

ACS Standard
Physical Chem
Exam Taken
Tuesday by
21 students

Score	%		
33	55.0		
32	53.3		
32	53.3		
32	53.3		
31	51.7		
29	48.3		
28	46.7		
28	46.7		
27	45.0		
27	45.0		
26	43.3		
25	41.7		
24	40.0		
23	38.3		
22	36.7		
21	35.0		
19	31.7		
19	31.7		
18	30.0		
16	26.7		
16	26.7		
Average	25.1	41.9	%
Last Year		38.6	%
Nat. Avg.		52	%

CHMY 361 How to *estimate* your final grade **Handout**

December 7, 2017

Total points = 700; Homework is worth 100; midterms = 100 each, and final =200

The total possible homework points =150, so:

Total % = (total HW/150 * 100 + total exam points)/700 (**after including your Final**)

Last year's letter grades were typical, but could be slightly different this year. T

Total % Grade (Estimate)

90-100	A
86-89	A-
80-85	B+
75-80	B
70-74	B-
68-70	C+
63-67	C
60-62	C-
50-59	D

20 pts) 1. State the 3 Laws of Thermodynamics in words and with a commonly used equation; indicate in a few words the importance of each. Define all symbols used.

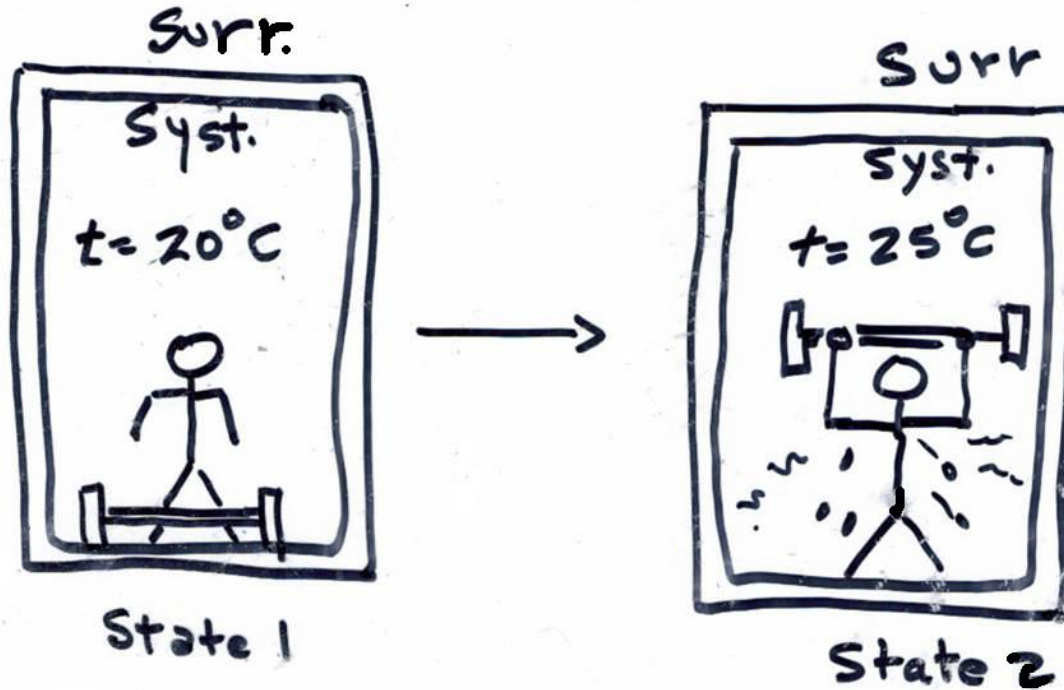
1st Energy of the Universe is conserved $\Delta U = q + w$

2nd Entropy of the universe increases for any natural process $\Delta S + \Delta S_{\text{surr}} \geq 0$
= only for equilibrium.

3rd Entropy of a perfect crystal at 0 Kelvin = 0 $S = k_B \ln W$

A little quiz

System = **insulated** room with weight lifter



Weight lifter works out and the room heats up
from 20°C to 25°C

Are ΔU , q , w positive, zero, or negative?

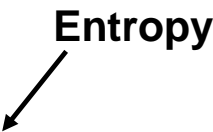
<u>Always True</u>	<u>Conditional</u>
$\Delta U = q + w$	Adiabatic: $q = 0$; $\Delta U = w$; Constant V: $\Delta U = \int_{T_1}^{T_2} C_V dT$ $\Delta U = C_V (T_2 - T_1)$ if C_V constant For ideal gas the above is always true (even if volume changes)
$H = U + PV$ $\Delta H = \Delta U + P_2 V_2 - P_1 V_1$	For $P = P_{\text{ext}} = \text{constant}$ 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 (even if pressure changes)
$dw_{\text{pv}} = -P_{\text{ext}} dV$ $w_{\text{pv}} = -\int_{V_1}^{V_2} P_{\text{ext}} dV$	for P_{ext} constant: $w_{\text{pv}} = -P_{\text{ext}} (V_2 - V_1)$; if isothermal reversible and ideal gas: $w_{\text{pv}} = -\int_{V_1}^{V_2} P dV = -nRT \ln \frac{V_2}{V_1}$ <u>Solids and Liquids</u> (volume changes are very small) $C_p \cong C_v$ and $\Delta H \cong \Delta U$

*Some useful state functions are **DEFINED** from other state functions. We are immediately concerned with **enthalpy $\equiv H = U + PV$ (by definition)**

Why?

