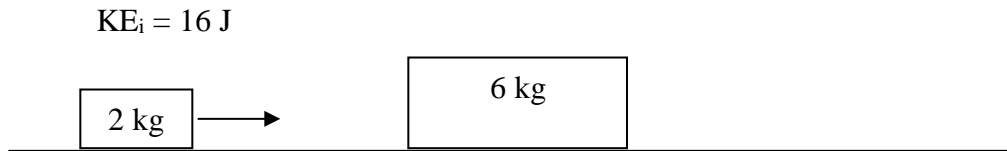


Colliding Blocks and Internal Energy

A 2 kg block having an initial kinetic energy of 16 J collides with a 6 kg block initially at rest.



- a) What is the initial momentum of the moving block?

$$KE = \frac{p^2}{2m} \text{ so } p = \sqrt{2mKE}. v = \frac{p}{m} = \frac{\sqrt{2KE}}{m} = 4 \frac{m}{s}.$$

- b) What is the final momentum of the pair, if they stick together after the collision?

No external force, momentum is conserved. $p_f = 8 \text{ kg} \frac{m}{s}$

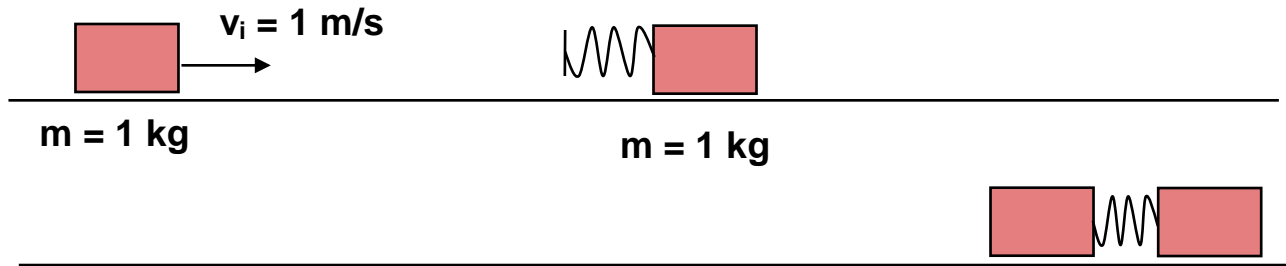
- c) Assuming as in part b that the blocks stick together, what is the kinetic energy of the combined 8 kg block?

It's now a single block of mass 8 kg. So, $KE = \frac{p^2}{2m} = 4J$.

- d) How much of the initial 16 J goes into other sorts of energy, *e.g.*, internal motion (vibrations and heat) of the blocks?

16 – 4J are unaccounted for. 12J must have gone into other sorts of energy.

We will see many times in this course the usefulness of modeling solids as collections of harmonic oscillators. Consider the following situation. We have two equal masses, 1 kg each. One of them is sitting at rest on a frictionless surface; this mass has on it a “sticky” spring. The other mass is traveling at 1 m/s towards the one at rest. When it makes contact with the sticky spring it becomes attached, and then the two masses behave as a(n oscillating) unit.



- a) What is the initial kinetic energy?

$$KE_i = \frac{1}{2}mv_i^2 = 0.5 \text{ J}$$

- b) What is the final center-of-mass kinetic energy after the collision? (Hint: What is the final center-of-mass momentum of the joined system?)

$$p_f = m_f v_f = 2mv_f = p_i = mv_i \rightarrow v_f = \frac{v_i}{2}$$

$$KE_f = \frac{1}{2}m_f v_f^2 = \frac{1}{2}(2m)\left(\frac{v_i}{2}\right)^2 = \frac{mv_i^2}{4} = 0.25 \text{ J}$$

- c) How much energy went into the vibrations about the center of mass? What *fraction* of the initial kinetic energy went into this vibrational energy?

