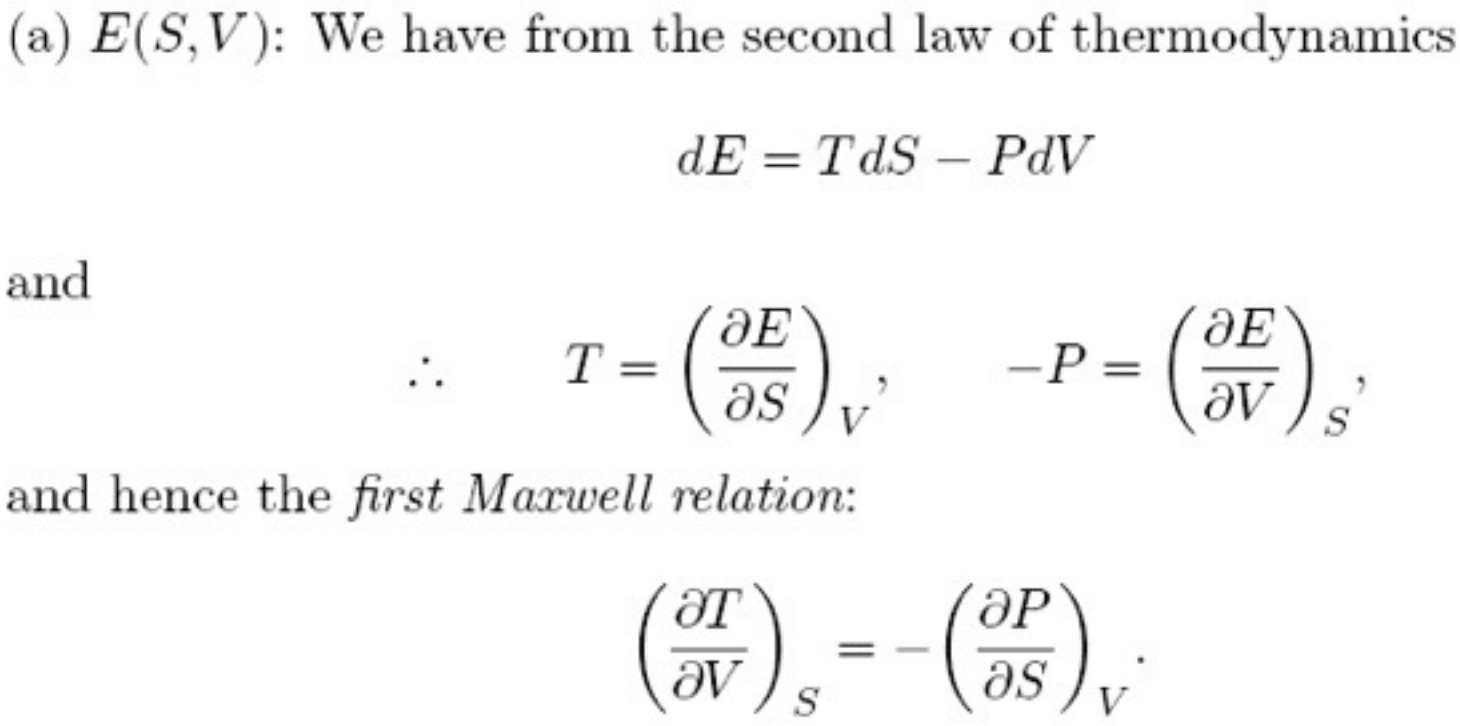
Classical Thermodynamics and Statistics

Thermodynamic Potentials

Internal Energy	$E(S,V)$
Enthalpy or Total Heat	$H(S,P) = E(S,V) + PV$ $(= G(T,P) + TS)$
Free Energy	$F(T,V) = E(S,V) - TS$
Free Enthalpy or Gibbs Function	$G(T,P) = E(S,V) - TS + PV$ $(= F(T,V) + PV)$

