Homework #

Class average = 73/93 = **78.6 % (very good)** for HW#1

Solutions will be posted later today
Objectives for Exam 1 are posted

We will review for the exam on Monday.
Have questions ready to ask in class.

The beginning of your **4 x 6 sheet for Exam 1**.

Always True	**Conditional**
$\Delta U = q + w$	**Adiabatic: q = 0 ; ΔU = w ;** **Constant V:** $\Delta U = \int_{T1}^{T2} C_v dT$ **$\Delta U = C_v (T_2 - T_1)$ if C_v constant** **For ideal gas the above is always true (*even if volume changes*)**
$H = U + pV$ $\Delta H = \Delta U + p_2V_2 - p_1V_1$	**For $p = p_{ext}$ = constant and pV work only:** $\Delta H = q = \Delta H = \int_{T1}^{T2} C_p dT$ **$\Delta H = C_P (T_2 - T_1)$ if C_P constant** **For ideal gas the above is always true (*even if pressure changes*)**
$dw_{pV} = -p_{ext}\mathbf{dV}$ $w_{pV} = -\int_{V_1}^{V_2} p_{ext}\mathbf{dV}$	**for p_{ext} constant: $w_{pv} = -p_{ext} (V_2 - V_1)$;** **if isothermal reversible and ideal gas:** $w_{pV} = -\int_{V_1}^{V_2} p\mathbf{dV} = -nRT\ln\frac{V_2}{V_1}$ **Solids and Liquids (volume changes are very small)** **Cp ≅ Cv and ΔH ≅ ΔU**

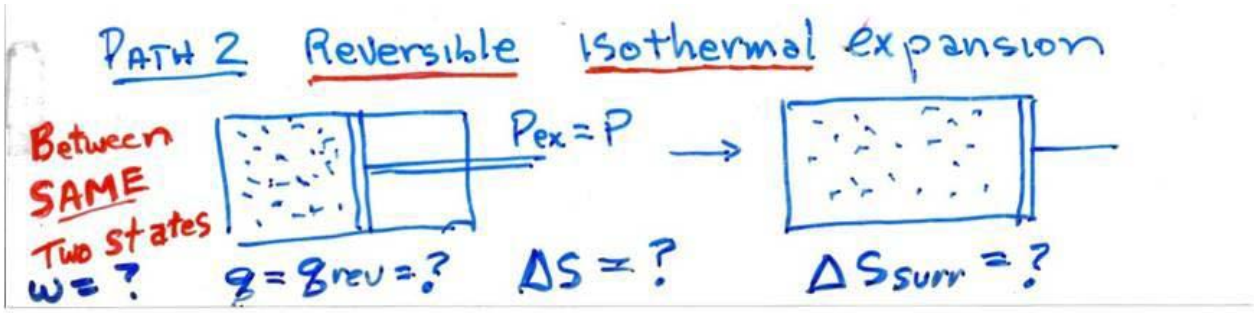
EXAMPLE: Ideal gas expanding, isothermally into vacuum:

Find $\Delta S = \frac{q_{rev}}{T}$ $\frac{J}{K}$

PATH 1 remove partition ($P_{ex} = 0$) $w = 0$, $q = 0$, $\Delta S = ?$, $\Delta S_{surr} = 0$

Find w,q, **ΔS , ΔS_{surr}**

How can we calculate **ΔS ?**



$$w_{pv} = -RT \ln \frac{V_2}{V_1} = -8.3145 * 298 * 0.693 = -1717 \text{ J}$$

q_{rev}=+1717

$\Delta S = = q_{rev}/T = R\ln 2$

$= 1717/298$ = 5.76 J/K

$\Delta S_{surr} = -q/T = R\ln 2$

$= -5.76$ J/K

$\Delta S_{UNIV} = 0$

The 3rd Law of Thermodynamics

In 1867, Ludwig Boltzmann earned his PhD for research on the kinetic theory of gases. Later, he began to see that entropy could be related to disorder, and he published the famous equation for ***absolute*** entropy

$S = k_B \ln W$ where **W is the number of quantum microstates** (the number of possible arrangements of the positions and velocities of the collection of molecules in the system—a truly enormous number –*while at* ***dynamic equilibrium***), and

k_B = Boltzmann's constant (= R/6x10^{23}) so has units of J K^{-1} $molecule^{-1}$

This, however, was well ahead of its time, and he died a discouraged man in 1906, just as the world of physics was waking up to the idea of atoms and molecules.

