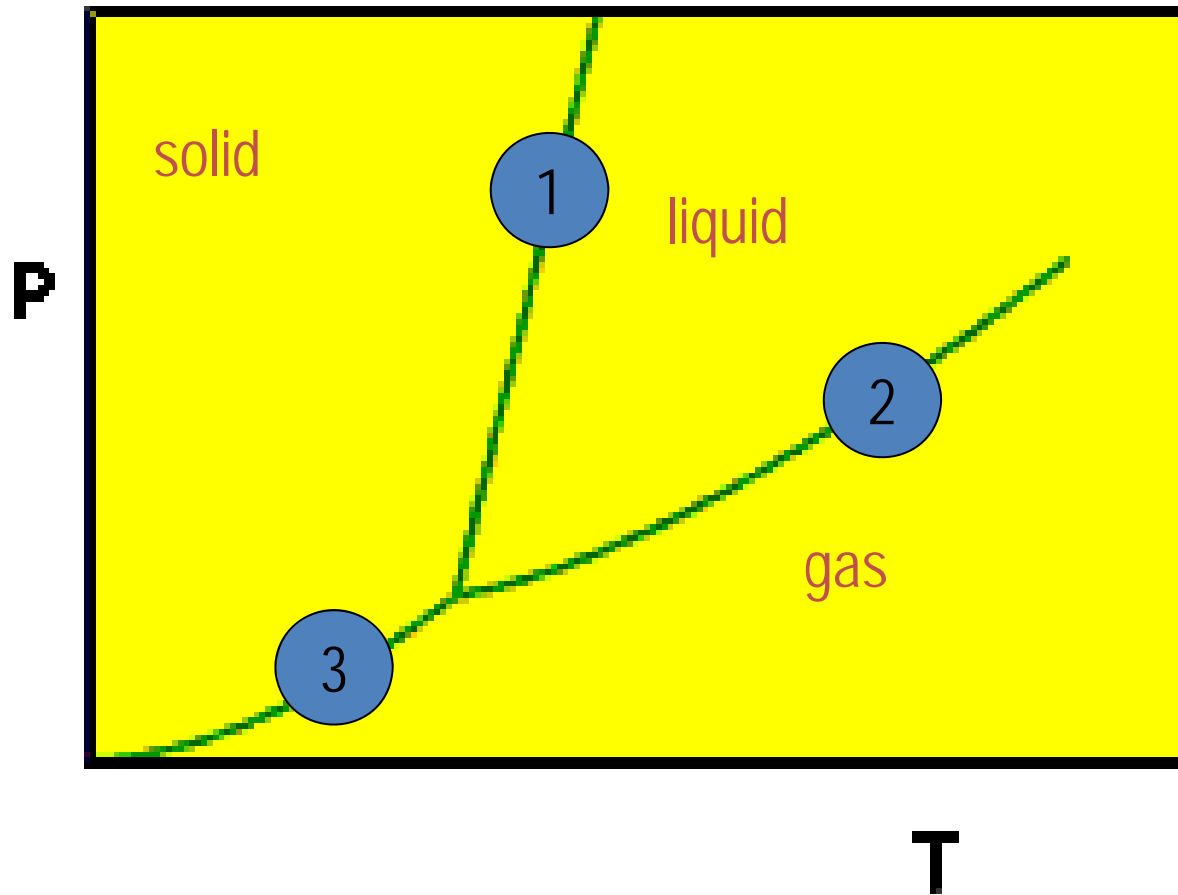
Vapor Pressure

- Clayperon I

$$\frac{dp}{dT} = \frac{\Delta_{12}H}{T \Delta_{12}V}$$

- For the phase transition $1 \leftrightarrow 2$,
 - $\Delta_{12}H$ is the change in molar enthalpy
 - measures intermolecular attraction
 - $\Delta_{12}V$ is the change in molar volume
 - measures randomness