Internal Energy



(a) $E(S,V)$: We have from the second law of thermodynamics

$$dE = T\,dS - P\,dV$$

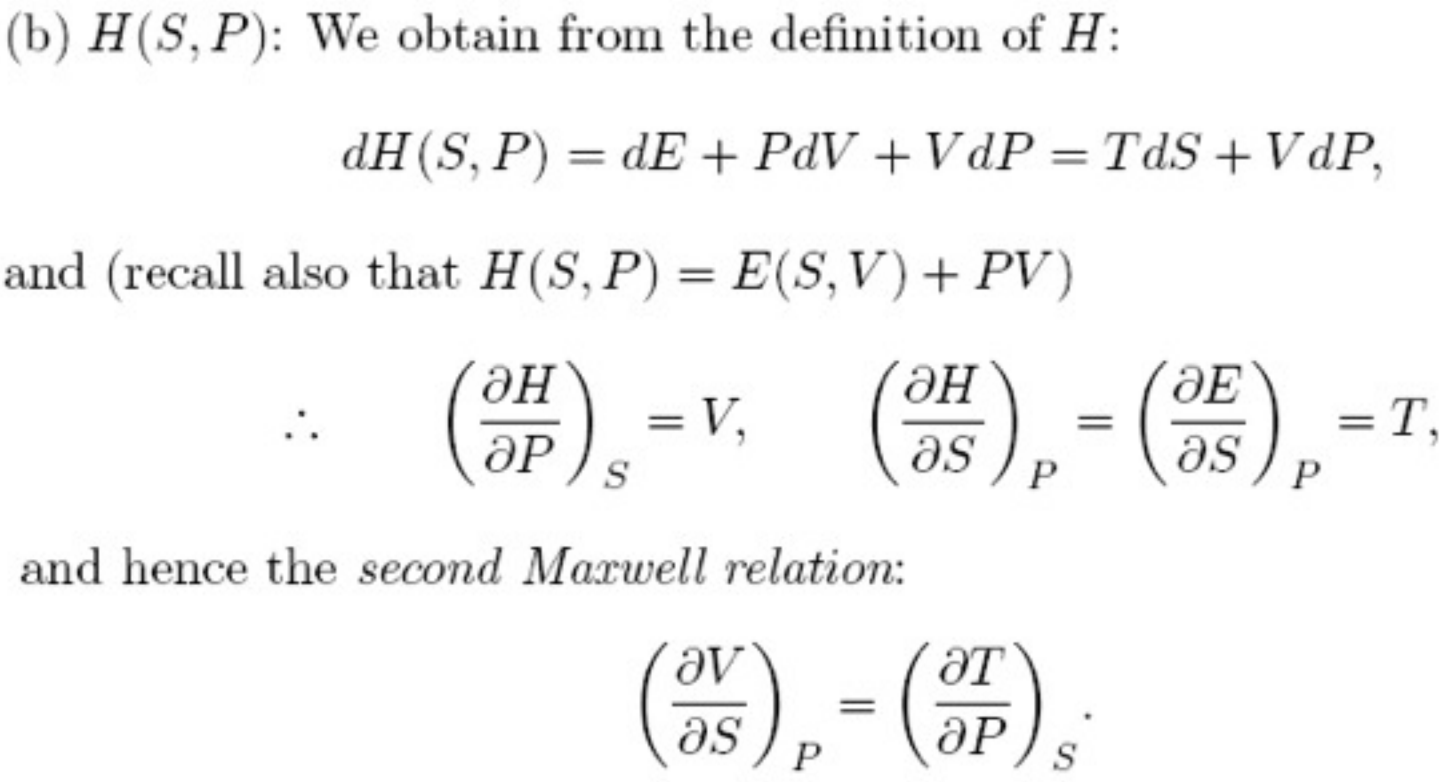
and

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

and hence the *first Maxwell relation:*

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

Enthalpy or Total Heat



(b) $H(S,P)$: We obtain from the definition of H:

