

Instructions:

- Please solve these problems ... putting your answer in the blank space.
- There are a few more problems than I'll ask for on your real test. In 2 hours I'll probably ask you to do 6 problems.
- Should an answer be wrong in the real test, you will have an opportunity to correct it ... by doing a calculation, open-book, showing your steps and reasoning and if you can, getting the correct answer at the end of your calculation.
- You can use your cheat sheets (maximum of 18 sides of paper) and a calculator.
- Good luck!

Useful data:Proton mass: $1.67 \times 10^{-27} \text{ kg}$ Electron mass: $9.11 \times 10^{-31} \text{ kg}$ Ideal gas constant $R = 8.31 \text{ J/mol} \cdot \text{K}$.Boltzmann's constant: $k = 1.38 \times 10^{-23} \text{ J/K}$ Planck's constant: $h = 6.63 \times 10^{-34} \text{ J s}$ $\text{eV} = 1.60 \times 10^{-19} \text{ Joule}$ Absolute zero: $0 \text{ K} = -273.15^\circ \text{C}$ speed of light: $c = 3.00 \times 10^8 \text{ m/s}$

Enthalpies and entropies of formation for selected compounds:

C (graphite): $\Delta H_f = 0 \text{ kJ}$, $\Delta S_f = 5.74 \text{ J/K}$ H_2 (gas): $\Delta H_f = 0 \text{ kJ}$, $\Delta S_f = 130.68 \text{ J/K}$ CH_4 (gas): $\Delta H_f = -74.81 \text{ kJ}$, $\Delta S_f = 186.26 \text{ J/K}$

Gaussian integrals:

$$\int_0^\infty e^{-ax^2} dx = \frac{\sqrt{\pi}}{2a^{1/2}} ; \int_0^\infty x e^{-ax^2} dx = \frac{1}{2a} ; \int_0^\infty x^2 e^{-ax^2} dx = \frac{\sqrt{\pi}}{4a^{3/2}}$$

1. What is the efficiency of an ideal engine that works between a hot temperature of 400K and a cold temperature of 300K?

Answer: _____

2. A particle can be in one of two energy states, $E_0 = 0$ or $E_1 = +\epsilon$. There is only one unique state with E_0 but there are 3 different states with energy E_1 . What is the Helmholtz free energy, F , for this single particle at temperature T ?

Answer: _____

3. Einstein solid A has $N_A = 1000$ particles, and initially has $E_A = 99$ energy quanta. Solid B has $N_B = 2000$ and initially has $E_B = 201$ energy quanta. What is the change in entropy ΔS that occurs after the two are put into thermal contact and reach equilibrium?

Hint: Since you can't use Mathematica, you will need the full Stirling's approximation. It would

be nice if it were on your cheat sheet. For this practice test, I'll give it:

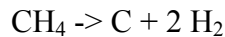
$$\ln N! = N \ln N - N + (1/2) \ln(2\pi N)$$

Answer: _____

4. A solid has an equation of state $P(T, V) = D[V_o - (1 - bT^2) V]$ where T is the temperature, V is the volume, and D, b, V_o are positive constants. By finding $\left(\frac{\partial S}{\partial V}\right)_T$ you can find how much heat, Q , the solid exchanges with the environment when compressed isothermally from volume V_o to volume V_I . What is Q ?

Answer: _____

5. Here is a chemical reaction converting methane to graphite and hydrogen gas:



Will this reaction go spontaneously at $T=298\text{K}$ and atmospheric pressure?

Answer: _____

6. In a very dilute plasma, electrons and protons can be treated as semi-classical ideal gasses. Suppose one has a gas of electrons in a container of size V , and that there are Γ_e states with energy less than E . In an identical container of volume V , how many energy states, Γ_p , are there for protons with energy less than E ?

Answer: _____

7. A Maxwell speed distribution yields an average speed of $\langle v \rangle = \sqrt{\frac{8kT}{\pi m}}$. Suppose we instead need the average inverse speed: $\langle 1/v \rangle$. Please find its value.

Answer: _____

8. A friend has just calculated the heat capacity, C , of a 2-level system with N

independent particles, each of which can have energy 0 or Δ . They find:

$$C = \frac{k e^{2\beta\Delta}}{(e^{\beta\Delta} - 1)^2}$$

Above, k is Boltzmann's constant and $\beta = 1/kT$. You look at this expression and say as kindly as possible "It's wrong." Without doing any calculation (like calculating this quantity yourself) tell your friend at least two things that suggest that their expression is wrong.