Vapor Pressure



$$\frac{dp}{dT} = \frac{\Delta_{12}H}{T \Delta_{12}V}$$

Vapor Pressure

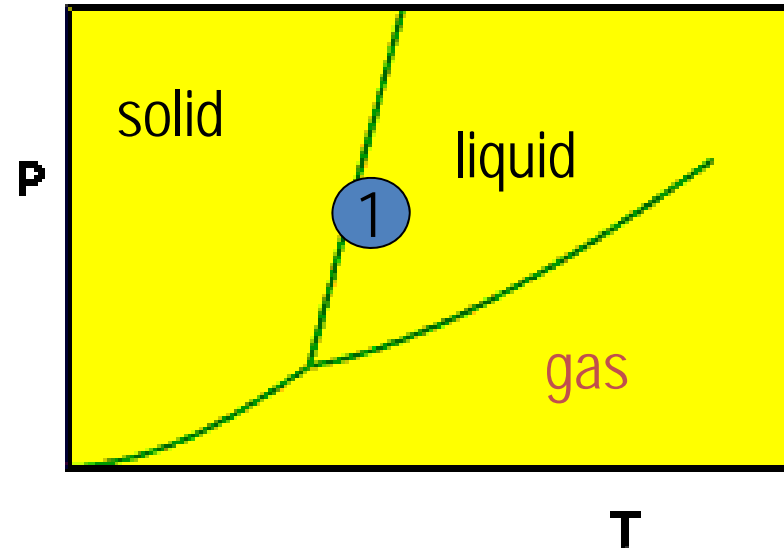
- Solid-liquid

1

- $\Delta_{12}H = \Delta_{\text{fus}}H$
 $\Delta_{\text{fus}}H$ is large

- $\Delta_{12}V = \Delta_{\text{fus}}V$
 $\Delta_{\text{fus}}V$ is small

- $\Delta_{\text{fus}}H / T \Delta_{\text{fus}}V$ is very large;
so is dp/dT



$$\frac{dp}{dT} = \frac{\Delta_{12}H}{T \Delta_{12}V}$$

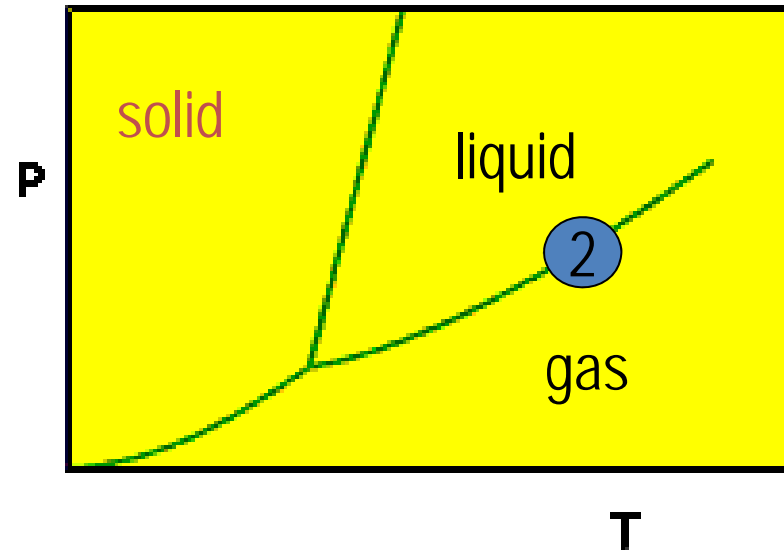
Vapor Pressure

- Liquid-gas 2

- $\Delta_{12}H = \Delta_{\text{vap}}H$
 $\Delta_{\text{vap}}H$ is large
($\Delta_{\text{vap}}H > \Delta_{\text{fus}}H$)

- $\Delta_{12}V = \Delta_{\text{vap}}V$
 $\Delta_{\text{vap}}V$ is large
($\Delta_{\text{vap}}V \gg \Delta_{\text{fus}}V$)

