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Exam #1

Biophysical Chemistry

Chemistry 130A

Spring 2001

Justify all your assumptions!

Show <u>all</u> your calculations!

Make sure all your conclusions are physically reasonable.

Keep track of units and significant digits!

Underline or Box all your final answers!

Exams in pencil won't be regraded.

1) 8
2) 9
3) +12
4) 9
5) 10

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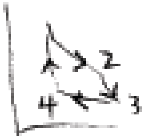
1. (9 pts) Thermodynamic Functions

(a) Each integral below represents taking a Carnot engine around one complete cycle. State whether or not the integral is equal to zero and why.

✓ 1. $\oint \frac{dq_{rev}}{T}$ Yes, $\oint \frac{dQ}{T} = \oint dS$; entropy is a state function and equals 0 for a cyclic process.

✓ 2. $\oint dw$ no, net work is done on the surroundings

$w = -nRT_H \ln\left(\frac{V_2}{V_1}\right) + -nRT_L \ln\left(\frac{V_4}{V_3}\right)$



✓ 3. $\oint \frac{dV}{V}$ Yes, $\Delta V = 0$ for a cycle.

✓ 4. $\oint (dq + dw) = \oint dE = 0$ Yes since Internal Energy is a state function.

✓ 5. $\oint dq$ No; $Q_H = Q_L + w$; $\oint dq = nRT_H \ln\left(\frac{V_2}{V_1}\right) + nRT_L \ln\left(\frac{V_4}{V_3}\right)$

(q is path dependent) $\neq 0$

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

$w \neq 0$ so $q \neq 0$

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(b) Which of the following are state functions and why?

✓ 1. **PVT** $PV = nRT$; PVT are state functions that depend on the conditions of a system. All systems at the same P, V, + T are in the same state.

✓ 2. **w/q**

w + q are not state functions, and $\frac{w}{q}$ does not result in a state function. (path dependent)

✓ 3. **q + w + PV** = $\Delta E + PV$; this equals ΔH and ΔH (enthalpy) is a state function that only depends on H_{final} and $H_{initial}$.

✗ 4. **E-TS** = $E - q = w$; work depends on the path taken. Not a state function

difference of 2 state

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2. (12 pts) Antidepressants and paths.

A pharmacist is considering the use of LiBr to treat manic-depressive patients after reading an advertisement in psychology today that said "Handel wrote The Messiah in seven days. Today he wouldn't have the problem. Lithium."

She is concerned that when solid LiBr is ingested with water, it might release enough heat to make the patient very uncomfortable. She is thinking of the following regimen: **Once Daily: Take 8.7 g of LiBr in 36mls of water.**

From her handy-dandy CRC she pulls out:

LiBr: 87 grams per mole

Water: 18 g/mol

ΔH for dissolving LiBr in water: -11.7 kcal/mol

C_p of LiBr in water is: 0.98 cal/(K g)

She then made the following assumptions: **1)** The LiBr and water mix in the stomach (and LiBr doesn't dissociate) **2)** The reaction occurs so quickly that no heat may leave the stomach (until later) **3)** Everything occurs at 1 atm.

(a) Write down the series of thermodynamic (and chemical) state changes for the process of taking the medication, dissolving of LiBr, and eventual release of heat to the surrounding.

1\. $\Delta H_{\text{dissolving}} = H_{LiBr(aq)} - H_{LiBr(s)} = -11.7 \frac{\text{kcal}}{\text{mol}}$ ✓

dissolving rxn

2\. $LiBr_{(s)} + H_2O_{(l)} \xrightarrow{} $ (produces heat) $LiBr(aq) + H_2O_{(l)}$ $\Delta H = -11.7 \frac{\text{kcal}}{\text{mol}}$

3\. $\Delta S_{\text{stomach}} = \frac{q}{T} = \frac{-\Delta H_{\text{dissolving}}}{T_{\text{stomach}}}$ $\Delta S_{\text{system}} = \frac{\Delta H_{\text{dissolving}}}{T_{\text{stomach}}}$

