

Homework # 1 Due Thursday in class

Guidelines:

1. *Obviously*, no two papers should be identical. **Credit cannot be given to 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 the next day (maybe) or on Mon
Due to shortage of TA help, I may not be able to grade every problem.
Sadly, I do not know which ones.

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

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

Typical expansion work problem: you are often only given 3 of the 4 variables.

You will have to use a form of $pV = nRT$ to find the unknown variable.

Most of the problems give p in *bars* and V in *L* so I prefer to use:

$pV = n$ **0.083145** *L bar mol⁻¹ K⁻¹ T* or if p in *atm*

$pV = n$ **0.0821** *L atm mol⁻¹ K⁻¹ T* to find the missing variable.

Then, to get the work:

If reversible isothermal : use $R = 8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$

$$w = -nRT \int_{V_1}^{V_2} \frac{dV}{V} = -nRT \ln \frac{V_2}{V_1}$$

If constant external pressure:

$$w = -p_{ext} (V_2 - V_1) \text{ bar L} \times \frac{8.3145 \text{ J mol}^{-1} \text{ K}^{-1}}{0.083145 \text{ bar L mol}^{-1} \text{ K}^{-1}}$$

$$w = -p_{ext} (V_2 - V_1) \text{ bar L} \times 100 \text{ J bar}^{-1} \text{ L}^{-1}$$

Problem 24 (c): see page 37 in text

Problem 28

(a) **Correction:** $D_r H^0$ should be ΔH^0 (a misprint I believe)

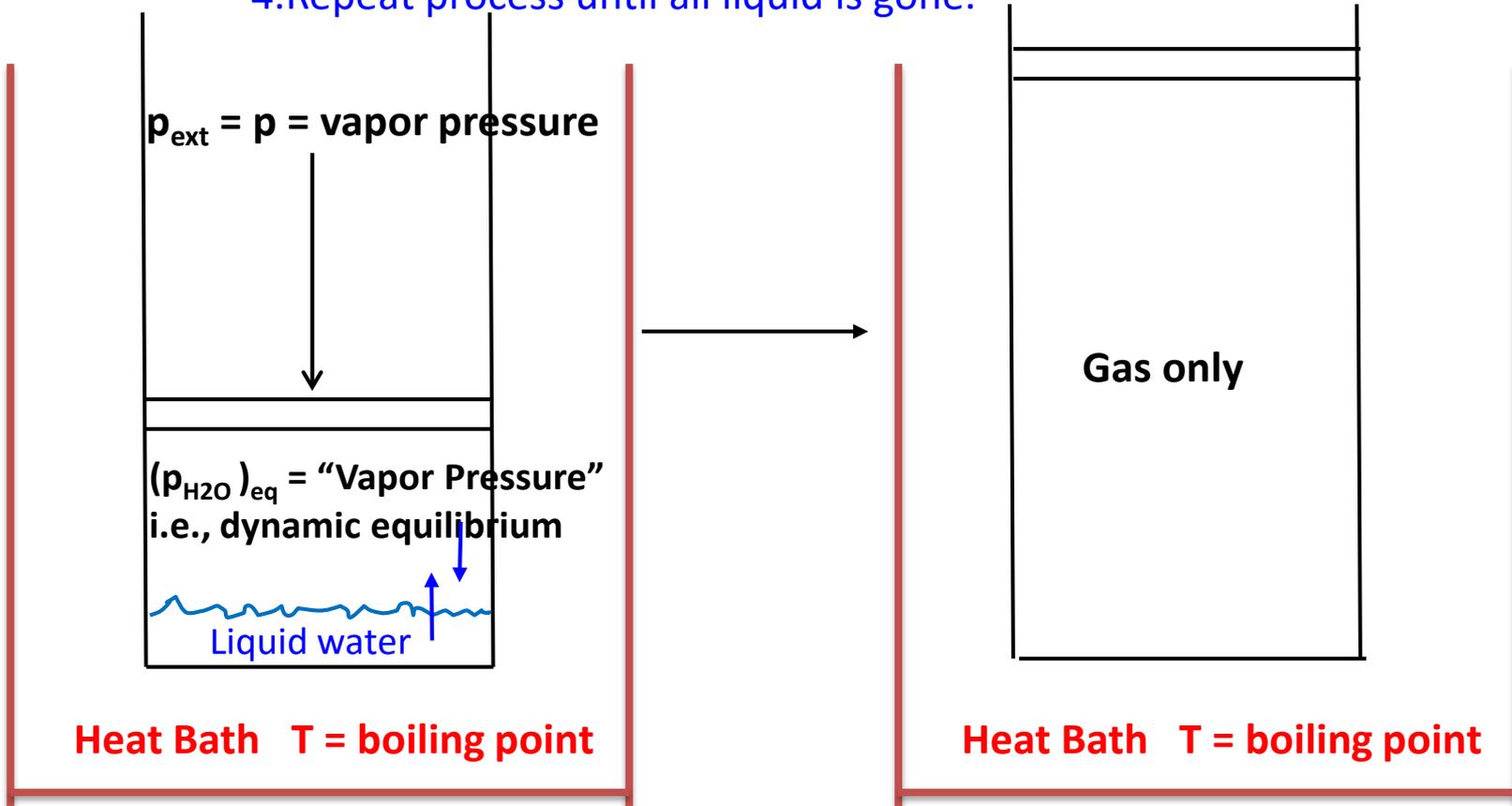
(b) (b) **Clarification:** “Energy equivalent” = ΔH^0 (in this case for 20 kg of sucrose for the reaction in (a))