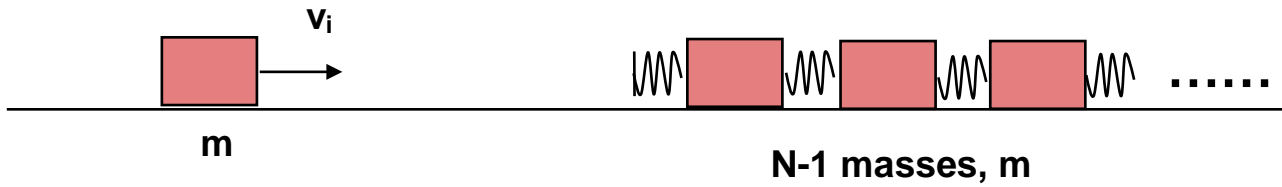
$$W_{on} = \Delta(E) = 0$$

$$E_f - E_i = 0$$

$$KE_f + U_{vib} - KE_i = 0$$

$$U_{vib} = 0.5 \text{ J} - 0.25 \text{ J} = 0.25 \text{ J}$$

Now consider the more general case with N-1 equal masses (all connected by springs). Again, a lone mass with velocity v_i knocks into them:



d) Use conservation of momentum to solve for v_f in this case.

$$p_f = m_f v_f = N m v_F = p_i = m v_i \rightarrow v_f = \frac{v_i}{N}$$

e) How much energy went into vibrational energy in this case?

$$U_{vib} = KE_i - KE_f = \frac{1}{2} m v_i^2 - \frac{1}{2} (N m) \left(\frac{v_i}{N} \right)^2 = \frac{1}{2} m v_i^2 \left(1 - \frac{1}{N} \right)$$

f) What is the *fraction* of energy that becomes vibrational? What is the numerical value when $N = 100$?

$$\frac{U_{vib}}{\frac{1}{2} m v_i^2} = \left(1 - \frac{1}{N} \right)$$

When $N=100$, 99% of the initial energy goes into vibrations.

The collision acts only on one block but the resulting motion involves all the blocks – random internal motion is called “thermal energy.”

Here we use "log" for log base 10, "ln" for log base e ("natural" logarithm).

The main math facts used in this review problem are:

I. $\ln(AB) = \ln(A) + \ln(B)$

II. $\ln(A^B) = B \ln(A)$

III. $\frac{d}{dx} e^u = e^u \frac{du}{dx}$

IV. $\frac{d}{dx} \ln(u) = \frac{1}{u} \frac{du}{dx}$

V. Chain rule: $\frac{d}{dx} f(u) = \frac{df}{du} \frac{du}{dx}$

Definitions:

$$x = e^{\ln(x)}$$

$$x = 10^{\log(x)}$$

a) What is $\log(0.01)$?

$$10^{-2} = 0.01, \log(0.01) = -2$$

b) Let $\ln(x) = 3.2$, and $\ln(y) = -7.2$. What is $\ln(xy)$?

$$e^x e^y = e^{x+y}, \ln(xy) = \ln(x) + \ln(y) = -4.0$$

c) Let $y = e^{306554}$. What is $\ln(y)$?

$$\ln(y) = 306554$$

d) Give an expression for $\frac{d}{dx} e^{35x}$.

$$35e^{35x}$$

e) Give an expression for $\frac{d}{dx} e^{-10x^2}$:

$$-20xe^{-10x^2}$$

f) Give an expression for $\frac{d}{dx} 5 \ln(3x)$.

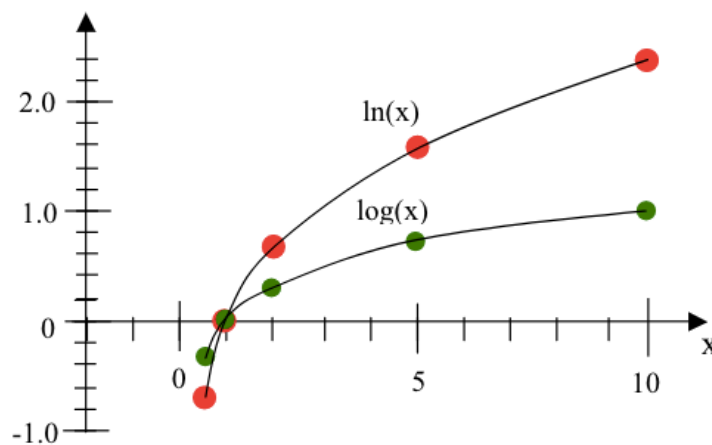
$$\frac{5}{x}$$

g) Plot a few points for $\log(x)$ and $\ln(x)$:

($x = 0.5, 1, 2, 5, 10$)

What about $x = 0$?

log not defined for $x = 0$.



Note $x = 10^{\log(x)}$ and $10 = e^{\ln(10)}$
 so $x = e^{\ln(x)} = e^{\ln(10)\log(x)}$ and
 $\ln(x) = \ln(10) \log(x) = 2.303 \log(x)$
 They are proportional.

h) Later in the course we will also need to know how to calculate:

$d(\ln N!)/dN$ for large enough N that we can treat $N!$ as a continuous function.