4\. $\boxed{\Delta H_{\text{dissolving}} = -\Delta H_{\text{surroundings}}}$ ✓

④

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(b) What is the **maximum** temperature reached in the stomach of the patient? Do you think this is ok? Show your thought process!

$$8.7\text{g LiBr} \times \frac{1 \text{ mol LiBr}}{87 \text{ g}} \times \frac{-11.7 \text{ kcal}}{1 \text{ mol LiBr}} = -1.17 \text{ kcal produced per dose}$$

$$+1.17 \text{ kcal} = \Delta H = q_{added} = m C_p \Delta T$$

$$+1.17 \text{ kcal} = (36\text{g } H_2O)\left(\frac{98 \text{ kcal}}{\text{K g}}\right)(\Delta T)$$

$$+{}_{\times}0332 \text{ K} = \Delta T$$

units mass −1

$$\left[36 \text{ mL } H_2O \times \frac{1\text{g } H_2O}{1 \text{ mL } H_2O} = 36 \text{ g } H_2O\right.$$

(assumption: density$_{H_2O \text{ at body T}}$ = 1g/mL)

⑤

* Assuming body T = 98°F = 36.67°C,

$$\text{Final T} = 36.67°\text{C} + {}_{\times}0332\,°\text{C} = \boxed{\overset{69.8}{\cancel{36.7}}\ °\text{C}}$$

This is ~~not~~ a major change in ~~Body T~~ stomach T, so LiBr in such doses is not ok, for the stomach.

3. (12 pts) Chemical Paths

+12

Perhaps the better antidepressant drug, Prozac, blocks the action of the neurotransmitter serotonin by competing for the serotonin binding site. At 20°C, the Prozac-receptor dissociation has an enthalpy of 1200 kJ/mol as measured by titration scanning calorimetry. The molecular weight of the Prozac-receptor complex is 42,000 g/mol

The difference in heat capacity between the complex (Prozac·Receptor) and the free molecules (Prozac+Receptor) has been determined to be $\Delta C_P = C_P^{complexed} - C_P^{uncomplexed} = 1.35$ J/(K gram). Calculate the ΔH per mole of reaction for dissociation of the Prozac-receptor complex at 37°C.

$$\Delta H_{dissoc}(20^\circ C) = 1200 \frac{kJ}{mol}$$

$$\begin{tikzcd}
\text{Pro-rec } (37^\circ C) \arrow[r, "\text{dissociation}"] \arrow[d, "\Delta H_1"] & \text{Pro + rec } (37^\circ C) \\
\text{Pro-rec } (20^\circ C) \arrow[r, "\Delta H_2", "\text{dissociation}"'] & \text{Pro+ rec } (20^\circ C) \arrow[u, "\Delta H_3"']
\end{tikzcd}$$

$$\Delta H_{dissoc}(37^\circ C) = \Delta H_1 + \Delta H_2 + \Delta H_3$$

$$= m C_{p\,comp} \Delta T + \Delta H_{dissoc}(20^\circ C) + m C_{p\,uncomp} \Delta T$$

$\left(\frac{1 \text{ mol}}{\text{Pro-rec}}\right)$

$$= \left(42000 \frac{g}{mol}\right) C_{pcomp} (20^\circ C - 37^\circ C) + 1200 \frac{kJ}{mol} + 42000 \frac{g}{mol} C_{puncomp} (37^\circ C - 20^\circ C)$$

$$= 42000 \frac{g}{mol} (37^\circ C - 20^\circ C)(C_{puncomp} - C_{p\,comp}) + 1200 \frac{kJ}{mol}$$

$$= 42000 \frac{g}{mol} (17 C^\circ)\left(-1.35 \frac{J}{K \cdot g}\right) + 1200 \frac{kJ}{mol}$$

$$= \boxed{236 \frac{kJ}{mol}}$$

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4. (10 pts) Entropy and other things

