Chem 130A EXAM#1 2/16/05
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Write solutions clearly on separate pages.

1. Answer true or false and provide your reason in 10 words or less.
   a. For any change of state, the sum of w + q is path independent. (5pt)
   TRUE: $w + q = \Delta U$ *and U is a state variable hence path independent*
   b. For any change of state, ΔS is path independent. (5pt)
   TRUE: since S is a state variable ΔS *is path independent*
   c. If heat is exchanged between a system and its surroundings at constant temperature during a reversible process, then ΔS for the universe = 0. (5pt)
   TRUE:
   $\Delta S_{universe} = 0$ *for all reversible processes (by definition of a reversible process)*
   $\Delta S_{universe} = (q_{rev}/T)_{sys} + (-q_{rev}/T)_{surr}$
   $T_{sys} = T_{surr}$
   d. For an irreversible expansion of a gas against a low external pressure (e.g. $P_{ex} < P_{int}$), the magnitude of the irreversible work must be greater than the work done for the same state change on a reversible path: $|w_{irr}| > |w_{rev}|$. (5pt)
   FALSE:

$$w_{irrev} = -\int_{v_i}^{v_f} P_{ext}\,dV = P_{ext}\Delta V \quad \text{(last expression for ideal gas)}$$

$$w_{rev} = -\int_{v_i}^{v_f} P_{\text{int}}\,dV = -nRT\ln\frac{V_f}{V_i} \quad \text{(last expression for ideal gas)}$$

even when not considering ideal gas;
in the reversible case $P_{int}=P_{ext}$ *at all times during the expansion*
and for the expansion to be spontaneous the following must be true:
$P_{int} \geq P_{ext}$
thus
$|w_{rev}| > |w_{irrev}|$

2. The following problem considers state changes of an ideal gas.
   a. A bubble of gas, with initial volume V_i, rises from the bottom of a lake (100m down where the pressure is 10 atm) to the surface (P = 1atm). Relate the final volume, V_f, to V_i assuming the initial and final temperatures are equivalent. (7.5pt)
   $10V_i = nRT$
   $V_f = nRT$
   $\Delta T=0$
   hence
   $V_i / V_f = 1/10$

   b. Write a more general expression relating V_i and V_f that includes the effect of a change in temperature. (full credit for the simplest relation) (7.5pt)
   $10V_i = nRT_i$
   $V_f = nRT_f$

$T_f \neq T_i$
hence
$V_f / V_i = 10T_f/T_i$

c. What is ΔS for the bubble, assuming initial and final temperatures are the same? (7.5pt)

$\Delta S = q_{rev}/T$

$$q_{rev} = -w_{rev} = \int_{v_i}^{v_f} P_{\text{int}} dV = nRT \ln \frac{V_f}{V_i}$$

$\Delta S = nR \ln(10)$

d. Obtain a more general expression for ΔS in terms of different initial and final temperatures, T_i and T_f, respectively. (If you need a parameter such as heat capacity, just incorporate C_p or C_v in your final answer and define it) (7.5pt)

For this break pathway into two pieces:

Step 1: $V_i \rightarrow V_f$ @ $\Delta T = 0$

$\Delta S_1 = nR \ln(V_f/V_i)$

using $PV=nRT$

$\Delta S_1 = nR \ln(10T_f/T_i)$

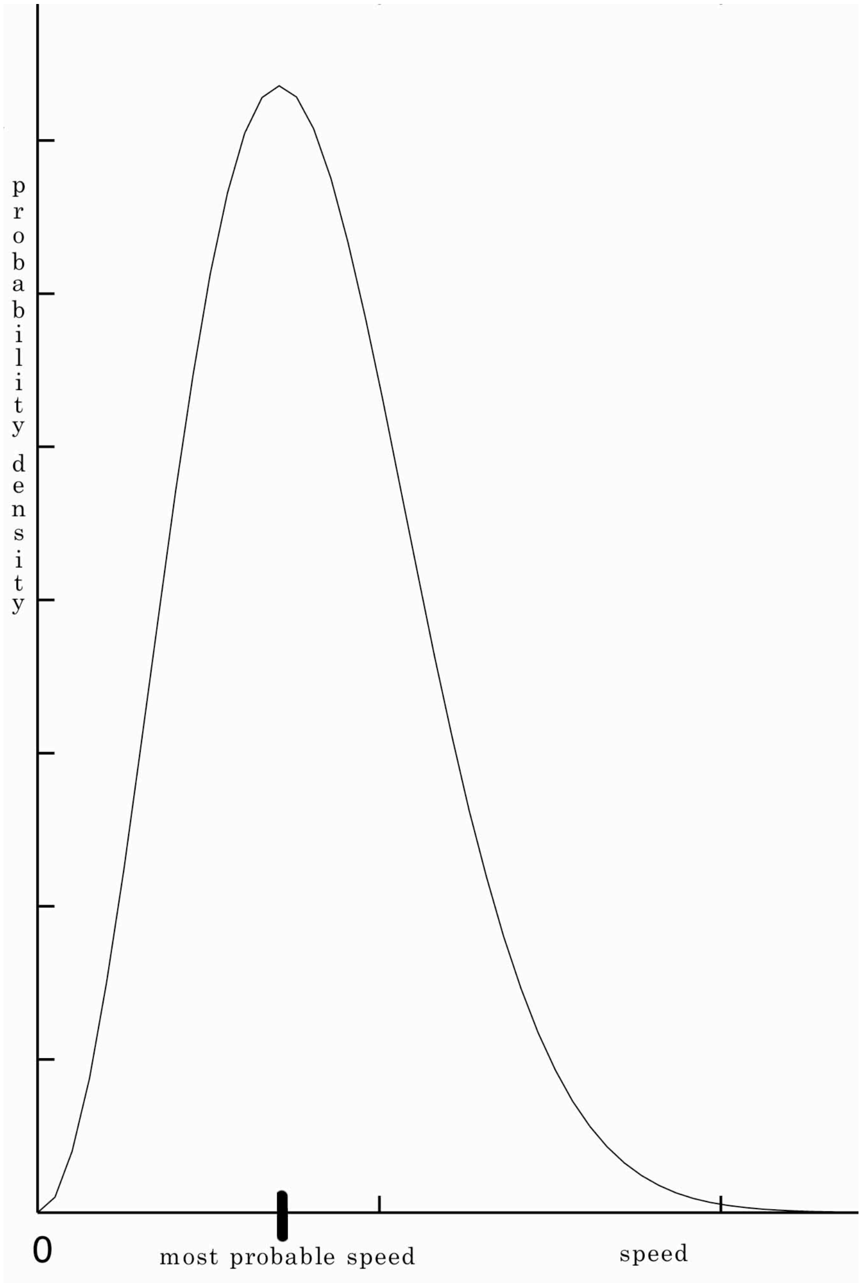
Step 2: $T_i \rightarrow T_f$ @ $\Delta V = 0$

$$\Delta S_2 = \frac{q_{rev}}{T} = \int_{T_i}^{T_f} \frac{C_V}{T} dT = C_v \ln(\frac{T_f}{T_i})$$

Sum of the two steps gives the overall ΔS:

$\Delta S = \Delta S_1 + \Delta S_2 = nR \ln(10T_f/T_i) + C_v \ln(T_f/T_i)$

3. Consider the molecular picture, or kinietic theory, of ideal gases.
    a. Sketch a plot the Maxwell *speed* distribution function taking care to properly label the axes. (Hint: is it probability or probability density?) (7.5pt)

