

Homework #1 Due tomorrow end of class.

Office Hours today?

I am free *** today EXCEPT 1-2:10 (but I want to find out which times I must be in my office)

***(If someone absolutely needs 12-1 please say so)

Homework # 1 Due Tomorrow in class

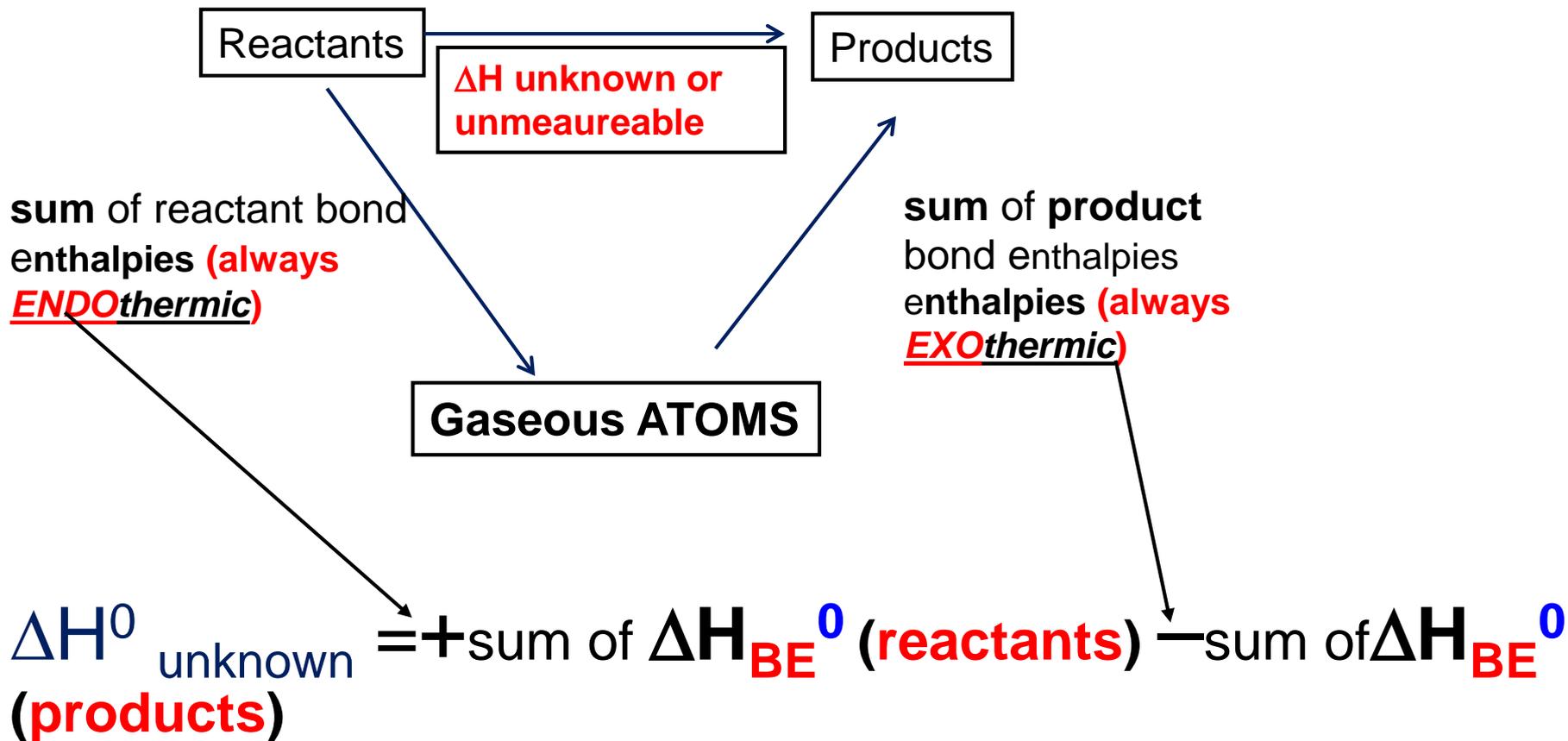
Guidelines:

1. *Obviously*, no two papers should be identical. **Credit cannot be given to essentially identical papers.**
2. OK to work in groups, but for mutual discussion purposes only.
Your paper is to reflect your own unique thoughts and understanding.
3. Bare, lonely answers without evidence of how they were obtained will not receive credit.
4. **Units should be indicated for all numbers**, and units should cancel to give the correct units for the answer. Units will be as important as numbers in the scoring.
5. Graded homework will be returned on Friday. (Exam #1 is on Tuesday)

“Bond Enthalpies (again)”

Another Exploitation of State Function Concept in Thermodynamics

Path does not matter. H is a STATE FUNCTION



Why the sign change???

