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**DO NOT OPEN THIS TEST BOOKLET UNTIL INSTRUCTED TO DO SO.
THIS IS A CLOSED-BOOK, NO-NOTES EXAM.**

- Please sit according to the seating chart.
- Include the correct sign and units (S.I.) on all problems.
- You may use a **non-graphing** calculator that does **not** do calculus. Please bring one.
- Partial Credit will be given on most problems, as long as you show your work. Answers without sufficient documentation of how the work was done may not be given full credit.
- The mean is often quite low on my exams. If you are having difficulty, don't freak out. Many parts of problems can be done independently, so if you get stuck, see if you can do another section. The questions are not arranged in order of difficulty.
- Only answers written in permanent ink will be re-graded upon request. Re-grade requests must be submitted within one week of when the corrected exams are available.
- If you run out of room and need to write on the back of a page, leave a note to the grader on the problem page regarding where the grader can find your additional work.
- You may **not** tear off this first page of equations. However, you **may** (carefully) tear out the second page, which has water constants.

$$work = \int force \cdot dist$$

$$F_{gravity} = mg$$

$$F_{spring} = k_{spring} (x - x_0)$$

$$\Delta P = \int \rho g dx$$

$$\text{Ideal Gas: } PV = nRT = Nk_B T$$

$$C_P - C_V = nR$$

Van der Waals:

$$\left(P + a \frac{n^2}{V^2} \right) (V - nb) = nRT$$

$$work_{P-V} = - \int_{V_i}^{V_f} P \cdot dV$$

$$|work|_{electric} = QV$$

$$V = IR, \quad I = Q/t$$

$$\text{Energy}_{photon} = h \cdot \nu$$

$$\text{Energy flux} = \sigma T^4$$

$$\text{where } \sigma = 5.67 \times 10^{-8} \text{ J/m}^2\text{sK}^{-4}$$

$$C_V = (dq)_V/dT$$

$$C_P = (dq)_P/dT$$

$$dU = dq + dw \text{ (1st Law)}$$

$$= TdS - PdV$$

(PV work only,
reversible)

$$H = U + PV$$

$$A = U - TS$$

$$G = U - TS + PV$$

$$S = k_B \ln (\# \text{ of config.})$$

$$dS = \frac{dq^{rev}}{T}$$

$$\Delta S_{mix} = -nR \sum_i x_i \ln x_i$$

$$\varepsilon_{Carnot} = \frac{T_{hot} - T_{cold}}{T_{hot}}$$

$$= \frac{-w_{total}}{q_I} = \frac{q_{II} + q_{III}}{q_I}$$

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

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

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

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

$$\Delta \bar{G}_{total} = \Delta \bar{G}^0 + (\bar{V}_{products} - \bar{V}_{react}) \Delta P_{products}$$

$$\Delta G = G_f - G_i = nRT \ln(P_f/P_i)$$

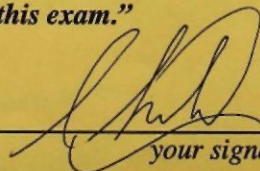
$$\Delta \bar{G}_{total} = \Delta \bar{G}^0 - (\bar{S}_{products} - \bar{S}_{react}) \Delta T_{products}$$

$$\left(\frac{dP}{dT} \right)_{eq} = \frac{S^\alpha - S^\beta}{V^\alpha - V^\beta} = \frac{\Delta S}{\Delta V} = \frac{\Delta H_{transition}}{T_{eq} \Delta V}$$

$$\ln \left(\frac{P_f}{P_i} \right) = - \frac{\Delta H_{vap}}{nR} \left(\frac{1}{T_f} - \frac{1}{T_i} \right)$$

G(giga) $\times 10^9$ M(mega) $\times 10^6$ k(kilo) $\times 10^3$ m(milli) $\times 10^{-3}$ μ (micro) $\times 10^{-6}$ n(nano) $\times 10^{-9}$ p(pico) $\times 10^{-12}$ f(femto) $\times 10^{-15}$

"I attest that I have neither given nor received any aid on this exam."


your signature

1) MULTIPLE CHOICE (2 points each) Put your single best answer for each question in each box.

- i) Most students use the equation $PV = nRT$ for gases in their first-year chemistry classes. The single best reason for this is because ...

- a) The equation is always true.
 b) The equation is always a good approximation (to within ~5% error).
 c) The equation is always valid when pressure is constant, and most undergraduate labs are at constant pressure.
 d) The equation is always valid when temperature is constant, and most undergraduate labs are at constant temperature.

Place the letter of your answer here:

+

B

- ii) Most students use the equation $\Delta G = \Delta H - T\Delta S$ in their first-year chemistry classes. The single best reason for this is because ...