Using only the meanings of "ln", "!", and " d/dN ", give a simple expression for $d(\ln N!)/dN$

$$d(N \ln N - N) = \ln N + \frac{N}{N} - 1 = \ln N$$

- a) What is the probability that you get a head (H) on a toss of a fair coin?

For a fair coin, the probability of heads or tails is equal, $P(H) = P(T)$.
Since $P(H) + P(T) = 1$, $P(H) = 1/2$.

- b) What is the average number of heads that would be expected on ten tosses of a fair coin?

The intuitive (and correct) answer is 5.
Mathematically, take ten tosses times the probability of heads per toss: $10 \times 1/2 = 5$.

- c) What is the probability that on those ten tosses you get HHHHHHHHHH?

The probability of heads on any toss is $1/2$. Each toss is independent of the others. For a sequence of independent events, the probability of the sequence is the product of the probabilities of the individual events. Therefore, the probability of getting 10 heads in 10 tosses is $1/2^{10} = 1/1024$.

- d) What is the probability that on those ten tosses you get HTTHTHHTTH?

Just as in part c, we have specified the number of heads and the order in which they appear, so this is just another sequence which also has the probability of $1/2^N$, where $N = 10$.

For the next two questions we no longer care what sequence we have, as long as the total number of heads is specified. This is described by the binomial distribution. The number of ways to have N_H heads in N tosses is:

$$C(N, N_H) = \frac{N!}{N_H!N_T!} = \frac{N!}{N_H!(N-N_H)!}$$

- e) What is the probability that you will get exactly 5 heads with 10 tosses?

$C(N = 10, N_H = 5) = \frac{10!}{5!5!} = 252$ is the total number of ways to get 5 heads. To get the probability we need to divide by the total number of arrangements possible for 10 coins:

$$P(N_H = 5) = C(N = 10, N_H = 5) = \frac{252}{2^{10}} = \frac{252}{1024} = 0.246$$

- f) What is the probability that you will get exactly 3 heads with 10 tosses?

$$P(N = 10, N_H = 3) = \frac{C(10,3)}{2^{10}} = \frac{120}{1024} = 0.117$$

The first law of thermodynamics says that $\Delta U = Q + W_{on}$. Now consider a system of gas molecules.

- a) Suppose we isolate the system so no heat flows in or out. How much work must we do to increase the internal energy of the system by 10 J?

No heat flow means $Q = 0$, therefore $W_{on} = \Delta U - Q = \Delta U = 10 \text{ J}$

- b) Now suppose that we allow for heat flow. If we do 20 J of work on the system, how much heat must be removed to keep the internal energy constant?

Holding the internal energy constant means $\Delta U = 0$, $Q + W_{on} = 0$, $Q = -W_{on} = -20 \text{ J}$
 Q is the heat flowing *in* to the system, therefore we must *remove* 20J of heat.

- c) Suppose that we do no work on the system. How much heat must be added to increase the internal energy by 15 J?

Doing no work means that $W_{on} = 0 \text{ J}$, therefore $Q = \Delta U - W_{on} = \Delta U = 15 \text{ J}$

- d) Suppose that we add 20 J of heat to the system, and in the process, it does 10 J of work. How much did the internal energy change?

Adding 20J of heat and doing 10J of work means that $Q = 20 \text{ J}$, $W_{on} = -10 \text{ J}$.
Thus we find $\Delta U = Q + W_{on} = 20 - 10 \text{ J} = 10 \text{ J}$ the internal energy increases by 10J.

Maximization of entropy means that the most probable condition is the one that always happens. When there are many things averaged together, the most probable thing becomes so much more probable than everything else that this is a *very* good approximation.

Suppose that we have a fair coin.

- a) If we flip the coin once, what is the probability that we find N_h heads?

N_h	Probability
0	$\frac{1}{2}$
1	$\frac{1}{2}$

- b) What about when we flip the coin twice?

Use $P(N_H, N) = \frac{C(N, N_H)}{2^N}$ with $N = 2$ in this case. See Week 1 Problem 4 solutions for detailed reasoning.