As 0 Kelvin is approached, all systems are in the zero point quantum mechanical energy level. For a perfect crystal in lowest energy level there is only 1 microstate : W=1

$S = k_B \ln 1 = 0$, i.e.,

The entropy of a perfect crystal at 0 K = 0.

(this is one form of the 3rd Law)

This means there is a basis for having *absolute* values for entropy, (unlike energy)

Table A.5
Appendix

Absolute entropies at 298 K

TABLE A.5 Inorganic Compounds*

	$\Delta_f H^\circ$ (kJ mol^{-1})	S° (J K^{-1} mol^{-1})	$\Delta_f G^\circ$ (kJ mol^{-1})
Ag(*s*)	0	42.55	0
$Ag^+(aq)$	105.79	73.45	76.80
AgCl(*s*)	−127.01	96.25	109.77
C(*g*)	716.68	158.21	669.21
C(*s*, graphite)	0	5.74	0
C(*s*, diamond)	1.90	2.38	2.90
Ca(*s*)	0	41.42	0
$CaCO_3$(*s*, calcite)	−1206.92	92.90	−1128.79
$Cl_2(g)$	0	223.18	0
$Cl^-(aq)$	−167.16	56.5	−131.23
CO(*g*)	−110.52	197.78	−137.01
$CO_2(g)$	−393.51	213.85	−394.36
$CO_2(aq)$	−413.80	117.6	−385.98

For ions in solution the S^0 values are arbitrarily set relative to $H^+(aq) = 0$
(thus, the ion S^0 will not make obvious physical sense)

Molecular Interpretation of Entropy

$S = k_B \ln W$ (Boltzmann ~1900)

Reversible isothermal expansion of ideal gas:

$$q_{rev} = -w_{rev} = nRT \ln \frac{V_2}{V_1}$$

Therefore,

$$\Delta S = \frac{q_{rev}}{T} = nR \ln \frac{V_2}{V_1} = nR \ln \frac{W_2}{W_1}$$

because the number of microstates is proportional to volume

$$\Delta S = nR \ln W_2 - nR \ln W_1 = S_2 - S_1, \textbf{\textit{ per mole}}$$

dividing by the number of molecules gives

$$\Delta S = k_B \ln W_2 - k_B \ln W_1, \textbf{\textit{ per molecule}}$$

ΔS from pure heating: dq = CdT

finding q_{rev} with heat capacity

$$\Delta S = \int_{T_1}^{T_2} \frac{dq_{rev}}{T} = \int_{T_1}^{T_2} \frac{CdT}{T} (done\ slowly) \approx C \int_{T_1}^{T_2} \frac{dT}{T}$$

This is heat capacity times the sum of fractional differences in T starting at T_1 and ending at T_2

and that is ??

$$\Delta S \approx C \ln \frac{T_2}{T_1}$$

$$\Delta S = C \ln \frac{T_2}{T_1}$$

over a small enough temperature range that C is effectively constant

Phase transitions at the transition temperature (e.g., melting point, boiling point,) are reversible, so:

$$\Delta S_{fusion} = \frac{\Delta H_{fusion}}{T_{mp}}$$

$$\Delta S_{vap} = \frac{\Delta H_{vap}}{T_{boiling}}$$

Absolute (Third Law) Entropy at any temperature T

(this is where the numbers in Table A.5 come from)

Below is the case in which there are 2 solid phases such as for N_2

$$S(T) = 0 + \int_0^{T_{tran}} \frac{C_P(solid\,1)}{T} dT + \frac{\Delta H_{transition}}{T_{trans}} + \int_{T_{trans}}^{T_{mp}} \frac{C_P(solid\,2)}{T} dT$$

$$+ \frac{\Delta H_{fusion}}{T_{mp}} + \int_{T_{mp}}^{T_{bp}} \frac{C_P(liquid)}{T} dT + \frac{\Delta H_{vap}}{T_{equil}} + \int_{T_{bp}}^{T} \frac{C_P(gas)}{T} dT$$