Bond Enthalpy is DEFINED as the:

Enthalpy of bond breaking (not making), i.e., always +

For the midterm and final **exams** in this course,
you will be allowed to bring a **4x6” card of notes (both sides)**

The beginning of **your 4 x 6 sheet(both sides)** for Exam 1. Use it for HOMEWORK

<u>Always True</u>	<u>Conditional</u>
$\Delta U = q + w$	<p>Adiabatic: $q = 0$; $\Delta U = w$; Constant V: $\Delta U = \int_{T_1}^{T_2} C_v dT$</p> <p>$\Delta U = C_v (T_2 - T_1)$ if C_v constant For ideal gas the above is always true (<u>even if volume changes</u>)</p>
$H = U + pV$ $\Delta H = \Delta U + p_2 V_2 - p_1 V_1$	<p>For $P = P_{ext} = \text{constant}$ and PV work only: $\Delta H = q = \Delta H = \int_{T_1}^{T_2} C_p dT$ $\Delta H = C_p (T_2 - T_1)$ if C_p constant For ideal gas the above is always true (<u>even if pressure changes</u>)</p>
$dw_{pV} = -p_{ext} dV$ $w_{pV} = -\int_{V_1}^{V_2} p_{ext} dV$	<p>for p_{ext} constant: $w_{pV} = -p_{ext} (V_2 - V_1)$; if isothermal reversible and ideal gas:</p> $w_{pV} = -\int_{V_1}^{V_2} p dV = -nRT \ln \frac{V_2}{V_1}$ <p><u>Solids and Liquids</u> (volume changes are very small) $C_p \cong C_v$ and $\Delta H \cong \Delta U$</p>

Partial Pressure ($p_{\text{H}_2\text{O}}$) for example.

Ideal gases behave ***independently*** (by definition) $pV=nRT$
 n is the number of moles. **Does not matter what kind of molecule.**

Therefore, $pV = (n_A + n_B + n_C) RT$ for a MIXTURE of gases A, B, C

$$p = \frac{nRT}{V} = \frac{n_A RT}{V} + \frac{n_B RT}{V} + \frac{n_C RT}{V} + \dots$$
$$= p_A + p_B + p_C + \dots$$

$$p_A = \text{partial pressure of gas A} = \frac{n_A RT}{V} = [A]RT$$

i.e., **partial pressure of gas A = p_A = the molar concentration of A x RT**

i.e., partial pressure is ***just a unit of concentration*** (in fact the **most commonly used** unit of concentration for gases).

NOTE: even though we started this conversation with a mixture of gases,

partial pressure has nothing to do with what other gases are present. (assuming ideal behavior)

Quiz: Air is 20% O₂ and 80% N₂

If the molar concentration of O₂ = 0.008 mol/L
and the molar concentration of N₂ = 0.032 mol/L
what is the partial pressure of O₂ if RT = 25 L atm ?

$$p_{O_2} = ?$$
$$= n/V RT = .008 \times 25 = 0.2 \text{ atm}$$

The answer has **NOTHING** to do with how much
N₂ is present

The p_{O_2} is just that pressure caused by the O₂
collisions with the walls.

That is the same as if no N₂ is present

Vapor Pressure

The *vapor pressure* of a pure liquid (at a certain temperature) is that *partial pressure* of the vapor that is in *equilibrium* with the liquid, at that temperature.

(also independent of other molecules present in the vapor)

For pure liquid A: “vapor pressure” = $[A(\text{gas})]_{\text{equil.}} RT = (p_A)_{\text{equilibrium}}$

Note: “Vapor pressure” of pure liquid is the *equilibrium constant* for the “reaction”: $\text{H}_2\text{O}(\text{pure liquid}) \rightarrow \text{H}_2\text{O}(\text{gas})$, for example.

Is the reaction endothermic or exothermic?

What does **LeChatelier’s Principle** say about which direction the equilibrium of this reaction will shift as temperature is raised?