$$dH(S,P) = dE + PdV + VdP = TdS + VdP,$$

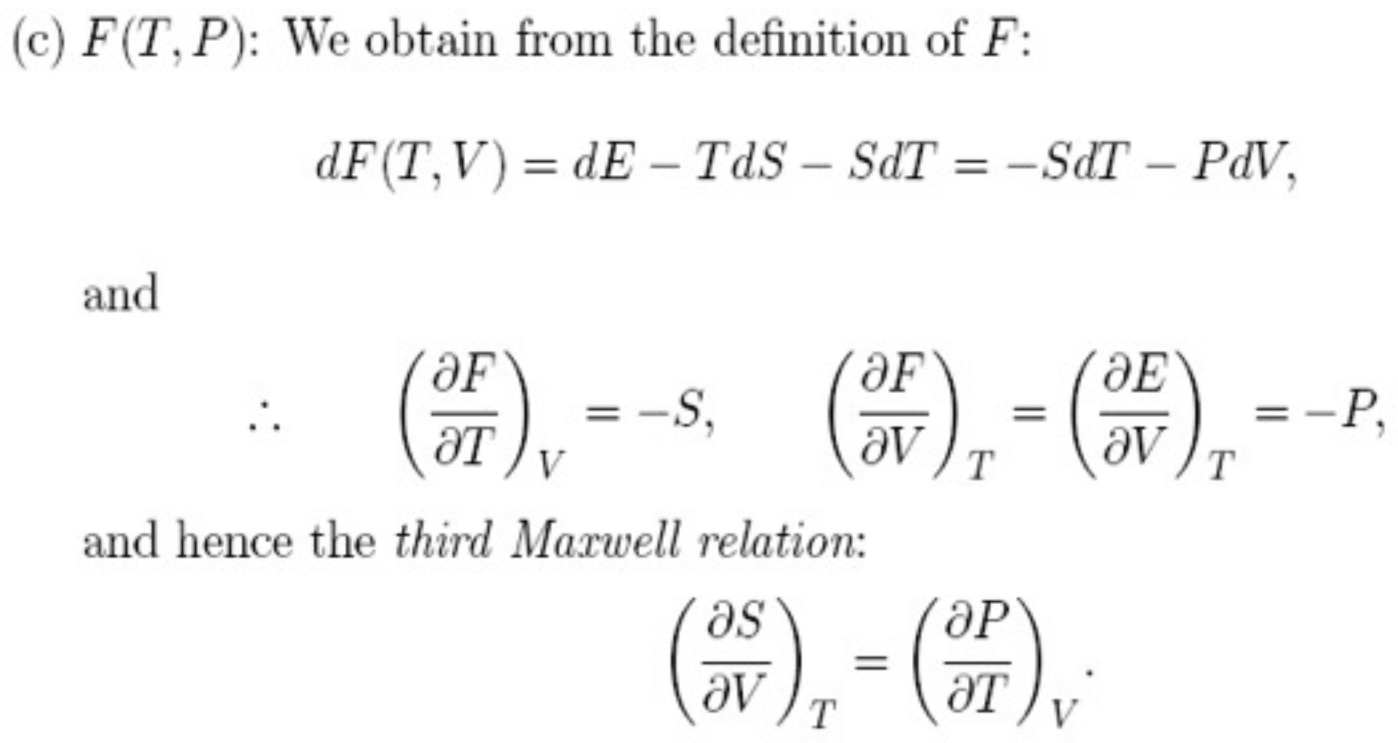
and (recall also that $H(S,P) = E(S,V) + PV$)

$$\therefore \qquad \left(\frac{\partial H}{\partial P}\right)_S = V, \qquad \left(\frac{\partial H}{\partial S}\right)_P = \left(\frac{\partial E}{\partial S}\right)_P = T,$$

and hence the *second Maxwell relation:*

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

Free Energy



(c) $F(T,P)$: We obtain from the definition of F:

$$dF(T,V) = dE - TdS - SdT = -SdT - PdV,$$

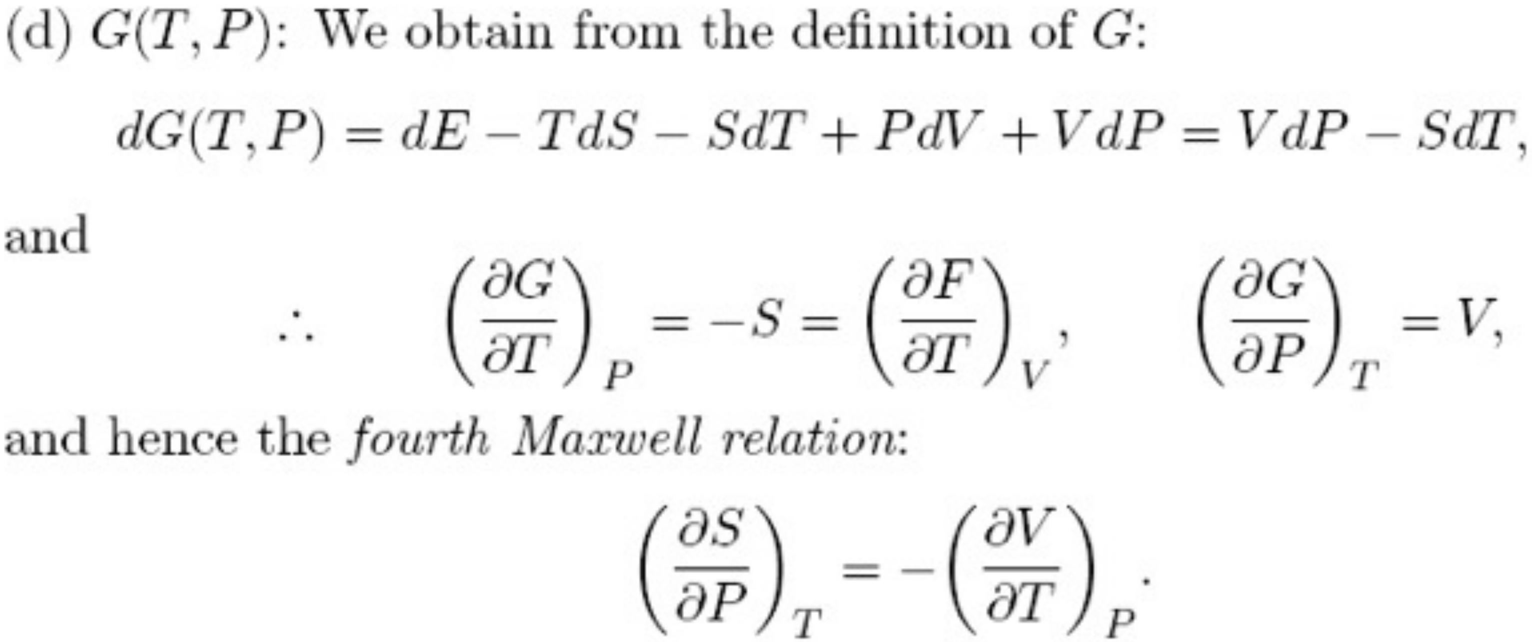
and

$$\therefore \qquad \left(\frac{\partial F}{\partial T}\right)_V = -S, \qquad \left(\frac{\partial F}{\partial V}\right)_T = \left(\frac{\partial E}{\partial V}\right)_T = -P,$$

and hence the *third Maxwell relation*:

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

Free Enthalpy or Gibbs Function



(d) $G(T, P)$: We obtain from the definition of G:

$$dG(T,P) = dE - TdS - SdT + PdV + VdP = VdP - SdT,$$

and

$$\therefore \qquad \left(\frac{\partial G}{\partial T}\right)_P = -S = \left(\frac{\partial F}{\partial T}\right)_V, \qquad \left(\frac{\partial G}{\partial P}\right)_T = V,$$

and hence the *fourth Maxwell relation*:

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

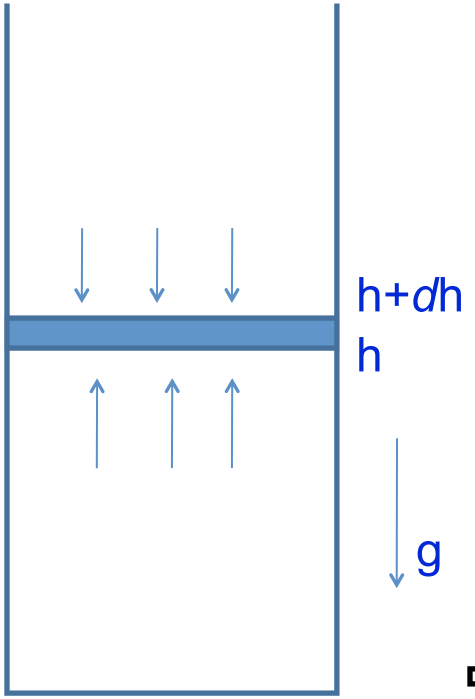
The Boltzmann Law

$$n = n_0 \exp(-E/kT)$$

Maxwell Velocity Distribution

$$f(v)dv = C \exp(-mv^2/2kT)\, dv$$

The exponential atmosphere



$$dP = P_{h+dh} - P_h = -nmg\,dh$$

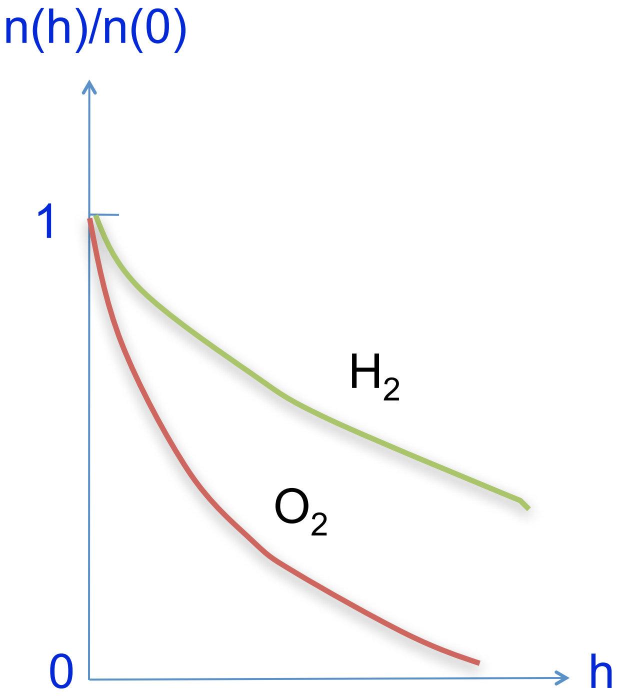
$$P = nkT$$

$$T = \text{Const.}$$

$$\therefore dP = kT\,dn = -nmg\,dh$$

$$dn/n = -mg\,dh/kT$$

$$\Rightarrow \quad n = n_0 \exp(-mgh/kT)$$



The Boltzmann Law

$$N_i = \frac{g_i}{e^{(\epsilon_i - \mu)/kT}} = N\frac{g_i e^{-\epsilon_i/kT}}{Z}$$

1. The elements are considered distinguishable in the way they can rearrange themselves among various energy states with equal probability.
2. The presence of one entity in a particular state is assumed in no way to inhibit or enhance the entrance of another identical entity.
3. Applied to classical gases.

Quantum Statistics

There are two main differences between quantum statistics and classical statistics:

1. In quantum statistics the energy levels are nearly always discrete. In classical statistics they are assumed to be continuous.

2. The counting of the number of arrangements of the elements is different in the two types of statistics. A dominant reason for this is the indistinguishability of the elements in quantum mechanics (resulting directly from the uncertainty relation). This is by far the most important effect.

When counting the number of arrangements of N elements in quantum statistics, we assume:

1.The elements are indistinguishable.

2. For Bose–Einstein statistics, any number of elements in the same state are allowed. For Fermi–Dirac statistics, at most 1 element in each state is allowed.

Bose–Einstein distribution

$$n_i = \frac{g_i}{e^{(\varepsilon_i - \mu)/kT} - 1}$$

$$f_{BE}(E) = \frac{1}{A\exp(E/k_B T) - 1}$$

1. The elements are indistinguishable, not obeying exclusion principle.

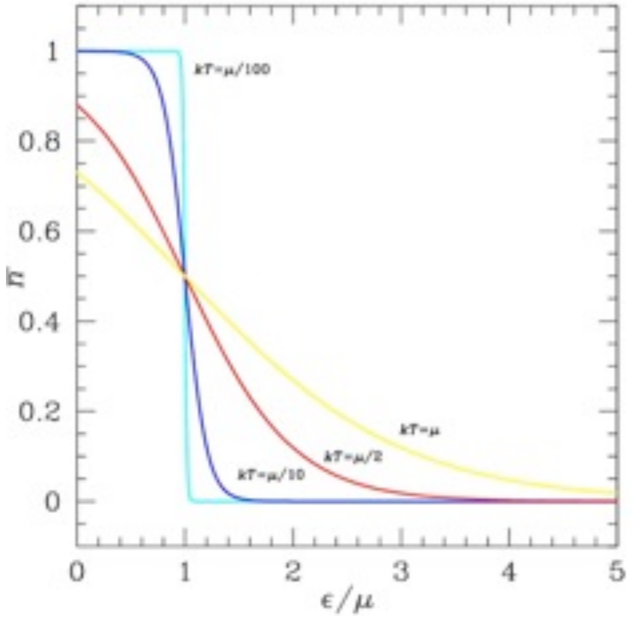
2. Applied to photon and phonon gases.