Because $\Delta H = q$ (if $P = P_{\text{ext}} = \text{constant}$ and there is only PV work) This is a common condition

Gibbs Free Energy = $G = H - TS$ (by definition)



because $\Delta G = -T\Delta S_{\text{univ}}$
(if T, and P constant and the process is doing only obligatory pV work)

and $\Delta G = \text{maximum useful (non-PV work) the system can deliver.$

(important in life processes), called **W_{other}** in this book.

Reversible Isothermal PV work (ideal gas)

$$p_{\text{ext}} = p = nRT/V \quad (\text{balanced forces})$$

An integral is just a

$$\text{Sum} \rightarrow w = -\int_{V_1}^{V_2} p_{\text{ext}} dV = -\int_{V_1}^{V_2} p dV = -\int_{V_1}^{V_2} \frac{nRT}{V} dV$$

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

Sum of fractional changes
= natural logarithm

ONLY if $p = p_{\text{ext}}$ = and ideal gas (but is common case)

What are ΔU and q ?

$\Delta U = 0$ (isothermal, ideal gas), therefore $q = -w$

CHAPTER 2: THE SECOND LAW

CONCEPTS:

- ENTROPY, S , is a measure of DISORDER
- In an isolated system ENTROPY INCREASES until EQUILIBRIUM IS REACHED

• 2nd LAW:

$$\underbrace{\Delta S + \Delta S_{\text{SURR}}}_{\text{UNIVERSE}} > 0 \text{ for actual process (spontaneous)}$$

$$\Delta S + \Delta S_{\text{SURR}} = 0 \text{ for a REVERSIBLE PROCESS (Equilibrium)}$$

∴ Calculate $\Delta S + \Delta S_{\text{SURR}} < 0$ THEN THE PROCESS IS IMPOSSIBLE

$$dS = \frac{dq_{\text{reversible}}}{T}$$

$$\Delta S = \frac{q_{\text{rev}}}{T} \text{ (constant } T)$$

$$\text{EFFICIENCY} = \frac{T_H - T_C}{T_H}$$

TRUE for ALL Heat engines
regardless of design & materials

REASON: A MORE EFFICIENT ENGINE COULD
DRIVE THE REVERSIBLE ONE IN
REVERSE, i.e., HEAT WOULD
SPONTANEOUSLY FLOW FROM
COLD → HOT !

THIS HAS NEVER BEEN SEEN TO HAPPEN

That would be a **violation of the Zeroth Law of Thermodynamics:**

The "People's Law". All people who ever lived are the scientists who established this "Law".

06:11.4 02:11-1 08:8-5
Old Exam question

State A \rightarrow State B Isothermal
 $T = 400 \text{ K}$

Path 1 irreversible $q = 12000 \text{ J}$

Path 2 reversible $q_{\text{rev}} = 8000 \text{ J}$

a) What is ΔS for path 1? ? $8000/400 = 20$

b) What is ΔS for path 2? $8000/400 = 20$

c) What is ΔS_{surr} for path 1? $-12000/400 = -30$

d) What is ΔS_{surr} for path 2? $-8000/400 = -20$

e) What is $\Delta S_{\text{UNIVERSE}}$ for path 1
(Is this path possible?) $20 - 30 = -10$
NOOOO

f) ΔS_{UNIV} for Path 2? 0

MOLECULAR INTERPRETATION

$$S = k \ln N$$

$k = \text{Boltzmann Constant}$

$$= \frac{R}{6 \times 10^{23}} = \frac{R}{N_{\text{Avo.}}}$$

$N = \# \text{ of microstates}^* \text{ available to system}$

* microstate = position & velocity vector
for each atom

SINGLE MOLECULE:

N is proportional to VOLUME ONLY

(20 pts) 9. From Table A.5, calculate ΔS_f° of $\text{CO}_2(\text{g})$.

$$\Delta S_f^\circ = \Delta S^\circ \text{ for } \text{C}(\text{gr}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$$

$$= S^\circ_{\text{CO}_2} - S^\circ_{\text{C}(\text{gr})} - S^\circ_{\text{O}_2}$$

$$= 213.74 - 5.74 - 205.138 = \boxed{+2.862 \text{ J/K}}$$

(b) reversible:

$$w = -nRT \ln \frac{V_2}{V_1} = -3 (8.3145 \text{ J mol}^{-1} \text{ K}) (300 \text{ K}) \ln \frac{25}{15} \quad \begin{array}{l} q + 3823 \text{ J} \\ w - 3823 \text{ J} \end{array}$$
$$= -3823 \text{ J}$$

$$\Delta S = \frac{q_{\text{rev}}}{T} = \frac{3823}{300} = +12.74$$

$$\Delta E \quad 0$$

$$\Delta H \quad 0$$

$$\Delta S \quad +12.74$$

$$\Delta S_{\text{surr}} \quad -12.74$$

(c) Do your results indicate that the process is spontaneous for the path in (a)? Explain.