If **ANYTHING is added** to a system at **equilibrium** it will be **USED**.

If heat is added (raise temperature), equilibrium will shift to **right**

“Heat” of vaporization means ΔH for vaporization

TABLE 2.2 Physical Properties* of Water, H_2O , $M = 18.0153 \text{ g mol}^{-1}$

Solid H_2O (ice)						
(at 0 C = 273.15 K, and 1 bar)						
Density (ρ) = 0.9167 g mL ⁻¹ = 916.7 kg m ⁻³						
Molar volume $V_m = 19.65 \text{ mL mol}^{-1} = 1.965 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$						
Vapor pressure = 0.00612 bar = 612 Pa						
Molar enthalpy of fusion (melting) $\Delta_{\text{fus}}H_m = 6007 \text{ J mol}^{-1}$						
Absolute molar entropy $S_m = 41.3 \text{ J mol}^{-1} \text{ K}^{-1}$						
Molar heat capacity at 1 bar ($C_{p,m}$) = 38.0 J mol ⁻¹ K ⁻¹						
Liquid H_2O						
Temperature (°C)	Density kg m ⁻³	Surface tension mN m ⁻¹	Vapor pressure (Pa)	Molar heat capacity $C_{p,m}$	Enthalpy of vaporization, kJ mol ⁻¹	Viscosity (mPa s)
0	999.8	75.65	612	76.01	44.91	1.792
20	998.2	72.74	2536	75.38	44.08	1.002
40	992.2	69.60	7370	75.29	43.27	0.653
60	983.2	66.24	19900	75.39	42.44	0.466
80	971.8	62.67	46120	75.61	41.56	0.354
100	958.3	58.91	101320	75.95	40.66	0.282
Absolute molar entropy $S_m = 63.3 \text{ J mol}^{-1} \text{ K}^{-1}$ at 273.15 K						
= 86.9 J mol ⁻¹ K ⁻¹ at 373.15 K						
Boiling point at 1 bar pressure: 372.76 K						
Gaseous H_2O (steam)						
(at 99.6°C)						
Absolute molar entropy $S_m = 195.8 \text{ J mol}^{-1} \text{ K}^{-1}$						
Molar enthalpy of vaporization (boiling) $\Delta_{\text{vap}}H_m = 40657 \text{ J mol}^{-1}$						
Molar heat capacity at 1 bar ($C_{p,m}$) = 36.5 J mol ⁻¹ K ⁻¹						

*Some of the properties listed will be defined and discussed in later chapters.

What does **LeChatelier's Principle** say about which direction this equilibrium of this reaction will shift as temperature is raised? If **ANYTHING** is added to a system at **equilibrium** it will be **USED**. If heat is added (raise temperature) equilibrium will shift to **right**

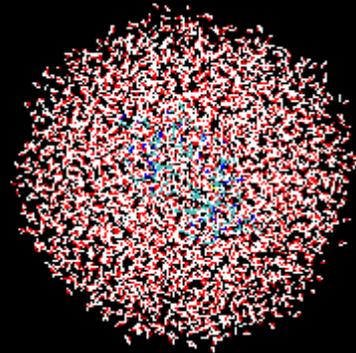
The vapor pressure of a liquid increases rapidly with increasing T because evaporation is endothermic, e.g., for water:

at 25 °C $(p_{\text{H}_2\text{O}})_{\text{eq}} = 0.0313 \text{ atm} = 100\% \text{ relative humidity}$

