41. Theory: thermodynamic laws

There are 3 laws " tricky "

1. $\Delta E_{univ} = \emptyset$ "energy is conserved in a ~~isolated~~ closed system"

2. $\Delta S_{sys} + \Delta S_{surr}$
   $\Delta S_{univ} \geq 0$ "entropy of an isolated system always increases"

3. $T_k \rightarrow \emptyset$ $S \rightarrow \emptyset$ for a perfect crystal
   absolute zero
   ___   ___   ___

42. Theory: systems, surroundings and signs

ΔG $\quad$ + nonspontaneous
$\quad\quad$ − spontaneous

ΔS_{univ} $\quad$ + spontaneous
$\quad\quad$ − nonspontaneous

$W = -\Delta n \varepsilon T$ $\quad$ + work done on system
$\quad\quad$ − work done on surroundings

$q = C\Delta T$ $\quad$ + heat in system (endothermic)
$\quad\quad$ − heat released to sur (exothermic)

$\Delta E = q + w$ $\quad$ varies with magnitude of q vs w s.t $q >> w$ would
$\Delta H = \Delta E + P\Delta V$ $\quad$ + become w is small, small $\Delta E \sim \Delta H$ and same sign
ΔS_{sys} $\quad$ − if disorder increases
$\quad\quad$ + if disorder decreases $\{$ state matter and
$\quad\quad$ $\#$ of particles $\}$

$\Delta S_{surr} = -\dfrac{\Delta H_{sys}}{T}$ $\quad \Delta H_{sys} \equiv$ opposite sign of ΔH_{sys}

I will give ym a series of rxns. ym
have to find which are ΔHf and which
are not.

1. have only elements in std state as
reactants $H_2(g)$, C graphite $Hg(\ell)$ etc
reactants rxns $\Rightarrow$

2. produce a mole of a single product

Travis bomb calorimeter calc.

So attach is here the first 42 words of
the problem. After that it is standard

$$\Delta H_{calc} = -\Delta H_{sur} = \underbrace{mc\Delta T}_{water} + \underbrace{C\Delta T}_{cal}$$

simple plus + chug, no tricks

47. Calculation: Hess' law and heats of formation   easy

$$\Delta H_r = \sum \Delta H_f \, products - \sum \Delta H_f \, reactants$$

Plus + chas using

I will give you a balanced chemical
equation and a bunch of ΔH_f data. You
plus + chug.

48. Calculation: Hess's law and combined reaction enthalpies   harder. These are NOT ΔH_f

I will give you 4 ΔH_r equations. You need
to flip/flop them and multiply by constants to
end up w.th The actual reaction I'm hunt.

$$\left.\begin{array}{l} rxn\ 1 \qquad \Delta H_{r_1} \sim \\ rxn\ 2 \qquad \Delta H_{r_2} \sim \\ rxn\ 3 \qquad \Delta H_{r_3} --- \\ rxn\ 4 \qquad \Delta H_{r_4} --- \end{array}\right\}$$

flip
flip
+
multiply
+ cancel

net rxn ΔH_r net $\boxed{\quad} \leftarrow$

49. Calculation: bond energies

I will give you a balanced chemical rxn.
You need to write Lewis structures for each rxn
and count the number of bonds. Then stick in
formula.

$$\Delta H_r = BE = \sum BE_r - \sum BE_p$$

to get answer. No tricks, just plug + chug.

plug + chug backward!!

50. Calculation: work calculation

I will give you a balanced chemical
reactions. You need to calculate W.

$$W = -\Delta n_g \cdot R \cdot T$$

Temp in K

8.314 J/mole·K or 2.0 cal/mole·K

Make sure your units cancel and plus is easy.
Also Δn_g is only for gas molecules.

$$\Delta E = q + w \qquad \Delta H = \Delta E + P\Delta V$$

I will give you very straight forward information about these two fundamental equations. you will make a simple conclusion.

Example: If no work is done, does $\Delta E = q$? yes

52. Problem: predicting entropy change in a chemical reaction

I will give a bunch of chemical rxns.
Be able to determine which have $\Delta S +$ a $\Delta S -$
based on

$$s \rightarrow \ell \rightarrow g \equiv \Delta S +$$

$$a \quad \text{`nmols of molecules in reaction} \equiv \Delta S +$$

and converse as well.

I will tell ym a phase transition. ym immediately While $\Delta G = 0$ so ("system" "melt" ↙ "evaporate")

$T = \dfrac{\Delta H}{\Delta S}$ ⟵ stick in numbers (w.TR units fixed and get T in K)

↳ $\Delta S = \dfrac{\Delta H}{T}$

Remember, T can only be positive so $\Delta H_{s,s'}$ & $\Delta S_{s,s'}$ must always be same sign in phase change.

Theory for S

↳ Which says that as $T \to \emptyset$ $S \to \emptyset$ for a perfect crystal. Any residual entropy is a fxn of the number of microstates of the system.

