Engineering Thermodynamics E115   Name:

This question is very easy + essential to understanding basics

1. The Three Laws of Thermodynamics (30 points)   *so cannot be lenient in grading*

(a) State the first law using variables, exact, and inexact differentials. (6 points)

(1pt) $dU = \delta q - \delta w$

must distinguish

if shown in 5th problem give full point

define and explain in words the terms used in your equation

4pts tot

$w =$ work $=$ force $\cdot$ distance $= \int_{initial}^{final} p\,dV$ (2pt); must have bounds correct (½ pt)

Must say path dependent (½ pt) for w; (½ pt) for q

$q =$ heat $=$ energy transfer between system and surroundings (1pt) (½pt)

$U =$ internal energy $=$ sum of kinetic and potential energies, where $KE = \sum_i^N m_i v_i$; must say path independent or function of state (½ pt)

Explain the sign convention. In other words, designate when something is done by a body or on a body. Or designate when something is done by the surroundings or on the surroundings.

(1pt) negative work done on a body
positive work done by a body

(1pt) heat into body positive q
heat out of body negative q

(b) State the second law using variables, exact, and inexact differentials (8 points)

(1pt) $dS = \frac{\delta q_{rev}}{T}$; not $\sum dS_i \geq 0$ this is something that follows from 2nd Law ; not $\sum dS_i = dS_{irr}$: also only follows from 2nd law

must distinguish

essential: this is the whole point of stating the second law at all

define and explain in words the terms used in your equation

$S =$ entropy; entropy is path independent or function of state (2pt)
↳ entropy is the measure of disorder or irreversibility (1pt)

$q_{rev} =$ max amount of heat transferred when process carried out reversibly (1pt)

$T =$ temperature ; temperature is a function of kinetic energy (1pt)

What does the second law tell us about a system in an adiabatic enclosure? Include discussion on reversible and irreversible processes.

The entropy of a system in an adiabatic enclosure can never decrease ; it increases during an irreversible process (1pt) and remains constant during a reversible process (1pt)

(c) Combine the First and Second Laws (8 points)

to obtain: $T = \left(\frac{\partial U}{\partial S}\right)_V$ and $P = (?)$?

(3pt) $\delta w = p\,dV$ $\delta q = T\,dS$

$dU = \delta q - \delta w$; $dU = T\,dS - P\,dV$

(1pt) const volume case:
$\frac{dU}{dS} = T\frac{dS}{dS}$ ∴ $\left(\frac{\partial U}{\partial S}\right)_V = T$

(4pt) const s case
$\frac{dU}{dV} = -P\frac{dV}{dV}$ ∴ $-\left(\frac{\partial U}{\partial V}\right)_S = P$

↑ must be partial derivatives

(d) State and explain the Third Law in words. (8 points)

option 1:
if $\left(\frac{\partial \Delta G}{\partial T}\right)_P$, $\left(\frac{\partial \Delta H}{\partial T}\right)_P \to 0$ as $T \to 0$ (2pt)

then ΔS, $\Delta c_P \to 0$ as $T \to 0$ (1pt)

Hence $\Delta S = 0$ at absolute zero temp (1pt)

option 2:
the entropy of any homogeneous substance which is in complete internal equilibrium (1pt) may be taken to be zero at 0 Kelvin (1pt)
↳ state of minimum possible constant energy (1pt)

Give one scenario when a substance is not at complete internal equilibrium at 0 Kelvin

p. 126 Gaskell   (4pt)

2. Helmholtz Free Energy Auxiliary Function and Equilibrium (30 points)

(a) State the definition of Helmholtz Free Energy using state variables (4 points)

$$A = U - TS \qquad \boxed{2pt}$$

In one sentence, describe conceptually the Helmholtz Free Energy

$\boxed{2pt}$ Useful work obtainable from closed thermodynamic system at constant T

(b) Take the exact differential of the Helmholtz Free Energy combined with the exact differential of the total internal energy dU=TdS-PdV (8 points)

to obtain: $S = -\left(\frac{\partial A}{\partial T}\right)_V$ and $P = (?)$?