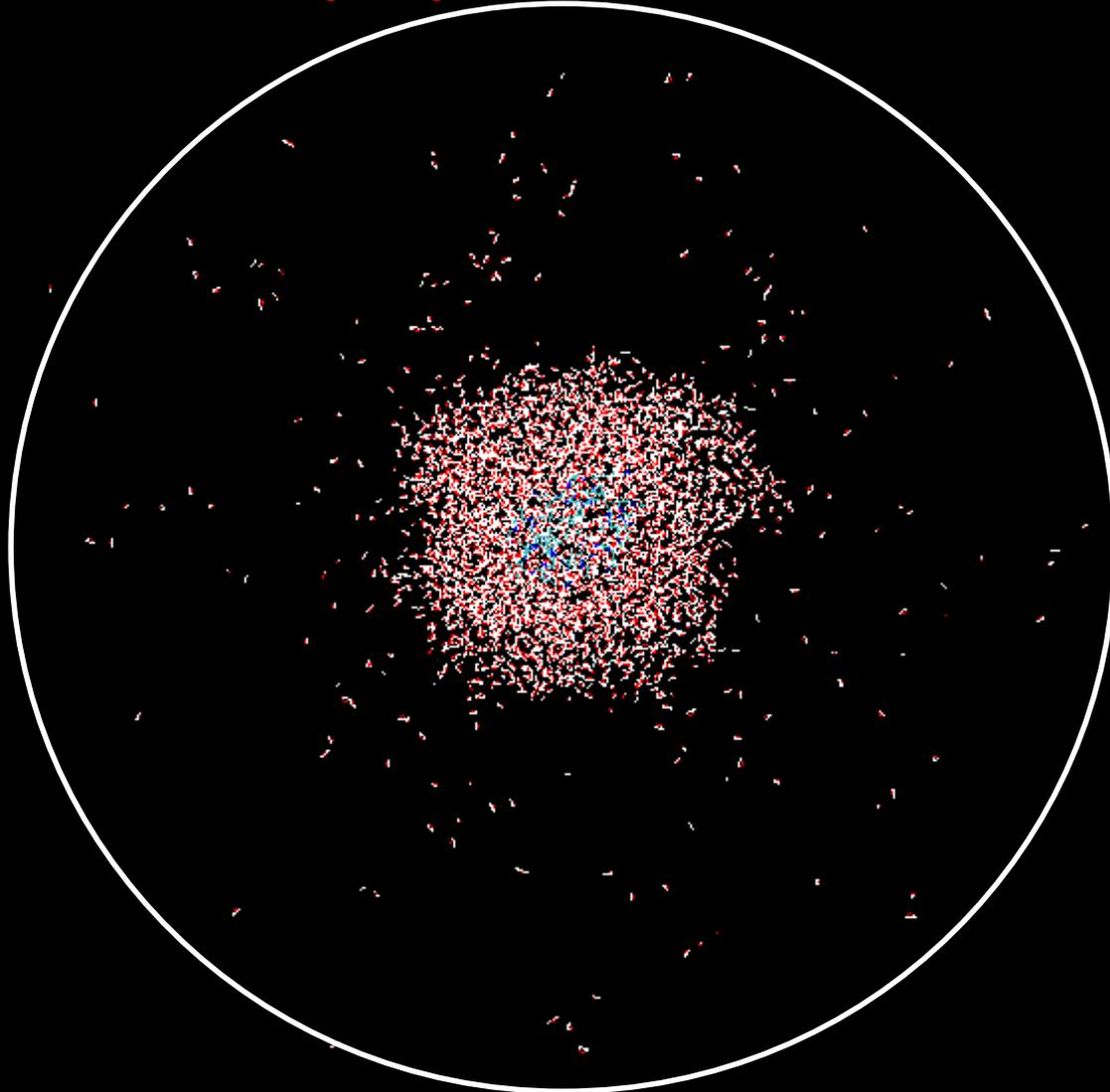
at 100 °C $(p_{\text{H}_2\text{O}})_{\text{eq}} = 1.0000 \text{ atm} = 100\% \text{ relative humidity}$
 $= 1.013 \text{ bar}$

Imagine a small water droplet with a few thousand water molecules. The oxygens are red and hydrogens are white. A small protein (blue) is in the center of the droplet. The drop is surrounded by a glass sphere.

Before evaporation



After **dynamic equilibrium** established. The partial pressure of water now = **“the vapor pressure”**



Vapor Pressure visualized:

Molecular Dynamics Simulation of evaporation from a small drop of water in the glass sphere.

[361 website Vapor Pressure Movie \(15th Grade Version\)](#)

- Simulation by Jose R. Tusell, CHARMM
- Graphics using VMD <http://www.ks.uiuc.edu/Research/vmd/>

Vapor Pressure Movie (4th Grade version)

<http://www.mhhe.com/physsci/chemistry/essentialchemistry/flash/vaporv3.swf>

Relative Humidity and Vapor Pressure (V.P.)

what happens to liquid water when? :

$p_{\text{H}_2\text{O}} < \text{V.P.}$ (relative humidity < 100%) **water evaporates**

$p_{\text{H}_2\text{O}} > \text{V.P.}$ (relative humidity > 100%) **water condenses**