- $\Delta_{\text{vap}}H / T \Delta_{\text{vap}}V$ is small;
so is dp/dT



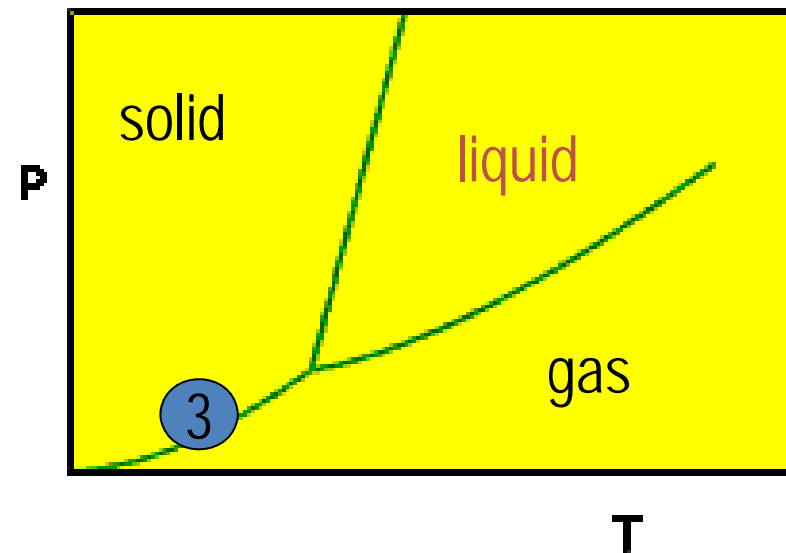
Vapor Pressure

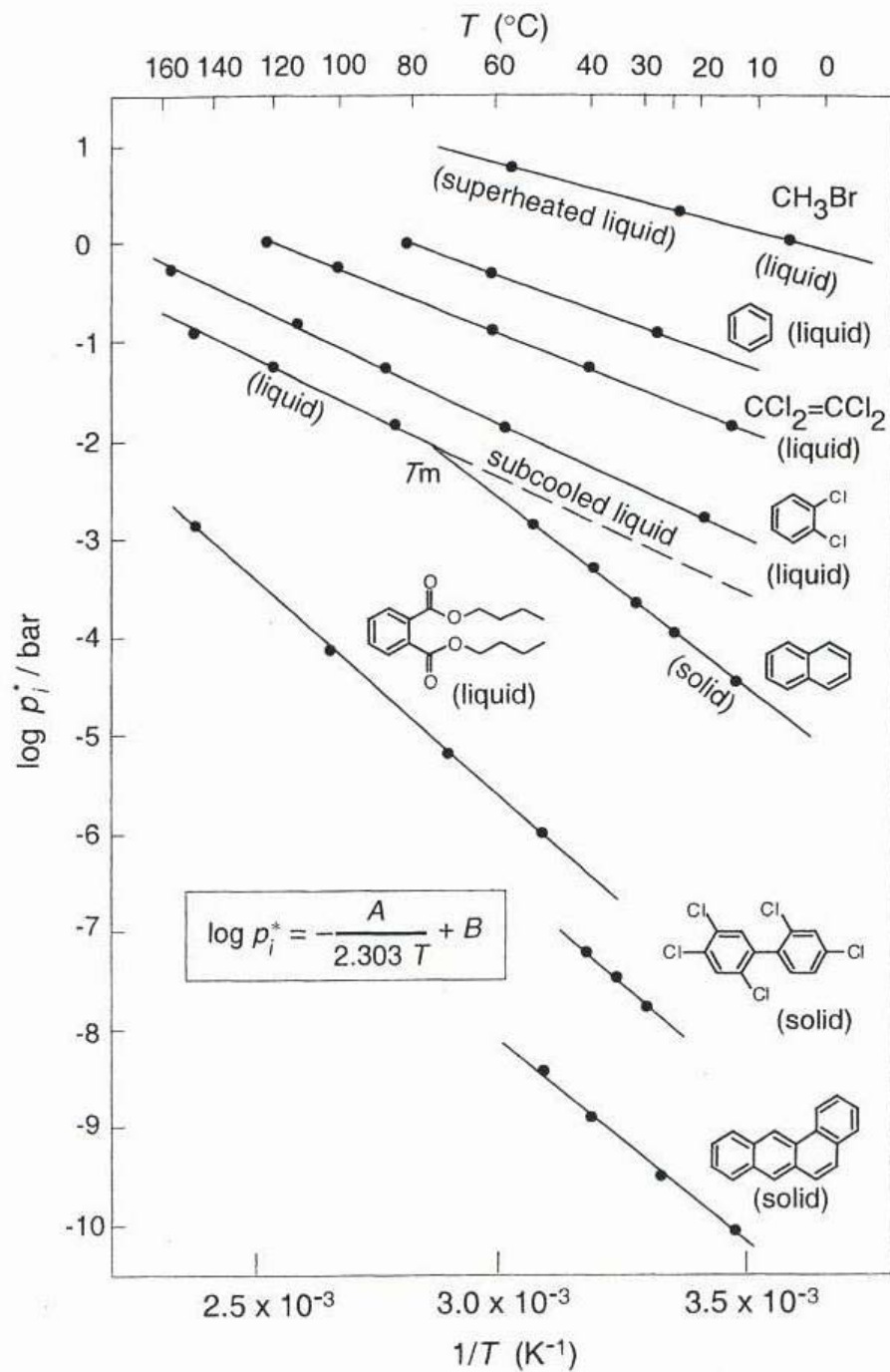
$$\frac{dp}{dT} = \frac{\Delta_{12}H}{T \Delta_{12}V}$$