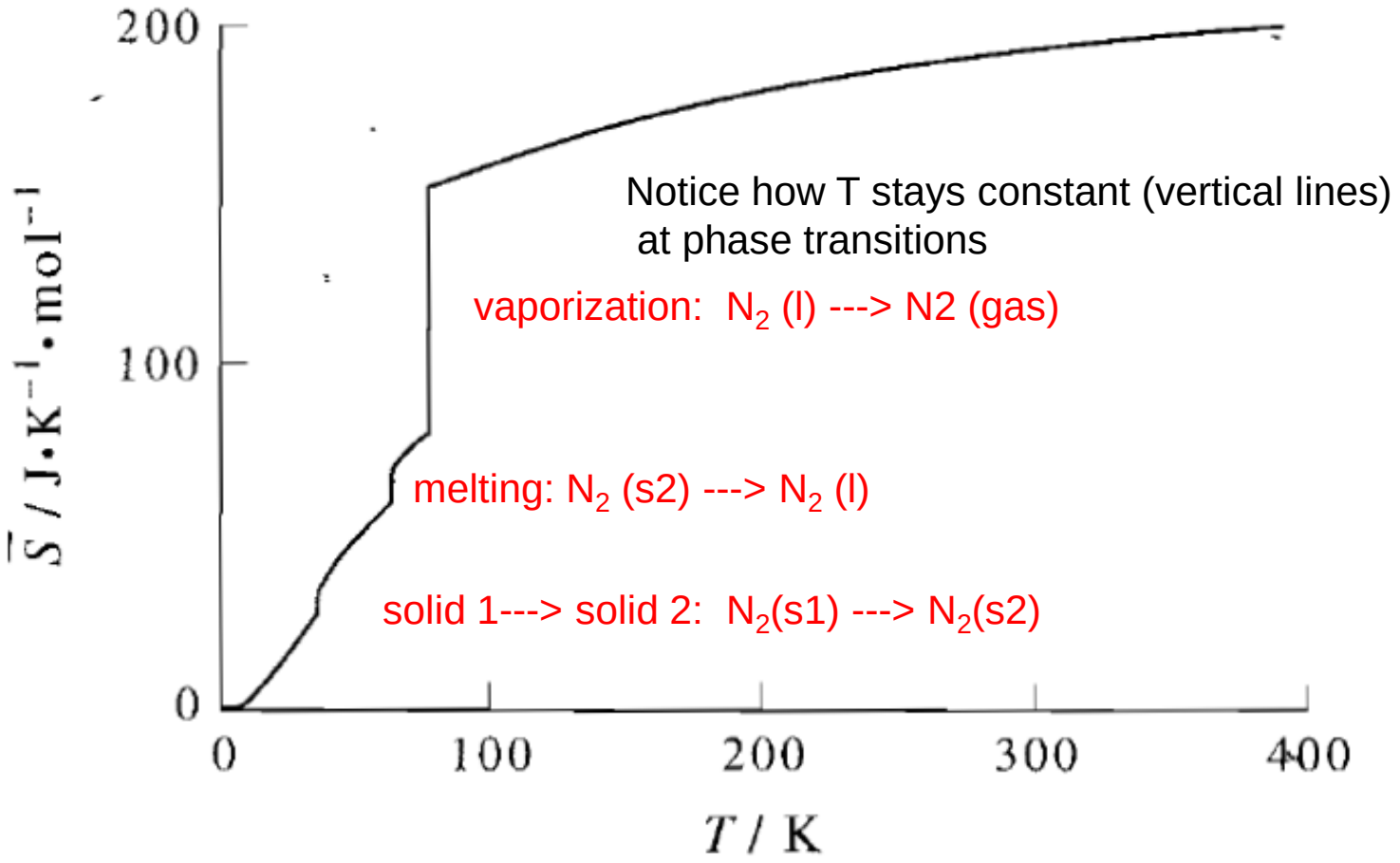


FIGURE 7.1
The molar entropy of nitrogen plotted against temperature from 0 K to 400 K.