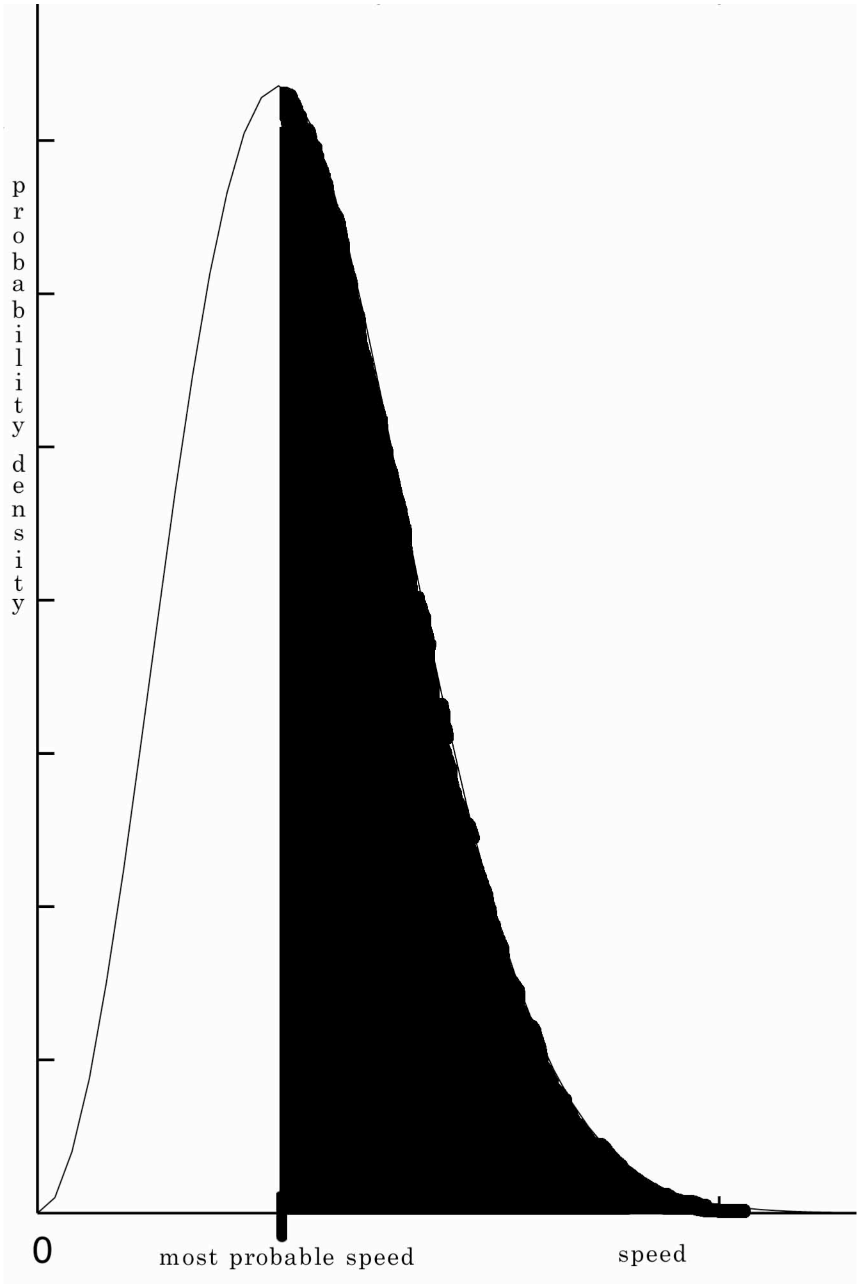


    b. Label the most probable speed on the your plot from part a. (7.5pt)