- Solid-gas

3

- $\Delta_{12}H = \Delta_{\text{sub}}H$
 $\Delta_{\text{sub}}H$ is very large
($=\Delta_{\text{fus}}H + \Delta_{\text{vap}}H$)
- $\Delta_{12}V = \Delta_{\text{sub}}V$
 $\Delta_{\text{sub}}V$ is large
($\Delta_{\text{fus}}V + \Delta_{\text{vap}}V$) $\sim \Delta_{\text{sub}}V$
- $\Delta_{\text{sub}}H/T \Delta_{\text{sub}}V$ is “medium”;
so is dp/dT





$$\ln P^0 = \frac{\Delta H_{vap}}{RT} + A$$

Liquids with no phase change
 Assuming ideal behavior
 $V_{liq} \ll V_{gas} \sim \text{constant}$

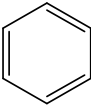
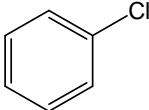
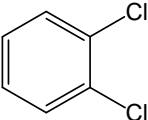
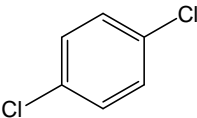
Vapor Pressure

- Clayperon II

$$\ln p^* = -\frac{\Delta_{12}H}{RT} + \frac{\Delta_{12}S}{R}$$

- enthalpy
 - breaking bonds in condensed phase
 - essentially no bonds formed in vapor phase
 - intermolecular interactions
 - van der Waals – major contribution to $\Delta_{12}H$
 - » varying electron distributions, dipole: induced dipole, dipole: dipole
 - polar – minor contribution – a few kJ mol^{-1}
 - hydrogen bonding – about 10-20 kJ mol^{-1}
- entropy
 - related to change in volume
 - greater volume = greater randomness = greater entropy

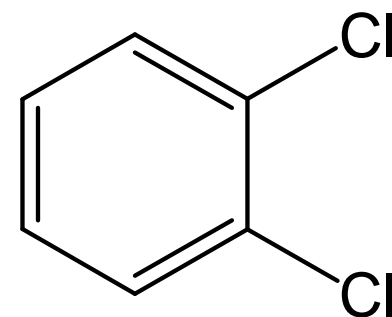
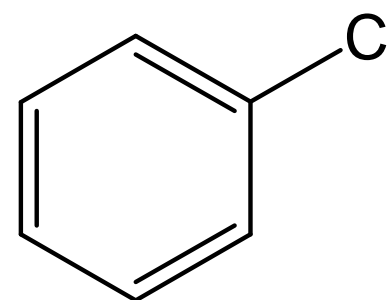
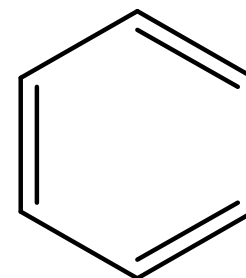
Vapor Pressure

compound	structure	T_b (K)	$\Delta_{\text{vap}}H(T_b)$ (kJ mol ⁻¹)	μ (D)
benzene		353	30.8	0
chlorobenzene		405	36.5	1.54
1,2-dichlorobenzene		454	40.6	2.50
1,4-dichlorobenzene		447	39.7	0