$p_{\text{H}_2\text{O}} = \text{V.P.}$ (relative humidity) = 100% **“nothing” happens**
(dynamic equilibrium)

in other words:

if $p_{\text{H}_2\text{O}} < \text{V.P.}$, air is ***unsaturated*** with water vapor

if $p_{\text{H}_2\text{O}} = \text{V.P.}$, air is ***saturated*** with water vapor

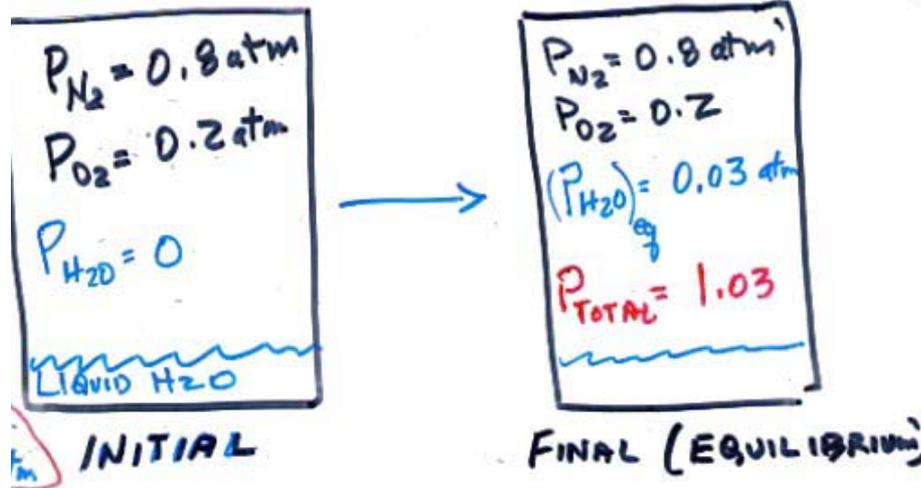
if $p_{\text{H}_2\text{O}} > \text{V.P.}$, air is ***super saturated*** with water vapor

entirely analogous to dissolving sugar in water.

Note: “Vapor pressure” of pure water is the **equilibrium constant** for the “reaction”:
 $\text{H}_2\text{O}(\text{pure liquid}) \rightarrow \text{H}_2\text{O}(\text{gas})$

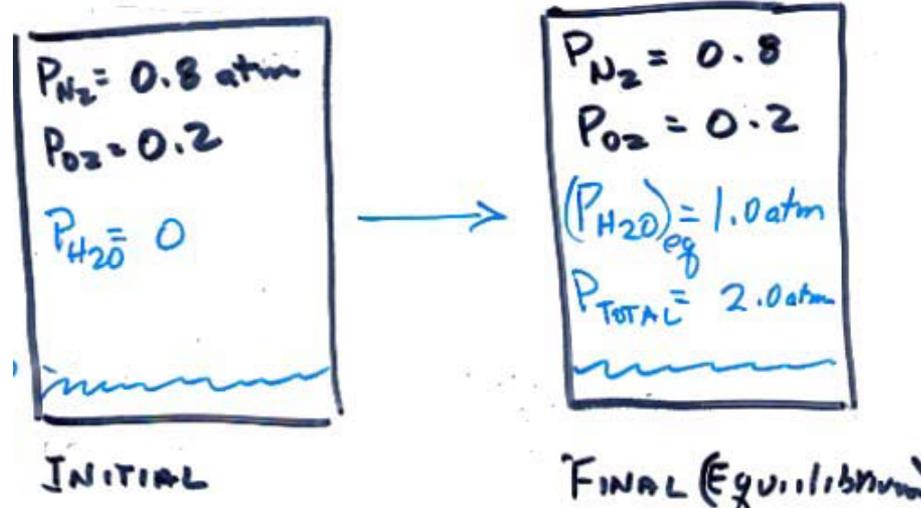
09 5-2
MORE PARTIAL PRESSURE ≠ "VAPOR PRESSURE"

Vapor pressure at 25°C = 0.03 atm



What are p_{N_2} , p_{O_2} and p_{H_2O} at equilibrium?

Vapor pressure at 100°C = 1.0 atm



What are p_{N_2} , p_{O_2} and p_{H_2O} at equilibrium?

If we reduce the volume by half what are p_{N_2} , p_{O_2} and p_{H_2O} at equilibrium?

1.6 0.4 and 1.0