$S = k \ln W$ ⟵ microstates and in a perfect crystal $W = \underline{\textcircled{1}}$ t(w·d

so $S = \emptyset$

$E_k = \frac{1}{2} kT$

$S = k \ln W$

I will give you a molecule and its number. You have to calculate S.

microstate $= W = (\# \text{ of orientations})^{\# \text{ of molecules}}$

• ln is natural log

$S = (\#)\text{molecules} \ k \ln(\#\text{ of orientations})$

• pull exponent out front

$S = (\#)\text{molecules} \ k \ln(\#\text{ of orientation})$

for a mole:
• $R = k N$
and $S = R \ln \#^{\# \text{ of orient}}$.

I already made you do this for ΔS at # 53 a phase change. where $\Delta G = 0$ so

$\Delta G = \Delta H - T\Delta S = 0$ so $\Delta H - T\Delta S = 0$

so $\Delta H = T\Delta S$

so $T = \frac{\Delta H}{\Delta S}$

you solve for T of the phase change

I made a catastrophic error in thinking you could do a real me of those on last exam. I apologize. Now it will be really simple.

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$$

$$\boxed{\dfrac{-\Delta H}{T}}$$

you needed calculate $\Delta H v$ & $\Delta S v$ yourself

I will give you simple data & you solve.

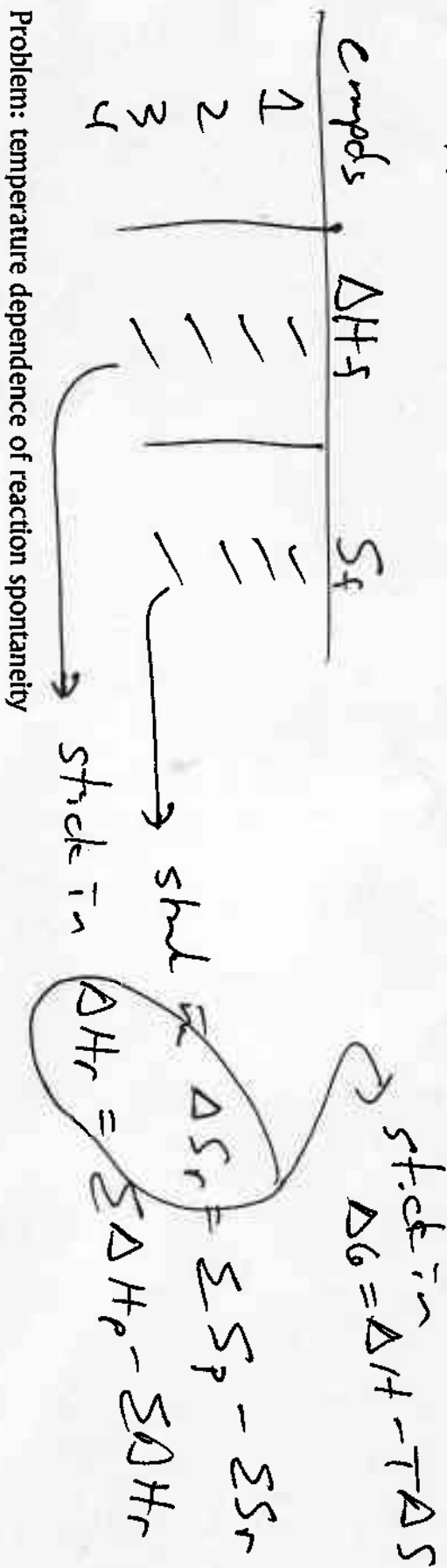I will give you a big table of ΔG_f data you need to spot the stable compounds.

If ΔG_f data

	ΔG_f
rxn 1	-100
rxn 2	+100
rxn 3	+50

∴ why #1 is stable because $\Delta G_f = \ominus$

59. Calculation: G°₀ from table values of Hf₀ and Sf₀

I will give you a balanced reaction
for a balanced reaction.

$\Delta G = \Delta H - T\Delta S$

Cmpds	ΔH_f	S_f
1		
2		
3		
4		

stick in
$\Delta G = \Delta H - T\Delta S$

$\Delta S_r = \Sigma S_p - \Sigma S_r$

should
$\Delta H_r = \Sigma \Delta H_p - \Sigma \Delta H_r$

60. Problem: temperature dependence of reaction spontaneity

$$\Delta G = \Delta H - T\Delta S$$

	ΔH	$T\Delta S$	
	$+$	$-$	never (never spon)
	$-$	$+$	always (always spon)
	$+$	$+$	only at high T
	$-$	$-$	only at low T

There
are
four
possibilities

I will give you the $\Delta H + \Delta S$ data,
you tell me the T dependence.

I will give you the $\Delta H + \Delta S$ data,
you tell me the T dependence.