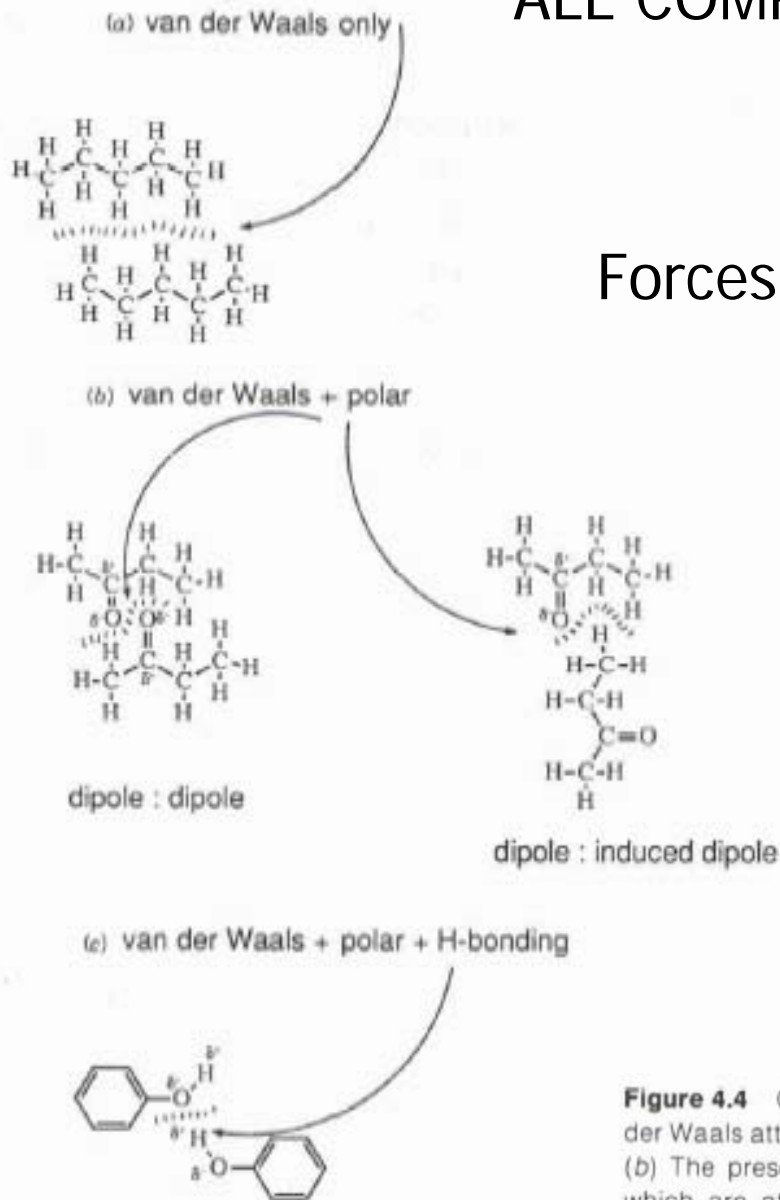
Vapor Pressure

- What kind of interaction is responsible for the increase in boiling point and enthalpy of vaporization in the series of benzene, chlorobenzene, and *o*-dichlorobenzene?

- A. van der Waals
- B. polar
- C. hydrogen bonding



ALL COMPOUNDS



Forces add up so \rightarrow size matters

Figure 4.4 Conceptualization of molecular forces and interactions. (a) Nonspecific or van der Waals attractions occur between all forms of matter, even nonpolar materials like pentane. (b) The presence of unevenly distributed electron densities gives rise to bond-size dipoles which are attractive to other dipoles or which induce electron redistribution in neighbor molecules and thereby establish dipole:induced dipole attractions. (c) Hydrogen atoms bonded to oxygen or nitrogen are available to be attracted to the nonbonded electrons of other oxygen or nitrogen atoms, establishing hydrogen bonds.