- a) The equation is always true.
 b) The equation is always a good approximation (to within ~5% error).
 c) The equation is always valid when pressure is constant, and most undergraduate labs are at constant pressure.
 d) The equation is always valid when temperature is constant, and most undergraduate labs are at constant temperature.

$$dG = dH - TdS = dH - Tds + SdT$$

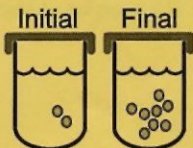
Place the letter of your answer here:

+

D

- iii) Cells are highly organized structures. Consider a system of a closed test tube containing two yeast cells, an aqueous glucose solution and some air. Soon there are eight yeast cells. The single **best** explanation of why this system does not violate the Second Law of Thermodynamics is that ...

- a) There are more ways to arrange 8 yeast cells than to arrange 2 yeast cells.
 b) The test tube is closed rather than isolated. Although the entropy of everything inside the tube decreases, the entropy of the surroundings increases.
 c) Mannan oligosaccharides, which are polymers, appear in yeast cell walls. More yeast means more polymers and more configurations.
 d) Growth of the yeast increases the temperature of the solution.
 e) The waste of the yeast has a higher entropy than the glucose it consumes.



Place the letter of your answer here:

+

E

- iv) A system undergoes a transition from having *zero* non-pressure-volume work to having *measurable* non-pressure-volume work. You may assume that everything that happens to the system is reversible. Which quantity does NOT change over this transition?

- a) dH
 b) dH for a system at constant P
 c) $dA - dU$
 d) dA
 e) dG

Place the letter of your answer here:

+

C

$$dG = U - TS + PdV$$

$$dA = dU - TS$$

$dA - dU = -TS$

no work term
no work taken into account

2)



(3 points total)

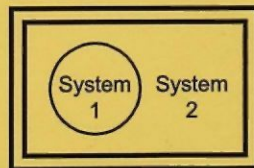
Rubber bands are made of long polymers. The rubber band in the figure is in contact with its surroundings and is initially stretched by a force. When the force is removed, the rubber band relaxes. During the relaxation... (Circle the single best answer for each part below.)

- i) ... the entropy of the polymers a) decreases. b) stays the same. **c) increases.** +
- ii) During the relaxation... **a) heat is transferred from the surroundings to the rubber.** + b) no heat is transferred. **c) heat is transferred from the band to the surroundings.**
- iii) Your upper lip is sensitive to heat. If you touch your lip to a stretched rubber band and then quickly relax the band, the nerves in your lip will sense that your lip has become... **a) cooler.** + b) no change. **c) warmer.**
- +3

$$\Delta S = \int \frac{dq_{\text{band}}}{T} + \int \frac{dq_{\text{surr}}}{T}$$

Not needed for this problem: To try this experiment at home, use the widest and thickest band possible.

- 3) Systems 1 and 2 are in contact with each other and isolated from their surroundings. A reaction occurs such that S_1 , the entropy of system 1, increases. What are all the conclusions you can make about S_2 , the entropy of system 2?



(Circle ALL possible answers below.) $\Delta S_1 \neq -\Delta S_2$ (2 points total)

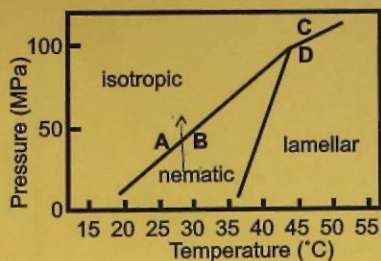
- generic rxn
 $q_1 = -q_2$
- a) S_2 can decrease as long as $|\Delta S_2|$ (the absolute value) is **greater than** $|\Delta S_1|$.
- b) S_2 can decrease as long as $|\Delta S_2|$ (the absolute value) is equal to $|\Delta S_1|$.**
- c) S_2 can decrease as long as $|\Delta S_2|$ (the absolute value) is **less than** $|\Delta S_1|$.
- d) S_2 can **increase** as long as $|\Delta S_2|$ (the absolute value) is **greater than** $|\Delta S_1|$.
- e) S_2 can **increase** as long as $|\Delta S_2|$ (the absolute value) is **equal to** $|\Delta S_1|$.
- f) S_2 can **increase** as long as $|\Delta S_2|$ (the absolute value) is **less than** $|\Delta S_1|$.
- g) S_2 can **remain at the same value.** ✓

+
 $S_2 > 0$
can increase
regardless
since
 $S_{\text{TOT}} > 0$ &
 $S_T = S_1 + S_2$
↓
(+)

$dU = 0$
 $dq = -dW$
 $\Delta S_{\text{TOT}} > 0$
isolated
system

4) In 2016, scientists made an aqueous mixture with 60% of one type of lipid, 20% of a second type, and 20% of a third type. They varied the pressure and temperature and found the three phases in the figure ("isotropic", "nematic", and "lamellar").