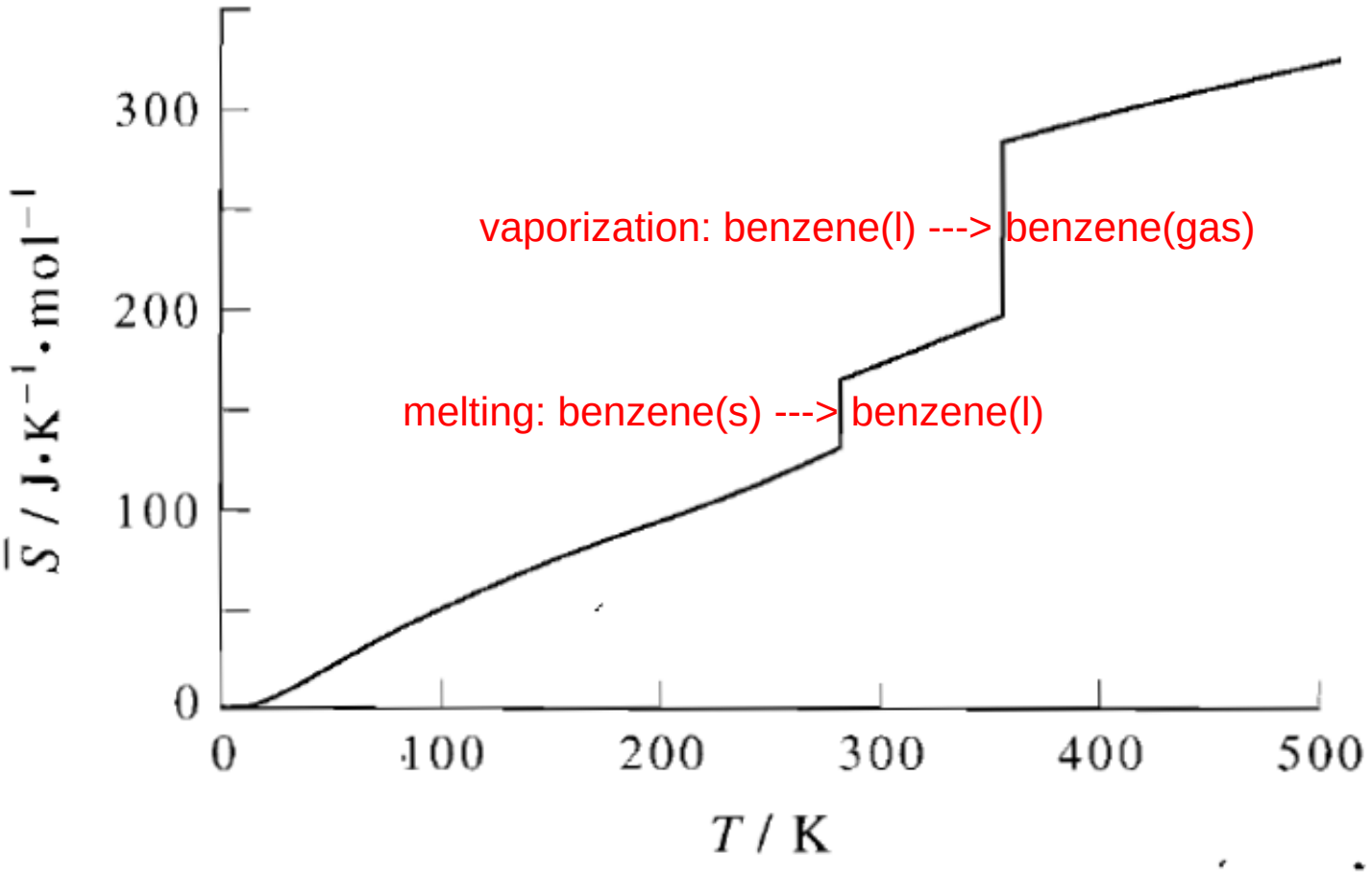


FIGURE 7.2
The molar entropy of benzene plotted against temperature from 0 K to 500 K.

THIRD LAW: ABSOLUTE ENTROPIES

	$\bar{S}^\circ$ J K^{-1}mol^{-1} at 298K	$\bar{S}^\circ$ at 0 K
Diamond	2.38	0
Graphite	5.74	0
Pb(s)	64.8	0
Al(s)	28.3	0
Al(l)	39	
$H_2O(l)$	69.9	
Al(g)	164	
$H_2O(g)$	189	
$N_2(g)$	192	
N(g)	153	