TABLE 4.1 Variations in Heats of Vaporization at Normal Boiling Points of Substituted Benzenes

Compound	Substituent(s)	$T_b(\text{K})$	$\Delta H_{\text{vap}}(T_b)$ ($\text{kJ}\cdot\text{mol}^{-1}$)	$\mu(\text{D})$
Benzene	— H	353	30.8	0
Methylbenzene (toluene)	— CH_3	384	33.2	0.4
Ethylbenzene	— CH_2CH_3	409	35.6	0.6
<i>n</i> -Propylbenzene	— $(\text{CH}_2)_2\text{CH}_3$	432	38.2	
<i>n</i> -Pentylbenzene	— $(\text{CH}_2)_4\text{CH}_3$	479	41.2	
<i>n</i> -Heptylbenzene	— $(\text{CH}_2)_6\text{CH}_3$	519	45.2	
<i>n</i> -Nonylbenzene	— $(\text{CH}_2)_8\text{CH}_3$	555	49.0	
Isopropylbenzene	— $\text{CH} \begin{matrix} \text{CH}_3 \\ \text{CH}_3 \end{matrix}$	439	37.5	
Vinylbenzene (styrene)	— $\text{CH}=\text{CH}_2$	418	37.0	
Fluorobenzene	— F	358	31.2	1.57
Chlorobenzene	— Cl	405	36.5	1.73
Bromobenzene	— Br	429	37.9	1.71
Iodobenzene	— I	462	39.5	1.42
1,2-Dichlorobenzene	2 x Cl	454	40.6	2.5
1,4-Dichlorobenzene	2 x Cl	447	39.7	0
Nitrobenzene	— NO_2	484	40.8	4.2
Aminobenzene	— NH_2	458	44.5	1.5
Hydroxybenzene	— OH	455	40.7	1.5
Benzylalcohol	— CH_2OH	478	50.6	1.7
Benzoic acid	— COOH	522	50.6	

$\text{H, C, S, I} < \text{N, Br} < \text{Cl} < \text{O} < \text{F}$

Vapor Pressure

$$\ln p^* = -\frac{\Delta_{12}H}{RT} + \frac{\Delta_{12}S}{R}$$





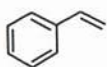
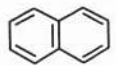
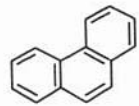

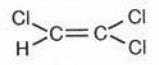
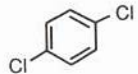
- Entropy of vaporization (liquid to gas)
 - Trouton (1884): $\Delta_{vap}S$ same for all liquids
 - $\Delta_{vap}S \sim 88 \text{ J mol}^{-1} \text{ K}^{-1}$
 - because $\Delta_{vap}H$ and T_b are related

$$\text{if } \Delta_{vap}G = 0, \text{ then } \Delta_{vap}S(T_b) = \frac{\Delta_{vap}H(T_b)}{T_b}$$

- Kistiakowsky (1923): $\Delta_{vap}S$ depends on T_b
 - Clayperon + ideal gas law

$$\Delta_{vap}S(T_b) = 36.6 + 8.31 \ln T_b \quad (\text{Eqn. 4-19})$$

TABLE 4.2 Constancy of Entropy of Vaporization at the Normal Boiling Point for Some Organic Compounds

Compound	Structure	T_b (K)	$\Delta S_{\text{vap}}(T_b)(\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})$			
			Observed	Kistiakowsky Prediction ^a	Intermolecular Forces ^b	
Pentane		309	83.3	84.2	vdW	
Pentadecane		544	90.8	88.9		
Benzene		353	87.0	85.4		
Toluene		384	86.6	86.0		
Styrene		418	88.7	86.8		
Naphthalene		491	88.3	88.1		
Phenanthrene		613	90.8	89.9		
Pyridine		389	90.4	86.2		
Methylene chloride	CH_2Cl_2	313	90.0	84.4		vdW + polar
Chloroform	CHCl_3	335	88.3	84.9		
Carbon tetrachloride	CCl_4	350	85.8	85.3		
Trichloroethylene		360	87.4	85.5		
<i>p</i> -Dichlorobenzene		447	89.1	87.3		