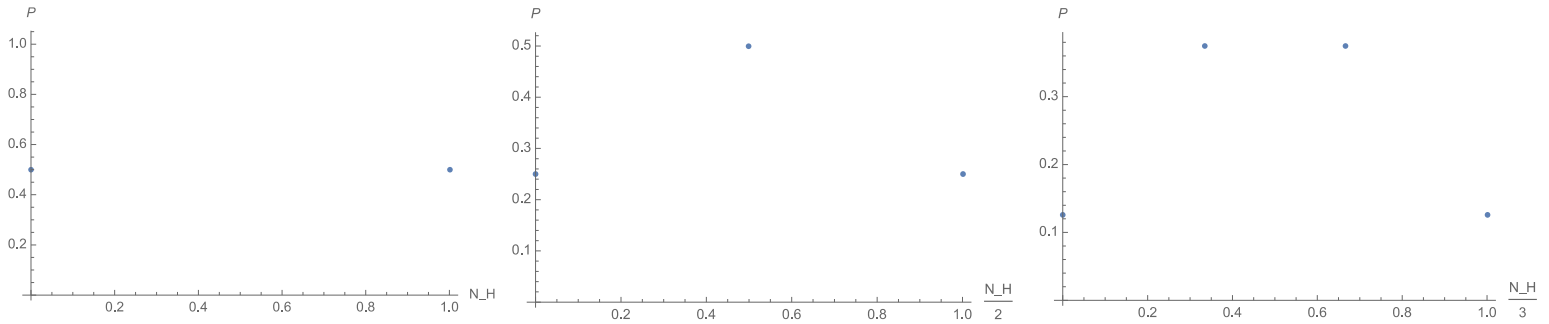
N_h	Probability
0	$C(2,0)/4 = \frac{1}{4}$
1	$C(2,1)/4 = \frac{1}{2}$
2	$C(2,2)/4 = \frac{1}{4}$

- c) And 3 times?

Use $P(N_H, N) = \frac{C(N, N_H)}{2^N}$ with $N = 3$ in this case

N_h	Probability
0	$C(3,0)/8 = \frac{1}{8}$
1	$C(3,1)/8 = \frac{3}{8}$
2	$C(3,2)/8 = \frac{3}{8}$
3	$C(3,3)/8 = \frac{1}{8}$

- d) Now let's suppose that we are interested in the average number of heads N_h that come up when we flip the coin N times: N_h/N . Make a plot of the probability of obtaining N_h/N for $N=1,2,3$



- e) When N becomes very large, what is the most probable value of N_h/N ? What is the chance that we will get a different value from the most probable?

From above you can see as N becomes larger, we get a probability distribution peaked around $\frac{N_h}{N} = \frac{1}{2}$ which gets narrower as N gets bigger.

Hence we see that the most probable value of $\frac{N_h}{N} \rightarrow \frac{1}{2}$ as $N \rightarrow \infty$, and the probability of getting a different value from $\frac{1}{2}$ goes to zero.

The formal mathematical statement is that:

$$\lim_{N \rightarrow \infty} P(N_h, N) = \lim_{N \rightarrow \infty} C(N_h, N)/2^N = \delta\left(\frac{N_h}{N} - \frac{1}{2}\right),$$

where $\delta(x)$ is the Dirac delta function.

Suppose that there are $N = 10^6$ gas molecules distributed in a box with many M states available per particle. That is, $M \gg N$. Assume M is proportional to the volume.

- a) by what factor does the total number of microstates go up if the volume of the box is increased 0.01% (a tiny amount)?

The number of microstates for N (independent) gas molecules with M states available is just $\Omega = M^N$. We know that $M \propto V$, hence

$$\frac{\Omega_f}{\Omega_i} = \left(\frac{V_f}{V_i}\right)^N = \left(\frac{V_i \cdot 1.0001}{V_i}\right)^{10^6} = (1.0001)^{10^6} = 2.674710993 \cdot 10^{43}.$$

- b) By how much does the entropy S increase in that expansion?

$$S_f - S_i = k_B \ln \frac{\Omega_f}{\Omega_i} = 99.995 \cdot k_B = 1.381 \cdot 10^{-21} \frac{\text{J}}{\text{K}}$$

In equilibrium, net entropy, S , is maximized as volume, V , is traded between two chambers A and B with numbers of particles N_A and N_B , both of which are big numbers.

The total S will be the sum of S_A and S_B , $S = S_A + S_B$

Let $S_A = N_A k \ln(V_A n_{AT})$ and $S_B = N_B k \ln(V_B n_{BT}) = N_B k \ln((V - V_A) n_{BT})$. Here “ n_{AT} ” and “ n_{BT} ” don’t depend on the volumes.

a) What’s dS/dV_A when S is maximized?