$\boxed{1pt}$ $dA = dU - SdT - TdS$

$\boxed{1pt}$ $= TdS - PdV - SdT - TdS$

$\boxed{1pt}$ $dA = -PdV - SdT$

$\boxed{2pt}$ for const V: $dA = -PdV - SdT$

$\boxed{3pt}$ for const temp
$dA = -PdV - SdT$

$-\left(\frac{\partial A}{\partial V}\right)_T = P$

$-\left(\frac{\partial A}{\partial T}\right)_V = S$ ↑ need partials

(c) Derive the equilibrium condition dA=0 for a constant temperature and volume system. (9 points)

Use $\Delta S = \frac{q}{T} + \Delta S_{irreversible}$

$\boxed{1pt}$ $(A_2 - A_1) = (U_2 - U_1) - (T_2 S_2 - T_1 S_1)$

$\boxed{1pt}$ $\underbrace{}_{q-w}$ $\underbrace{}_{-T\Delta S \text{ for isotherm}}$

$\boxed{1pt}$ $\Delta S = \frac{q}{T} + \Delta S_{irr} \rightarrow q = T(\Delta S - \Delta S_{irr})$

$\boxed{1pt}$ $w = 0$ for const volume

$(A_2 - A_1) = T(\Delta S - \Delta S_{irr}) - T\Delta S$

$\boxed{1pt}$ $dA + TdS_{irr} = 0$

$\boxed{1pt}$ for reversible $dS_{irr} = 0$
$dS_{irr} > 0$ for spontaneous

$\boxed{1pt}$ ∴ equilibrium requires that $dA = 0$

include a short discussion below on spontaneity regarding equilibrium

$\boxed{2pt}$ nothing spontaneous can occur when A reaches minimum value

(d) Using the result from part (b), evaluate one of Maxwell's equations (9 points)

Recall, for Z=Z(x,y) that $\left(\frac{\partial L}{\partial y}\right)_x = \left(\frac{\partial M}{\partial x}\right)_y$ where $L = \left(\frac{\partial Z}{\partial x}\right)_y$, $M = \left(\frac{\partial Z}{\partial y}\right)_x$

$\boxed{1pt}$ $\begin{cases} Z = A \\ X = T \\ Y = V \end{cases}$

$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$ $\boxed{4pt}$

$\boxed{2pt}$ $\begin{cases} L = -S \\ M = -P \end{cases}$

↑ need this maxwell's equation not any other of the three since this one only follows from part (b)

Why is the change in the Helmholtz Free Energy independent of the order of differentiation?

$\boxed{2pt}$ It is a state function

3. Gibbs Free Energy Auxiliary Function and the Gibbs-Duhem Equation (30 points)
(a) State the definition of Gibbs Free Energy using state variables (4 points)

(2pt) $$G = H - TS \quad \text{or} \quad G = U + PV - TS$$

In one sentence, describe conceptually the Gibbs Free Energy

(2pt) usefulness of process-initiating work obtainable (at const T and P)
or
max amount of non-expansion work that can be extracted (+1 EC) explain non-expansion work

(b) Let $G = G(T, P, n_i, n_j, n_k, \ldots n_I)$ where $n_i, n_j, n_k, \ldots, n_I$ are the number of moles present of species $i, j, k, \ldots, L$ respectively, and I is the total number of species present. (16 points)
What is the exact differential of the Gibbs Free Energy?

need to be at least $T, n_i, \ldots$ $T, P, n_j, \ldots$

typo note: G_I also used

(6pt) $$dG = dG(T, P, n_i, n_j, n_k, \ldots n_I) = \left(\frac{\partial G}{\partial T}\right)_{P, n_i, n_j \ldots n_I} dT + \left(\frac{\partial G}{\partial P}\right)_{T, n_i, n_j \ldots n_I} dP + \left(\frac{\partial G}{\partial n_i}\right)_{T, P, n_j, n_k \ldots n_I} dn_i$$
$$+ \left(\frac{\partial G}{\partial n_j}\right)_{T, P, n_i, n_k \ldots n_I} dn_j + \cdots + \left(\frac{\partial G}{\partial n_I}\right)_{T, P, n_i, n_j, \ldots n_{I-1}} dn_I$$

need to show ellipsis or etc. taking dG w.r.t. all species

What is the exact differential for constant composition (i.e. constant $n_i, n_j, n_k, \ldots, n_I$) ?
(you do not need to derive the auxiliary function like in question 2b)

$dG = dH - TdS - SdT$

(2pt) $dG = dG(S, P, T, V) = -SdT + VdP$ from memory   or rederive: $dH = dU + PdV + VdP$
                                                         $dU = TdS - PdV$ combined law
                                                   ↳ $dH = TdS + VdP$