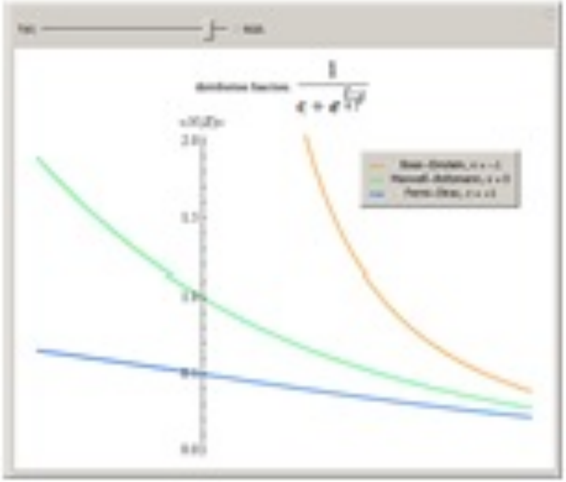
Fermi–Dirac (F–D) distribution

$$\bar{n}_i = \frac{1}{e^{(\epsilon_i - \mu)/kT} + 1}$$

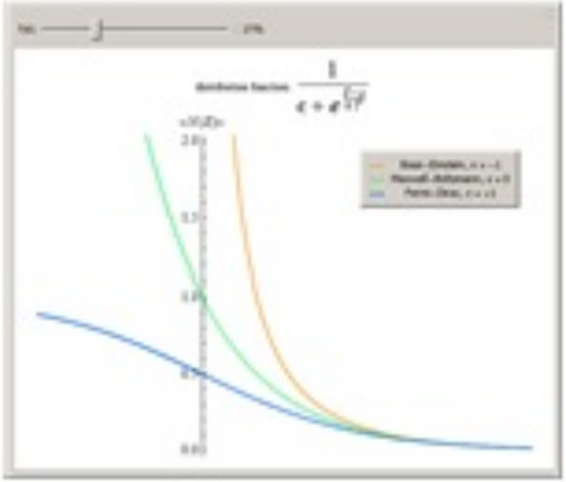
1. The elements are indistinguishable, obeying exclusion principle.

2. Applied to electron gas.

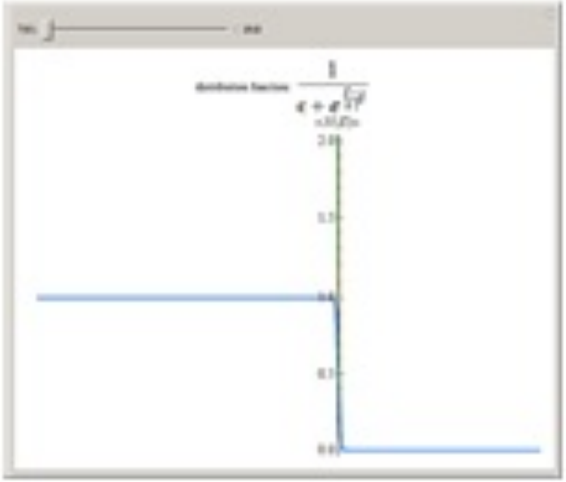




T high



T medium



T low

— B-E

— Boltzmann

— F-D

Homework#9 (Nov. 15, 2010):

(a)Determine the order of magnitude of the fraction of hydrogen atoms in a state with principle quantum number n = 2 to those in state n = 1 in a gas at 300 K.

(b)Take into account the degeneracy of the states corresponding to quantum numbers n = 1 and 2 of atomic hydrogen and determine at what temperature approximately one atom in a hundred is in a state with n = 2.