(6 points total)



i) From points A and B in the figure, the isotropic to nematic transition appears to be...

~~a) Exothermic~~

b) Endothermic

c) Neither exothermic or endothermic

~~$\Delta V < 0$~~

final vol $> V_0$

$$\frac{dP}{dT} = \frac{\Delta H}{T_{eq} \Delta V}$$

$$V_I < V_N$$

$$V_N - V_I > 0$$

(-)

$$\frac{dP}{dT} =$$

ii) From points C and D in the figure, the isotropic phase has a...

a) Smaller molar volume than the lamellar phase

b) Bigger molar volume than the lamellar phase

c) Volume that is equal to the volume of the lamellar phase

+

smaller slope
0.2

iii) Which transition is associated with the largest value of $\frac{\Delta V}{\Delta S}$?

a) The isotropic to lamellar transition

b) The isotropic to nematic transition

c) The nematic to lamellar transition

$$\frac{dT}{dP} = \frac{\Delta V}{\Delta S} = \left(\frac{dP}{dT}\right)^{-1}$$

I \rightarrow N

I \rightarrow L

N \rightarrow L

0.05

Source: C. Knight, A. Rahmani, M.R. Morrow, 2016, Effect of an anionic lipid on the barotropic behavior of a ternary bicellar mixture, *Langmuir*, 32, 10259-10267. (The lipid mixture is DMPC-d₅₄/DMPG/DHPC.)

5) Changes in volume (V) and pressure (P) can result in changes in entropy (S).

Because entropy is a state function, the entropy change in this situation could be written as:

$$dS = \left(\frac{\partial S}{\partial V}\right)_P dV + \left(\frac{\partial S}{\partial P}\right)_V dP \quad \left(\frac{\partial S}{\partial V}\right)_P = \left(\frac{\partial P}{\partial T}\right)_S$$

Which expression(s) below could be used to substitute for $\left(\frac{\partial S}{\partial V}\right)_P$ in the equation above?

(Circle the single best answer below.)

(2 points total)

a) C_V ideal gas

b) $nR \ln \frac{V_f}{V_i}$

~~c) $\left(\frac{\partial P}{\partial T}\right)_V$~~

d) $\frac{nR}{T}$ gas

e) C_P

f) $nR \ln \frac{P_f}{P_i}$

g) $\left(\frac{\partial P}{\partial T}\right)_S$

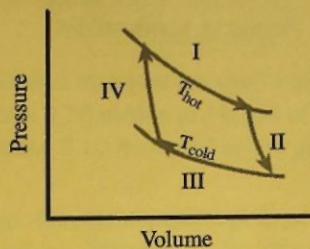
h) Options b and c

Great!

6) A particular "heat engine" power plant produces 1000 megawatts of power (1 megawatt = 10^6 J/s).

Its boiler is at 500°C , and its cooling stage is in a cold Northwest river at 10°C .

(13 points total)



i) What is the efficiency of the power plant?

$$\epsilon = \frac{T_h - T_c}{T_h} = \frac{773 - 283 \text{ K}}{773 \text{ K}} = 0.634$$

+3

place your answer here:

63.4%

ii) How much heat/second is expelled into the river?

q_{III} !

$$\epsilon = \frac{-W_{\text{TOT}}}{q_{\text{I}}} \quad \& \quad q_{\text{I}} + q_{\text{III}} = -W_{\text{TOT}} \quad \therefore \quad q_{\text{I}} = -(W_{\text{TOT}} + q_{\text{III}})$$

$$\therefore \quad \epsilon = \frac{-W_{\text{TOT}}}{-(W_{\text{TOT}} + q_{\text{III}})}$$

$$\epsilon(W_{\text{TOT}}) + \epsilon q_{\text{III}} = W_{\text{TOT}} \quad \therefore \quad \epsilon q_{\text{III}} = W_{\text{TOT}}(1 - \epsilon)$$

$$\epsilon(W_{\text{TOT}}) - W_{\text{TOT}} =$$

$$q_{\text{III}} = \frac{W_{\text{TOT}}(1 - \epsilon)}{\epsilon} = \frac{1 \cdot 10^9 \frac{\text{J}}{\text{s}}(1 - 0.634)}{0.634}$$

place your answer here:

+6

$5.78 \cdot 10^8 \text{ J/s}$

iii) In order to maintain the cooling stage at 10°C , engineers have designed the power plant to continually take in cold water from the river and to expel used, warmer water back into the river. If regulations permit no more than a 5°C increase in the temperature of the water from when it is taken into the power plant to when it is expelled, how much water must flow through the plant to operate it? Express your answer in (metric tons of water)/(second), where 1 metric ton = 10^3 kg.

$$5.78 \cdot 10^8 \text{ J/s} = q = \int m C dT = m C_{\text{H}_2\text{O}} \left(\frac{\Delta T}{\cancel{\text{K}}} \right)$$

$$5.78 \cdot 10^8 \text{ J/s} = m \cdot 4.184 \frac{\text{kJ}}{\text{kg}\cdot\text{K}} \cdot \frac{1000 \text{ J}}{1 \text{ kJ}} \cdot 5 \text{ K}$$

$$2.76 \cdot 10^4 \frac{\text{kg}}{\text{s}} = m$$

$$2.76 \cdot 10^4 \frac{\text{kg}}{\text{s}} \cdot \frac{1 \text{ metric ton}}{10^3 \text{ kg}} =$$

+4

place your answer here:

27.6 metric tons/second



	Argon	N ₂
Molar Cp in J/(mol·K)	20.8	29.1
Molar mass in g/mol	39.9	28.0

- 7) A thermally insulated box with rigid walls is initially divided into two unequal volumes. The volume on the left of the divider is 2.0 L and contains 0.20 moles of N₂ gas at 200°C. The volume on the right of the divider is 1.0 L and contains 0.10 moles of argon gas at 100°C.

(18 points total)

- i) The gases undergo a two-step process. In the first step, the gases exchange heat through the divider until they reach a uniform temperature. What is ΔS for this step?

$$* (n_{Ar} = P_{Ar} V_{Ar})$$

$$* n_{Ar} C_{Ar} = 0.10 \text{ mol} \cdot \frac{20.8 \text{ J}}{\text{mol K}}$$

$$= 2.08 \text{ J/K}$$

$$* n_{N_2} C_{N_2} = 0.20 \text{ mol} \cdot \frac{29.1 \text{ J}}{\text{mol K}}$$

$$= 5.82 \text{ J/K}$$

$$\Delta V = 0 \text{ for system}$$

$$dq_v = 0 \text{ for system}$$

$$\text{use } \bar{C}_v = \bar{C}_p - R$$

for heat capacity

$$q_{Ar} = -q_{N_2}$$

$$\int n C dT = -\int n C dT$$

$$n_{Ar} C_{Ar} (T_f - T_{Ar}) = -n_{N_2} C_{N_2} (T_f - T_{N_2})$$

$$n_{Ar} C_{Ar} T_f - n_{Ar} C_{Ar} T_{Ar} = n_{N_2} C_{N_2} T_{N_2} - n_{N_2} C_{N_2} T_f$$

$$T_f (n_{Ar} C_{Ar} + n_{N_2} C_{N_2}) = n_{N_2} C_{N_2} T_{N_2} + n_{Ar} C_{Ar} T_{Ar}$$

$$T_f = \frac{n_{N_2} C_{N_2} T_{N_2} + n_{Ar} C_{Ar} T_{Ar}}{n_{Ar} C_{Ar} + n_{N_2} C_{N_2}}$$

~~$$T_f = \frac{5.82 \text{ J/K} (473 \text{ K}) + 2.08 \text{ J/K} (373 \text{ K})}{5.82 + 2.08 \text{ J/K}}$$~~

$$T_f = \frac{(5.82 \text{ J/K})(473 \text{ K}) + (2.08 \text{ J/K})(373 \text{ K})}{5.82 + 2.08 \text{ J/K}}$$

$$T_f = 446.67 \text{ K} = 173.67^\circ \text{C}$$

$$\Delta S_{TOT} = \Delta S_{Ar} + \Delta S_{N_2} = \int \frac{dq_{Ar}}{T} + \int \frac{dq_{N_2}}{T} = \int \frac{n_{Ar} C_{Ar} dT}{T} + \int \frac{n_{N_2} C_{N_2} dT}{T}$$

$$= n_{Ar} C_{Ar} \ln \frac{T_f}{T_{Ar}} + n_{N_2} C_{N_2} \ln \frac{T_f}{T_{N_2}}$$

$$= (2.08 \frac{\text{J}}{\text{K}}) \ln \frac{446.67 \text{ K}}{373 \text{ K}} + (5.82 \frac{\text{J}}{\text{K}}) \ln \frac{446.67 \text{ K}}{473 \text{ K}}$$

$$\Delta S_{TOT} = 0.0416 \text{ J/K}$$

+12

Great
Job

place your answer here:

0.0416 J/K

Continued on the next page...