Comparing the two previous differentials, what are the state functions entropy and volume? ↳ $dG = VdP - SdT$

(+1 EC) for rederive

(2pt) $$S = S(G, T, P, n_i, n_j, n_k, \ldots, n_I) = -\left(\frac{\partial G}{\partial T}\right)_{P, n_i, n_j \ldots n_I}$$ from comparing dT terms

(2pt) $$V = V(G, T, P, n_i, n_j, n_k, \ldots, n_I) = \left(\frac{\partial G}{\partial P}\right)_{T, n_i, n_j \ldots n_I}$$ from comparing dP terms

Introduce a chemical potential μ_i for changing composition

(2pt) $$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T, P, n_j \ldots n_I}$$ from remaining terms

describe in words the meaning of chemical potential for a thermodynamic system:

(2pt) p. 97 Gaskell   or   potential energy absorbed/released during chemical reaction
or slope of free energy of the system w.r.t. change in number of moles just of that species

(c) Eliminate G to obtain the Gibbs-Duhem Equation which relates all the intensive properties of a system. (10 points)
Use only the variables (n, μ, V, P, S, T) and a summation over the total number of present species I.

(2pt) $$G = \sum_{i=1}^{I} \mu_i n_i \text{ for constant } T, P \qquad\qquad dG = -SdT + VdP + \sum_i \mu_i dn_i \text{ (2pt)}$$

note: we can look at how state functions change w.r.t. one variable when all others are held constant because state functions are path independent

(2pt) $$dG = \sum \mu_i dn_i + \sum n_i d\mu_i = 0 \qquad \text{when taken to be in equilibrium}$$
$$\sum \mu_i dn_i = -\sum n_i d\mu_i$$

following Gaskell's derivation on p. 217 will give same relation when $G = Q'$; $\overline{Q}_i = \mu_i$ he just does it more generally

if temp, pressure, and composition all change at once, we can think of an equivalent

(4pt) $$\sum_i^{I} n_i d\mu_i = -SdT + VdP$$

process where T changes, then P changes, then composition changes

4. Configuration Entropy (30 points)

(a) What is the conceptual definition of configuration entropy? (4 points)

(2pt) number of specific ways a system may be arranged
or measure of disorder

*not degree of irreversibility ↳ for thermal entropy

In statistical mechanics, what is the equilibrium state of a system?

(2pt) state of maximum entropy

(b) Consider the scenario shown below. We have six identical diamond particles, four identical circle particles, and two identical triangle particles confined to a grid. The particles are currently prevented from migrating due to partitions A and B. Also assume the particles are prevented from rotating. (8 points)

Partition A   Partition B
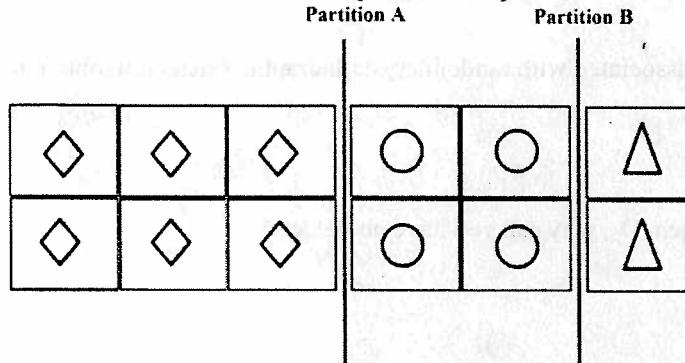
The initial state is shown. What is the number of distinguishable arrangements? Leave your answer as an integer and not in factorial form.

(1pt) Exactly one distinguishable arrangement.
Not 3! : No matter how the particles migrate it will always look like shown

What is the value of configuration entropy? Include units.