Yes; $\Delta S + \Delta S_{\text{surr}} > 0$ \therefore spontaneous by
2nd Law.

At constant T and P, the Gibbs Free Energy is king.

Definition: $G = H - TS$

$$\Delta G = \Delta H - \Delta(TS) \quad \text{always true}$$

But, most useful for **constant T and $P = P_{\text{ext}} = \text{constant}$**

so that: $\Delta(PV) = P \Delta V$ and $\Delta(TS) = T \Delta S$; then

**non-PV
 ("other") work**

$$\Delta G = \Delta U + p\Delta V - T\Delta S = q - P_{\text{ext}}\Delta V + w_{\text{useful}} + p\Delta V - T\Delta S$$

but, $\Delta S_{\text{surr}} = -q/T$ so $q = -T \Delta S_{\text{surr}}$

$$\Delta G = -T(\Delta S + \Delta S_{\text{surr}}) + w_{\text{useful}} \quad (w = -p_{\text{ext}}\Delta V + w_{\text{useful}})$$

$$\Delta G = -T\Delta S_{\text{univ}} + w_{\text{useful}} \quad \text{if T and p constant}$$

$$\Delta G = -T\Delta S_{\text{univ}} + w^* \text{ if T and P constant}$$

Two limits most often used:

1. If $w_{\text{useful}} = 0 \rightarrow \Delta G = -T\Delta S_{\text{univ}}$

so a negative ΔG means spontaneous process (because ΔS_{univ} is positive) i.e, what you already know and use, but what is ***NOT always true if useful work is involved***

2. Reversible: $\rightarrow \Delta G = w_{\text{useful}} \text{ (reversible)}$

here, $w_{\text{useful}} \text{ (rev)}$ is the most negative possible w (meaning most work system can do, or least work done on the system to force a non-spontaneous process to proceed backwards.) i.e., even if ΔG is negative, the process will not be spontaneous if w_{useful} is equal to, or more positive than ΔG

(20 pts) 2.

a) From $dH = TdS + VdP = \left(\frac{\partial H}{\partial S}\right)_P dS + \left(\frac{\partial H}{\partial P}\right)_S dP$ b)

$$\left(\frac{\partial H}{\partial S}\right)_P = T$$

$$\left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial T}{\partial P}\right)_S$$

20 pts) 1. (12 pts) If an isothermal, constant volume spontaneous process clearly creates a final state that is more ordered than the initial state, and if $P = P_{\text{ext}} = \text{constant}$, and there is PV work only, tell whether the following are positive, 0, or negative. Indicate your reasoning very briefly.

q - w 0 ΔE - ΔH - ΔS - ΔG -

$$\Delta H = q$$

$$\Delta G \leq 0 \quad \text{spontaneous}$$

$\Delta S < 0$ ordering.

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

- +

 ↑

 -

$$w = 0 \quad \Delta U = 0 \quad w = -P_{\text{ext}} \Delta V$$

$$\Delta E = q + w = -$$

↓₀

- (15 pts) 3. Supercooled (much below freezing point) water suddenly turns to ice in an *isolated* chamber at constant pressure, and eventually comes to equilibrium. Tell whether the following are positive, zero, or negative. Give a brief justification for each of your answers. If it is not possible to unequivocally know the answer for any of these, indicate this and say why.

$$q \underline{0} \quad w \underline{0} \quad \Delta T \underline{+} \quad \Delta U \underline{0} \quad \Delta H \underline{?} \quad \Delta S \underline{+} \quad \Delta G \underline{?} \quad \Delta S_{\text{surr}} \underline{0} \quad \Delta S_{\text{univ}} \underline{+}$$

* see below *

$q, w, \Delta U = 0$ because isolated

$\Delta T = +$ exothermic & isolated.

$\Delta S = \Delta S_{\text{univ}} = +$ it happened and isolated

$\Delta S_{\text{surr}} = 0$ isolated

$\Delta H = \Delta U + \Delta(PV) = 0 +$ what you assume for ΔPV

$\Delta G = \Delta H - T\Delta S = ?$ if you make no assumption about ΔPV or if $\Delta PV = \text{neg.}$
 $= \text{negative}$ if you assume $\Delta PV = 0$