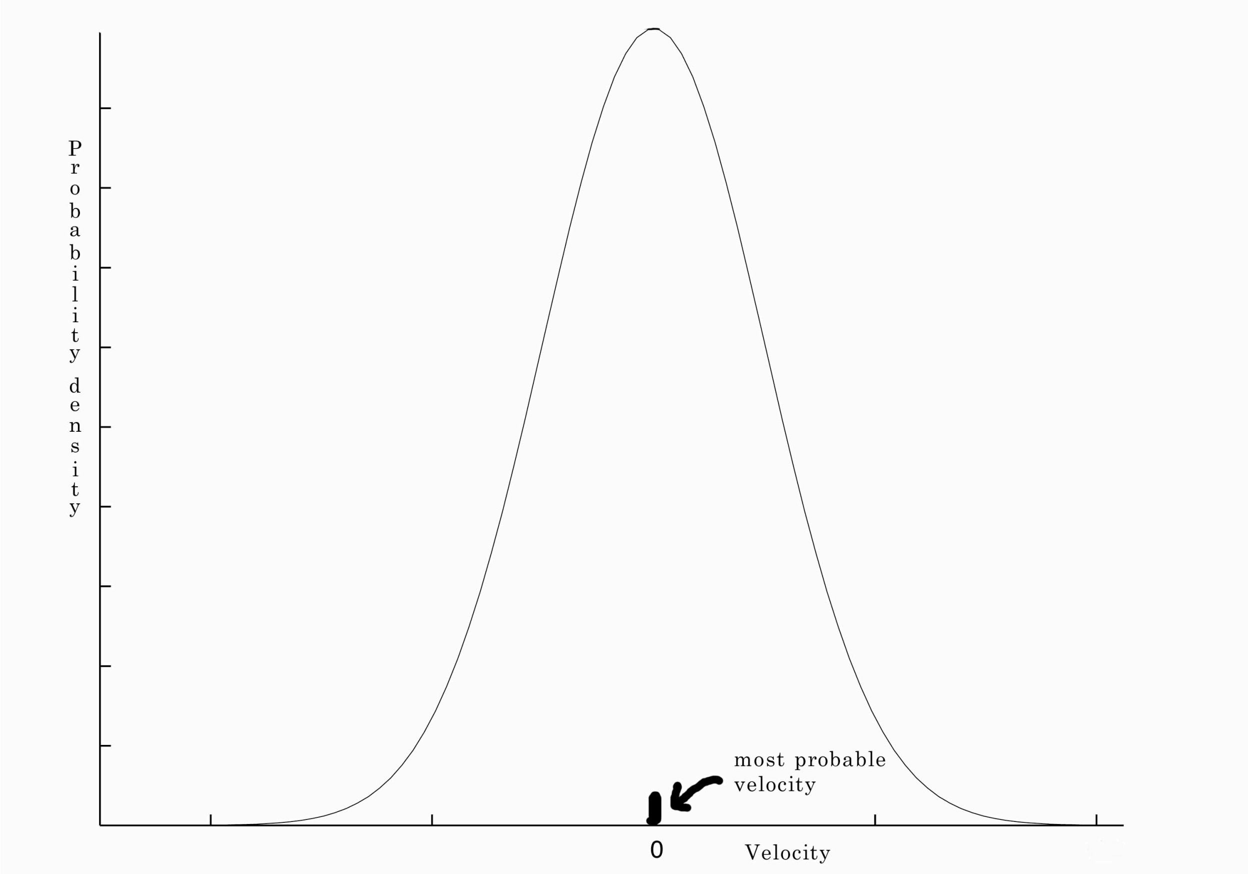
See most probable speed tick mark on X axis (speed axis)

c. Write an expression representing the probability that a molecule chosen at random is going faster than the most probable speed. Sketch this on the plot as well. (Write down any necessary integrals, but don't solve them) (7.5pt)

$$P(c > c_{mp}) = \int_{c_{mp}}^{\infty} f(c)dc = \int_{c_{mp}}^{\infty} 4\pi c^2 \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(-\frac{mc^2}{2kT}\right)dc$$



d. Now consider the Maxwell *velocity* distribution in one dimension and repeat parts a – c for this. Full credit for finding the simplest solution. (7.5pt)



note that this a symmetric function about zero and thus the most probable velocity is at zero ($v_{mp}=0$).

$p(v>v_{mp}) = 1/2$ if you are consider the sign of the velocity

If however you are thinking only about the magnitude (absolute value) of the velocity then $p(|v|>|v_{mp}|)=1$

$$P(v_x > v_{x,mp}) = \int_{v_{x\,mp}}^{\infty} f(v_x)dv_x = \int_{v_{x\,mp}}^{\infty} \left(\frac{m}{2\pi kT}\right)^{1/2} \exp\left(-\frac{mv_x^{\ 2}}{2kT}\right)dv_x$$

4. Chemical hand warmers are popular among back-country skiers and mountaineers. These contain a chemical that reacts with O_2 in the air, releasing heat over a prolonged period of time.
    a. What must be the sign of ΔH for this reaction? (10pt)

It must be negative since heat is being released by the system to the surroundings

    b. If C_p(products) of this reaction were significantly greater than C_p(reactants), would the hand warmer give off more heat to its surroundings at body temperature (37 °C) or at –20 °C? Explain your answer quantitatively, using principles and laws we have discussed. (10pt)

More heat is released at -20°C

$$\begin{tikzcd}
R \arrow[r, "\Delta H_1"] \arrow[d, "(37+20)*C_p(R)"'] & P & @\ T=-20 \\
R \arrow[r, "\Delta H_2"] & P \arrow[u, "(-20-37)*C_p(P)"'] & @\ T=37
\end{tikzcd}$$

$\Delta H_1 = (37+20)*C_p(R) + \Delta H_2 + (-20-37)*C_p(P)$

$\Delta H_1 = (37+20)*[\ C_p(R) - C_p(P)\ ] + \Delta H_2$

Since $C_p(P) > C_p(R)$
$\Delta H_1 < \Delta H_2$

thus more heat is *released by the system* at -20°C than at 37°C