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(a) Give a formula for the probability that all N molecules of an ideal gas are in one half of a box and not the other. Compare the probability when N equals four to when N is equal to Avagadro's number. What are the implications of this in cells when a protein is present at small numbers (5-10 copies)? (Think, for example, about cell division.)

probability $= \left(\frac{1}{2}\right)^N$ each molecule has $\frac{1}{2}$ chance of being in $\frac{1}{2}$ of the box

$N=4: \left(\frac{1}{2}\right)^4 = \frac{1}{16}$

$N = 6.02 \times 10^{23} : \left(\frac{1}{2}\right)^{6.02 \times 10^{23}}$ = much, much greater than.

* when a protein is in small quantities in a cell, it has a relatively higher chance of being at 1 end of the cell. when the cell divides, all the protein may go to 1 daughter cell but not the other. This could alter the functions of both cells

(b) The second law of thermodynamics states that any system and its surroundings must continually increase in entropy. However, living organisms constantly create highly ordered structures from less-ordered raw materials. Do living organisms violate the second law? Explain.

1

The 2nd law only states that $\Delta S_{univ} \geq 0$, so as ΔS_{cells} decreases, $\Delta S_{environment}$ increases at least as much to compensate for the decrease in entropy caused by the functioning of cells (division, DNA replication, etc).

The chemical energy ~~The~~ produced from chemical rxns is partially released as heat, which causes an entropic increase in the surroundings.

4

(c) Do you get more work out of a reversible or irreversible expansion of an ideal gas? Why?

irreversible: $P_{ex} < P_{int}$ rev: $P_{ex} = P_{int}$

$w = -P_{op}\Delta V$ $w_{irrev} = -P_{ex}\Delta V$ $w_{rev} = -P_{ex}\Delta V = -P_{int}\Delta V$

compare

$|w_{irrev}| < |w_{rev}|$ since $P_{ex} < P_{int}$ for irreversible processes.

Thus, reversible expansion produces $\boxed{\text{more work.}}$

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5. (17 pts) Non-ideality

A crazed physicist has made an electron gas in the laboratory. He theorizes, for reasons he doesn't wish to divulge, that the internal energy of this gas is:

$$E(V,T) = (3/2)nRT + X(\frac{n}{VT})$$

over some temperature range, with X a positive constant (in units of J*L*K/mol). This second term might describe a repulsive interaction among the electrons in the gas.

The heat capacity of this gas is given by $C_V = (\frac{\partial E}{\partial T})_V = (3/2)nR - X\frac{n}{VT^2}$

5/7 **(a)** Recall that $C_V = (3/2)nR$ for an ideal gas. Does the form of C_V above make sense, in light of the fact that our nonideal gas has repulsive interactions? Explain.

The electron gas has repulsive interactions due to the negative charges of the electrons. A lower C_v (since $\frac{Xn}{VT^2}$ is subtracted from $\frac{3}{2}nR$) means the gas increases in T with less energy. This makes sense because there are no attractive interactions between electrons, making them relatively easy to increase the energy of.

✓

(b) Intuitively, we expect $C_V > 0$ always (because increasing the temperature of a system should increase its energy). Is the C_V above physically reasonable in this sense? Explain.

For C_v to be negative, $\frac{3}{2}nR < X\frac{n}{VT^2}$. Assuming that T is on an absolute scale, $X\frac{n}{VT^2}$ will always be small unless $0<T<1K$. For realistic cases, Cv will be positive.

2/7 **(c)** For an ideal gas, ΔE for an isothermal expansion is 0. Will ΔE for our nonideal gas be greater than, less than, or equal to zero when it undergoes an isothermal expansion?

Keeping T constant will ~~keep~~ not ~~prev~~ prevent C_v from changing because V is changing. However, as ΔE is defined,

$\Delta E = nC_v\Delta T$

if $\Delta T = 0$, then $\Delta E = 0$ as well. ΔE is solely dependent on ΔT.