Vapor Pressure

$$\ln p^* = -\frac{\Delta_{12}H}{RT} + \frac{\Delta_{12}S}{R}$$

- Entropy of vaporization (liquid to gas)
 - Fishtine (1963): corrections for polar effects

$$\Delta_{vap}S(T_b) = K_F (36.6 + 8.31 \ln T_b) \quad (\text{Eqn. 4-20})$$

- Myrdal et al. (1996): correction for molecule flexibility and polar effects

$$\Delta_{vap}S(T_b) = 86.0 + 0.4\tau + 1421HBN \quad (\text{Eqn. 4-21})$$

effective number
of torsional
bonds

hydrogen bond
number

Vapor Pressure

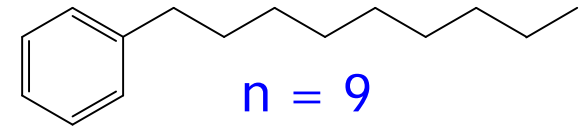
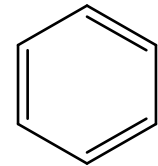
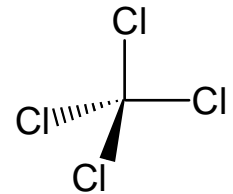
$$\ln p^* = -\frac{\Delta_{12}H}{RT} + \frac{\Delta_{12}S}{R}$$

- Entropy of melting (solid to liquid)
 - $\Delta_{fus}S$ sensitive to molecular structure
 - increase in V
 - translation, rotation
 - increase in “flexibility”
 - internal bending
 - structural contributions to $\Delta_{fus}S$
 - rigid, spherically symmetric
 - rigid
 - flexible chain

Vapor Pressure

$$\ln p^* = -\frac{\Delta_{12}H}{RT} + \frac{\Delta_{12}S}{R}$$

- Entropy of melting (**solid to liquid**)
 - Reid et al. (1977): symmetry, rigidity, flexibility
 - rigid, spherically symmetric
 - $\Delta_{\text{fus}}S_{\text{translation}} \sim 14 \text{ J mol}^{-1} \text{ K}^{-1}$
 - rigid
 - $\Delta_{\text{fus}}S_{\text{tran}} + \Delta_{\text{fus}}S_{\text{rotation}} \sim 56.5 \text{ J mol}^{-1} \text{ K}^{-1}$
 - flexible (internal chain $n > C_5$)
 - $\Delta_{\text{fus}}S_{\text{tran}} + \Delta_{\text{fus}}S_{\text{rot}} + \Delta_{\text{fus}}S_{\text{internal}} \sim$
 $\Delta_{\text{fus}}S(T_m) \sim 56.5 + 10.5(n-5) \text{ J mol}^{-1} \text{ K}^{-1}$



Vapor Pressure

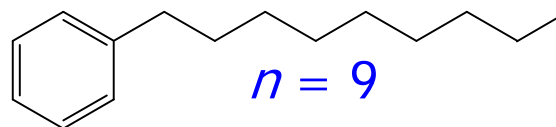
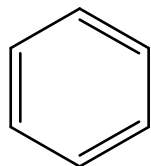
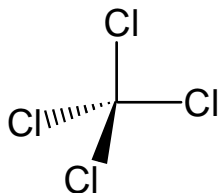
$$\ln p^* = -\frac{\Delta_{12}H}{RT} + \frac{\Delta_{12}S}{R}$$

- Entropy of melting (solid to liquid)
 - Myrdal and Yalkowsky:

$$\Delta_{fus}S(T_m) = 56.5 + 9.2\tau - 19.2\log \sigma$$

effective number of torsional bonds rotational symmetry number

- does not work well for small spherical or H-bonding molecules



NOT A GOOD WAY TO ESTIMATE OR PREDICT!

Thinking about your project/presentation

- **Anthropogenic environmental disasters**
 1. **Bhopal: the Union Carbide gas leak**
 2. **Jilin chemical plant explosions 2005**
 3. **Seveso: Italian dioxin crisis 1976**
 4. **World Trade Center Toxic Dust 2001**
 5. **Major oil spills of the 20th and 21st century**
 6. **The Love Canal chemical waste dump**
 7. **View-Master factory in Beaverton, Oregon**
 8. **Brio Superfund Site**
 9. **Whole in the Ozone layer**
 10. **Kanemi Yusho oil poisoning 1968**
 11. **DWH Incident**