} Liquids

$\Delta \bar{S}^\circ_{vap} = +119$ J K^{-1}mol^{-1}

$N_2(g) \rightarrow 2N(g)$ $\quad \Delta\bar{S}^\circ = 2(153) - 192$

$= +114$ J K^{-1}mol^{-1}

Chemical Reactions =Business as usual

Consider a generic chemical reaction

aA + **b**B → **c**C + **d**D

where the a,b,c,d = the stoichiometric numbers

and **A,B,C,D** are chemicals

Enthalpy changes:

$\Delta_r H^0 = c\,\Delta_f H^0(C) + d\,\Delta_f H^0(D) - a\,\Delta_f H^0(A) - b\,\Delta_f H^0(B)$

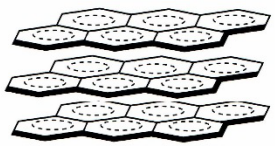
Unlike for Enthalpy, we have absolute standard entropies: no Δ_f

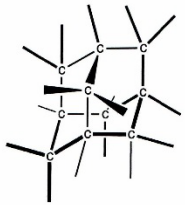
$\Delta_r S^0 = cS^0(C) + dS^0(D) - aS^0(A) - bS^0(B)$

the hardness of an element; in hard solids the molecules are more rigidly confined to lattice positions and have lower entropies than in soft solids. Contrast graphitic carbon, which is arranged in two-dimensional planes that can easily slide between each other, with the more rigid three-dimensionally network-bonded structure of diamond (see sidebar, 298 K, 1 bar).

Phase	Entropy	Property
Diamond	2.38 J $K^{-1}mol^{-1}$	Hard
Graphite	5.74 J $K^{-1}mol^{-1}$	Soft

graphite





diamond

All entropies increase as the temperature is raised since increasing molecular motion increases the possible positions and configurations of the molecules.

Interpreting entropy as a measure of disorder helps us to understand and predict entropy changes in reactions. In the gas phase, if the number of product molecules is less than the number of reactant molecules, entropy decreases. If the number of gas molecules increases, entropy increases. Two examples at 25°C and 1 bar are shown as follows. The superscript in $\Delta_r S^\circ$ specifies that the values are for reactions in which all reactants and products are in their standard states, which we will define later.

Reaction	$\Delta_r S^\circ_m$(J K^{-1} mol^{-1})
$2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$	−88.8
$PCl_5(g) \rightarrow PCl_3(g) + Cl_2(g)$	170.3

If the number of molecules is unchanged by the reaction, a small change in entropy—either positive or negative—is expected. For reactions in solution, it is more difficult to predict the entropy change because of the potentially large effects of the solvent. Two solute molecules may react to form one product molecule, but unless we know what is happening to the solvent—whether it is being ordered or disordered—we cannot predict the change in entropy. However, we can rationalize and interpret the measured results. A few examples of reactions carried out at 25°C, 1 bar are as follows:

Reaction	$\Delta_r S^\circ_m$(J K^{-1} mol^{-1})
$CO_3^{2-}(aq) + H^+(aq) \rightarrow HCO_3^-(aq)$	+148.1
$NH_4^+(aq) + CO_3^{2-}(aq) \rightarrow NH_3(aq) + HCO_3^-(aq)$	+146.0
$OH^-(aq) + H^+(aq) \rightarrow H_2O(l)$	+80.8
$NH_4^+(aq) + HCO_3^-(aq) \rightarrow CO_2(aq) + H_2O(l) + NH_3(aq)$	+94.2
$NH_3(aq) + H^+(aq) \rightarrow NH_4^+(aq)$	+2.1
$HC_2O_4^-(aq) + OH^-(aq) \rightarrow C_2O_4^{2-}(aq) + H_2O(l)$	−23.1
$CH_4(aq) \rightarrow CH_4(CCl_4)$	+75

For the first four reactions, neutralization of charges occurs. Because a charged species tends to orient the water molecules around it, charge neutralization results in disorientation of some of the solvent molecules and an increase in entropy. The next two reactions involve transfer of charge but no neutralization. The entropy changes are small as a consequence. The last reaction involves the transfer of a nonpolar methane (CH_4) molecule from a polar solvent (H_2O) to a nonpolar solvent (CCl_4). The large positive ΔS is primarily the result of the ordering of water molecules around a nonpolar molecule. Removal of the nonpolar molecule results in the randomization of the water molecules and hence a positive ΔS. The ordering of water molecules around nonpolar moieties is important for many reactions in aqueous media, such as the