(c) Hint: convert kJ from part (b) per 10,000 m² per hour to kW/m². (recall 1 W = 1 Js⁻¹.)

Problem 10 d

“A liquid at its boiling point is converted reversibly into its vapor, at constant T and 1 bar pressure” (boiling point = temperature at which the vapor pressure = p_{ext})

1. Reduce p_{ext} a tiny amount (so it will be reversible)
2. Gas expands and $p_{\text{H}_2\text{O}} < \text{vapor pressure}$.
3. A tiny amount of liquid evaporates until equilibrium is reached again.
4. Repeat process until all liquid is gone.



Vapor Pressure

The “*vapor pressure*” of a pure liquid H₂O (at a certain temperature) is that *partial pressure* = $p_{\text{H}_2\text{O}}$ (i.e., *concentration* in units of pressure) of the vapor that is in *equilibrium* with the liquid, at that temperature.

For pure liquid A: “vapor pressure” = $[A]_{\text{equil.}} RT = (p_A)_{\text{equilibrium}}$
(that is another form of the IDEAL GAS LAW)

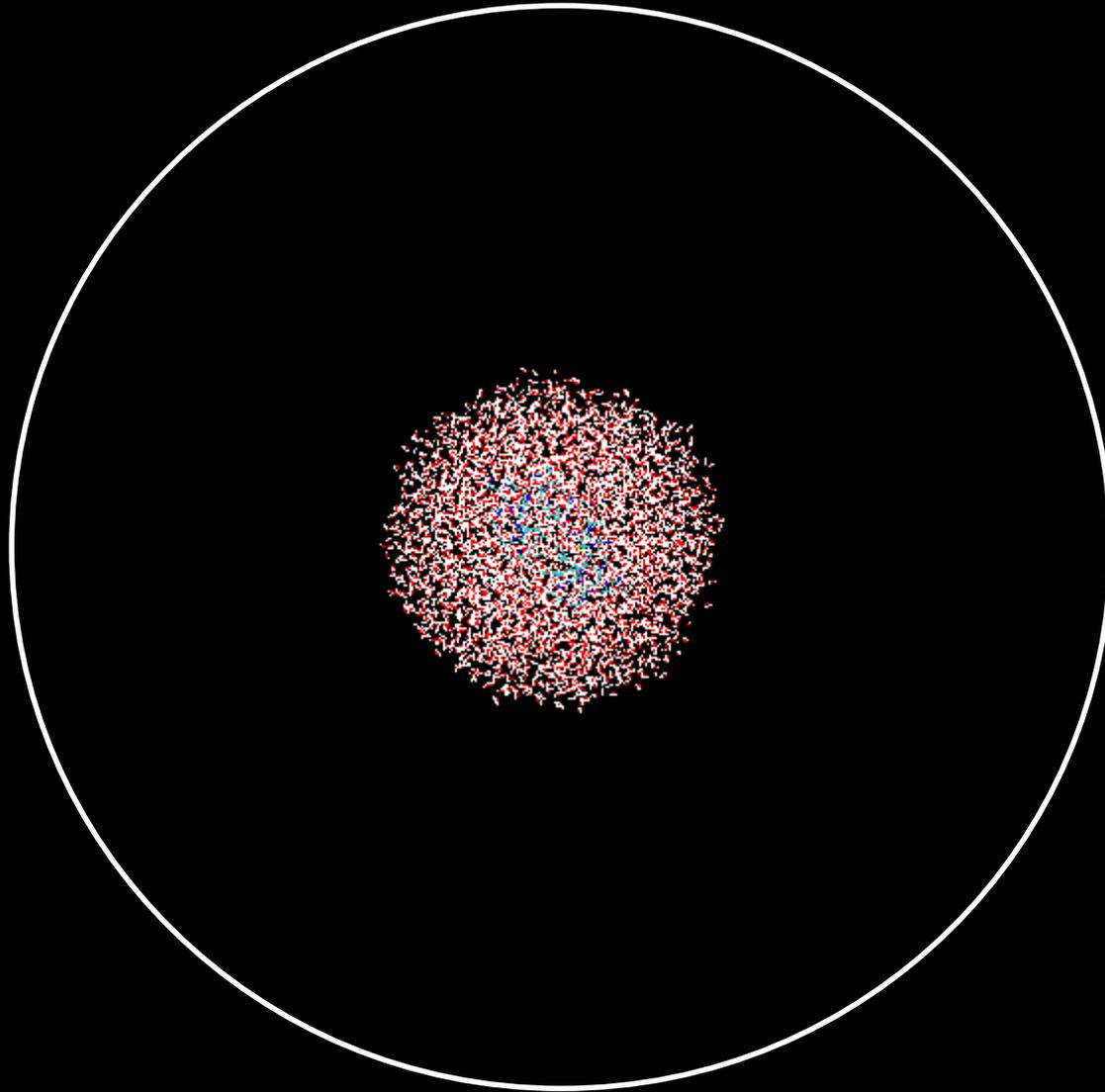
Note: “Vapor pressure” of pure liquid is the *equilibrium constant* for the “reaction”: **H₂O(pure liquid) → H₂O(gas)**, for example.