(1pt) $S = k \ln \Omega$

$= k \ln 1 = 0 \; J/K$ (1pt)

Partition A is removed so the diamond and circle particles randomly migrate. What is the number of distinguishable arrangements? Leave your answer as an integer and not in factorial form.

$$\Omega = \frac{N(circle + diamond)!}{N(circle)! \; N(diamond)!} = \frac{10 \cdot 9 \cdot 8 \cdot 7 \cdot 6 \cdot 5 \cdot 4 \cdot 3 \cdot 2}{\underbrace{4 \cdot 3 \cdot 2}_{circle} \; \underbrace{6 \cdot 5 \cdot 4 \cdot 3 \cdot 2}_{diamond}} = 210$$

(2pt)   (1pt)

Then Partition B is removed and all the particles randomly migrate. What is the number of distinguishable arrangements? Leave your answer as an integer and not in factorial form.

$$\Omega = \frac{N(circle + diamond + triangle)!}{N(triangle)! \; N(circle)! \; N(diamond)!} = \frac{12 \cdot 11 \cdot 10 \cdot 9 \cdot 8 \cdot 7 \cdot 6 \cdot 5 \cdot 4 \cdot 3 \cdot 2}{\underbrace{2}_{triangle} \cdot \underbrace{4 \cdot 3 \cdot 2}_{circle} \; \underbrace{6 \cdot 5 \cdot 4 \cdot 3 \cdot 2}_{diamond}}$$

(1pt)

$= 630$
$\cdot 22$
1260
$+12600$

$= 13860$

(2pt)

13860

(c) Consider a chemically pure solid of carbon monoxide CO beginning at finite temperature then cooled to a frozen crystalline lattice at 0 Kelvin. (10 points)
Conceptually or algebraically, what is the entropy associated with the distribution of vacant lattice sites?

(2 pt) • vacancies disseapear by diffusing to the free surface of the crystal
or
• non equilibrium concentrations of vacancies can be frozen in causing non-zero entropy at 0k

Conceptually or algebraically, what is the entropy associated with random crystallographic orientation?

(3 pt) 180° rotated lattice defect

CO   CO   CO   CO
OC   CO   CO   give rise to non zero entropy
CO   CO   CO   CO   at 0k
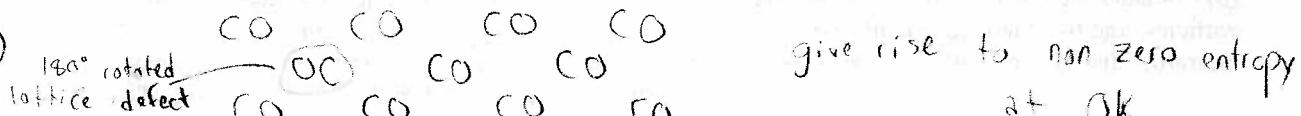
When does the entropy associated with random crystallographic orientation obtain its maximum value?

(2 pt) max entropy at equal numbers of molecules oriented in opposite directions

If you have frozen Oxygen, O$_2$, why can you have no defects?

(3 pt) 180° rotated lattice molecule does not give rise to defect

OO   OO   OO   OO
OO   OO   OO   OO
OO   OO   OO   OO

(d) Which of the following two reactions is more exothermic? (8 points)

↳ gives off energy

$$C_{(graphite)} + \frac{1}{2} O_{2(g)} \rightarrow CO_{(g)} \text{ at } 1000K$$

$$C_{(diamond)} + \frac{1}{2} O_{2(g)} \rightarrow CO_{(g)} \text{ at } 1000K$$
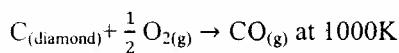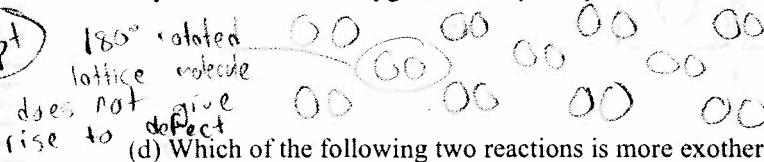
Note that diamond is more tightly packed than graphite due to being aligned Face Centered Cubic.
Include a brief discussion of Enthalpy in justifying your answer.

(3 pt) $H = U + PV$

$\sum_{i}^{N} m v_i^2$ same for both reactions

$N_{Diamond} > N_{carbon}$ in same volume and pressure

$H_{diamond} > H_{carbon}$
hence diamond reaction more exothermic

(2 pt)

(more energy released that goes into the CO$_{(g)}$)

Explain which reaction is more spontaneous.

(3 pt) $G = H - TS$

↑ higher for diamond

lower for diamond since diamond has lower entropy since it is neatly packed with low disorder

$G_{diamond} > G_{carbon}$

$G \sim$ process initiating work
∴ diamond more spontaneous

(+4pt EC) for getting both parts of (d) fully correct
↳ more long and difficult than I initially noticed
(+2pt EC) for getting only one part of (d) correct