...continued from the previous page

ii) In the second step, the divider between the volumes is removed, and the molecules distribute uniformly throughout the total volume. What is ΔS for this step?

this is ΔS of MIXING

$$\Delta S = -nR \sum x_i \ln x_i$$

$$\Delta S = -nR (X_{N_2} \ln X_{N_2} + X_{Ar} \ln X_{Ar}) *$$

$$\begin{aligned} \Delta S &= -(0.3 \text{ mol}) (8.314 \frac{\text{J}}{\text{mol K}}) \left(\frac{2}{3} \ln \frac{2}{3} + \frac{1}{3} \ln \frac{1}{3} \right) \\ &= -(0.3 \text{ mol}) (8.314 \frac{\text{J}}{\text{mol K}}) (-0.6365) \end{aligned}$$

$$\Delta S = 1.58759 \text{ J/K}$$

↳ positive, which makes sense for mixing

$$* X_{N_2} = \frac{n_{N_2}}{n_{N_2} + n_{Ar}} = \frac{0.2}{0.3}$$

$$X_{Ar} = \frac{n_{Ar}}{n_{Total}} = \frac{0.1}{0.3}$$

+5

Great job!

place your answer here:

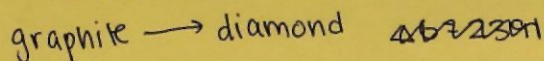
1.59 J/K

8) In the movie "The Adventures of Baron Munchausen", the character Vulcan crushes coal (graphite) between his hands to make a diamond for his wife, Venus. You may assume that the reaction occurs at a constant temperature and the chunk of coal has a mass of 0.200 kg.

	\bar{H}^0 (J/mole)	\bar{G}^0 (J/mole)	\bar{V} (volume/mole)
diamond	1863	2391	3.42 cc/mole = 3.42×10^{-6} m ³ /mole
graphite	0	0	5.33 cc/mole = 5.33×10^{-6} m ³ /mole

What pressure does Vulcan need to achieve between his hands to turn graphite into diamond?

(6 points total)



$$\Delta \bar{G}^0 = 2391 \text{ (J/mol)}$$

$$\Delta \bar{V} = \left(3.42 \cdot 10^{-6} \frac{\text{m}^3}{\text{mol}} - 5.33 \cdot 10^{-6} \frac{\text{m}^3}{\text{mol}} \right) = -1.91 \cdot 10^{-6} \frac{\text{m}^3}{\text{mol}}$$

For this coal: $\Delta V = \Delta \bar{V} \cdot n = -1.91 \cdot 10^{-6} \frac{\text{m}^3}{\text{mol}} \cdot \frac{0.200 \text{ kg}}{0.012 \text{ kg/mol}} = -3.183 \cdot 10^{-5} \text{ m}^3$

~~$\frac{\Delta P}{\Delta T} = \frac{\Delta H_{\text{transition}}}{T_{\text{eq}} \Delta V}$~~ not @ equilibrium

$$\Delta \bar{G}_{\text{total}} = \Delta \bar{G}^0 + (\bar{V}_{\text{prod}} - \bar{V}_{\text{react}}) \Delta P_{\text{prod}}$$

\downarrow equil.

$$0 = \Delta \bar{G}^0 + \left(-1.91 \cdot 10^{-6} \frac{\text{m}^3}{\text{mol}} \right) (P_f - 10^5 \text{ Pa})$$

$\uparrow P_f = \text{atmospheric pressure}$

$$\Delta \bar{G}^0 = 1.91 \cdot 10^{-6} \frac{\text{m}^3}{\text{mol}} (P_f - 10^5 \text{ Pa})$$

$$\frac{2391 \text{ J/mol}}{1.91 \cdot 10^{-6} \text{ m}^3/\text{mol}} + 10^5 \text{ Pa} = 1.252 \cdot 10^9 \text{ Pa}$$

$$dG = dU - TdS - SdT + PdV + VdP$$

$$dG + dW - TdS - SdT + PdV + VdP$$

$$= -SdT + VdP$$

$$dG = VdP$$

$$dG = W (PdV)$$

$$J = \text{Pa} \cdot \text{m}^3$$

$$\therefore \text{J/m}^3 = \text{Pa} \quad \checkmark$$

(+7) Great job!

place your answer here:

$$1.252 \cdot 10^9 \text{ Pa}$$

Source: Values for ΔH and ΔG are from the Argonne National Laboratories' website:

https://atct.anl.gov/Thermochemical%20Data/version%201.118/species/?species_number=951