Answer: _____

Answer: _____

Answers:

1. Answer: $\eta = 0.25$

which can be found as $(T_H - T_C)/T_H$

2. Answer: $F = -kT \ln[1 + 3e^{-\epsilon/kT}]$

which can be found via

$$Z(T, V, 1) = \sum_E g(E) e^{-\beta E} \text{ and}$$

$$F = -kT \ln Z$$

3. Answer: $\Delta S = 3.07k$

which can be found by this argument:

The multiplicity of Einstein solid i , where $i = A$ or B , is $\Omega_i = (E_i + N_i - 1)! / [E_i! (N_i - 1)!]$.

We get initial entropy as $k \ln(\Omega_A \Omega_B)$. Final entropy is $k \ln(\Omega)$ where we use

$N = N_A + N_B$ and $E = E_A + E_B$ in the final state. If we had Mathematica we could use

these numbers as is ... or even use Mathematica's "Binomial" function. If we are restricted to hand calculator, Stirling's approx. works for these numbers, giving accuracy to about 5 decimal places. *(This turns out to require a lot of numbers entered correctly into a calculator. I'll try to choose a less time consuming numerical task on a real test!)*

Thus: the initial entropy is $998.41k$, the final is $1001.48k$, making the difference

$\Delta S = 3.07k$ where k is Boltzmann's constant.

Note 1: Because these numbers are big but not huge, we actually do need that last term in Stirling's approx.: $\log[2 \pi N]$ or we would have too little precision to get this answer to 5 sig figs.

Note 2: In equilibrium, the mean number of quanta in side A is going to be $E_A = 100$, and in B, $E_B = 200$. If we took the entropy of just that most-likely state, and added one more figure to our calculation using the full Stirling Approximation, we'd get $S = 998.414k$ which is only a tiny bit higher than the entropy of the initial system: $S = 998.410k$. If you made the mistake of just taking S for that that most-likely state, you'd get a really tiny change in entropy, instead of the right answer. Take home message: Equilibrium allows fluctuations from the mean, so true equilibrium entropy for the merged system is higher than entropy of any state of the separated system, even the most likely one ☺

4. Answer: $Q = DbT^2 [V_I^2 - V_o^2]$

which can be found this way:

We use a Maxwell relation:

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

We can find the RHS which is $\left(\frac{\partial P}{\partial T}\right)_V = 2bDTV$. We equate this quantity with the LHS. We then say that Q is the integral of $T dS$. In other words:

$$Q = T \int_{V_o}^{V_I} \left(\frac{\partial S}{\partial V}\right)_T dV = T \int_{V_o}^{V_I} \left(\frac{\partial P}{\partial T}\right)_T dV$$

which results in the answer:

$$Q = DbT^2 [V_I^2 - V_o^2]$$

5. Answer: No

We argue this by using $\Delta G = \Delta H - T\Delta S$ applied to whole reaction ... with ΔG positive for products and negative for reactants. Thus $\Delta G = 50.7 \text{ kJ}$, a positive number so the reaction will not go spontaneously. ΔG is the change in an "availability" and it must be negative if a process is to proceed spontaneously.

6. Answer: $\Gamma_p = 78,500 \Gamma_e$ (to three sig fig's)

We find this by thinking about counting particle states in a box. The number of single-particle states with energy less than E is:

$$\Gamma(E) = \frac{4\pi}{3} \frac{V}{h^3} (2mE)^{3/2}$$

All we need from this formula is the mass dependence in the number of states: $\Gamma \sim m^{3/2}$, so we use the ratio of their masses to find: $\Gamma_p / \Gamma_e = (m_p / m_e)^{3/2}$. These masses are given at the start of the test ... and yields this answer to three sig figs.

7. Answer: $\langle 1/v \rangle = \sqrt{\frac{2m}{\pi kT}}$

We get this answer by using the Maxwellian speed distribution, where the probability density of observing a speed v is:

$$4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} v^2 e^{-\frac{mv^2}{2kT}}$$

We want to take the expectation value of $1/v$ which would be

$$\langle 1/v \rangle = \int_0^\infty 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} v e^{-\frac{mv^2}{2kT}} dv$$

This is not a bad integral ... in fact the integrand is a perfect differential once you change variables to $u = v\sqrt{m/2kT}$. You could do it on your own, though I did give it to you at the start of the test under the heading of "Gaussian integrals". Doing the integral out (as you would on a test correction) gives you the answer.

8. Answer: The $T \rightarrow 0$ limit should be zero according to the third law. Instead, it goes to a constant, k . Also, the $T \rightarrow \infty$ limit of C for a system with a finite number of levels should be zero, but instead it (weirdly) goes to infinity as T^2 . Also, the "heat capacity" is an extensive quantity – and should be proportional to N . (These are three things; you only need to find two. Perhaps you found one that I missed?)