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

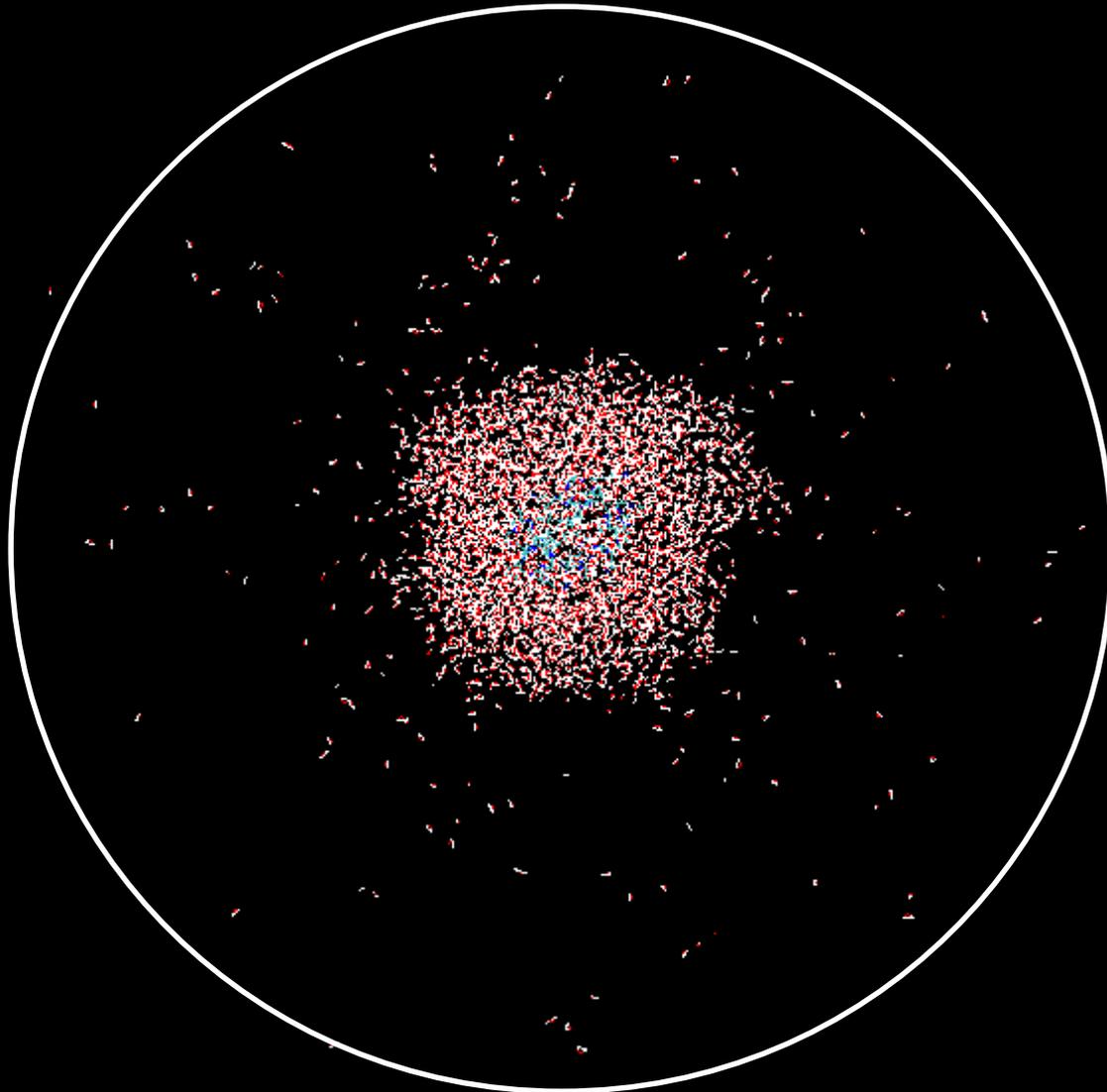
at 25 °C $(p_{\text{H}_2\text{O}})_{\text{eq}} = 0.0313 \text{ atm} = 100\% \text{ relative humidity}$

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

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.



After dynamic equilibrium established. The partial pressure of water now = "the vapor pressure"



Vapor Pressure Movies

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

Molecular Dynamics Simulation of evaporation from a small drop of water

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

<http://www.chemistry.montana.edu/callis/documents/courses/chmy361/movies/waterdrop27aug15.avi>

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 what is the partial pressure of O₂ if RT = 25 L atm ?

$$p_{O_2} = ?$$

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

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”:
 $\text{H}_2\text{O}(\text{pure liquid}) \rightarrow \text{H}_2\text{O}(\text{gas})$

Boiling Point : when applied Pressure = “Vapor Pressure”

Why is Boiling Point when $p_{\text{ext}} = \text{“Vapor Pressure”}$

First: What **is** boiling?

What will happen if you heat water that is absolutely pure liquid (no micro bubbles)?

Answer: It will **superheat**. When a particle of dust (containing air) falls in, the water will instantly boil vigorously (sometimes **too** vigorously!)

Boiling is when liquid **evaporates into bubbles** and they rise to the surface. This requires $V.P. > p_{\text{ext}}$.

Table 2.2 5th Edition (this year)

Liquid H₂O

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


(What is this pressure? (=1 atm))

Boiling point at 1 bar pressure: 372.76 K (99.6°C)

Boiling point a 1 atm pressure: 373.16 K (100 °C)

“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.