When S is maximized, $dS = 0$, so $\frac{dS}{dV_A} = 0$.

b) Write dS_A/dV_A as a function of V_A .

$$\frac{dS_A}{dV_A} = \frac{N_A k}{V_A}$$

c) Write dS_B/dV_B as a function of V_B .

$$\frac{dS_B}{dV_B} = \frac{N_B k}{V_B}$$

d) Given $V_B = V - V_A$, write dS_B/dV_A as a function of V_A .

Use: $S_B = N_B \cdot k \cdot \ln[(V - V_A) \cdot n_{BT}]$

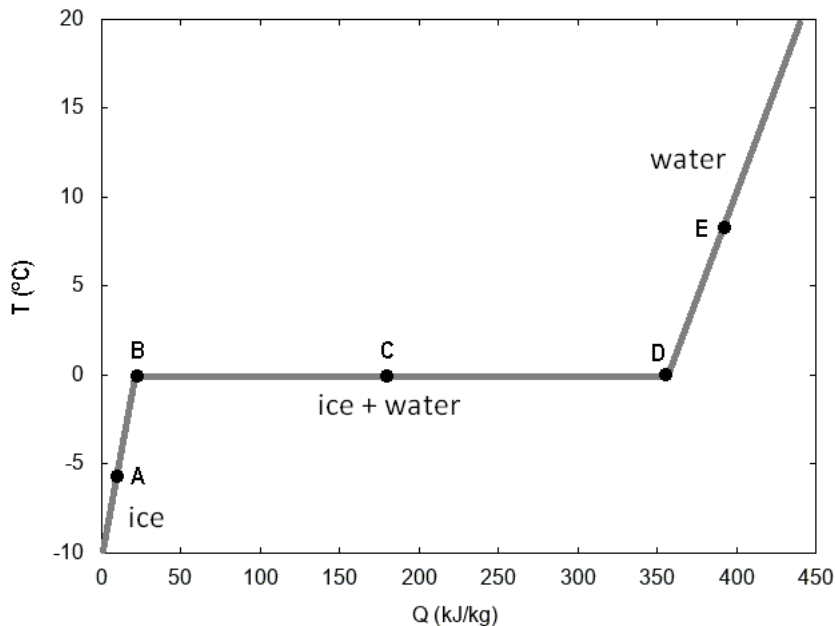
$$\frac{dS_B}{dV_A} = -\frac{N_B k}{V - V_A}$$

e) Find V_A that maximizes S .

$$\frac{dS}{dV_A} = 0 = \frac{d(S_A + S_B)}{dV_A} = \frac{dS_A}{dV_A} + \frac{dS_B}{dV_A} = k \left(\frac{N_A}{V_A} - \frac{N_B}{V - V_A} \right)$$

$$\frac{N_A}{V_A} = \frac{N_B}{V - V_A} \quad \text{so} \quad N_A(V - V_A) = N_B V_A \quad \Rightarrow \quad V_A = V \left(\frac{N_A}{N_A + N_B} \right)$$

The specific heat of liquid water is $\sim 4.2 \text{ kJ/K} \cdot \text{kg}$. The latent heat of fusion is 333.5 kJ/kg .



a) 1 J of heat is added to 1 kg of liquid water initially at $T=0^\circ\text{C}$.

- i. Which point in the Q vs T diagram does this correspond to initially?

D

- ii. How much does the temperature increase?

The graph shows that for the liquid water the temperature rises linearly with the thermal energy Q . So, in this case, the heat capacity $C = \frac{dQ}{dT}$ is temperature independent. The heat capacity is given by the specific heat times the total mass: $C = c \cdot m$

We have : $\Delta T = \Delta Q / C$ and

$$\Delta T = \frac{1 \text{ J}}{\frac{4200 \text{ J}}{\text{K kg}} * 1 \text{ kg}} = 2.38 \cdot 10^{-4} \text{ K}$$

- iii. How much does the entropy of the water increase?

Here we have $dU = dQ$, so $dS = \frac{dQ}{T} = c \cdot m \frac{dT}{T}$ and

$$\Delta S = c \cdot m \int_{T_i}^{T_f} \frac{dT}{T} = c \cdot m \ln \frac{T_f}{T_i} = 3.66 \cdot 10^{-3} \frac{J}{K}$$

where $T_f = T_i + \Delta T = 273.15 \text{ K} + 2.38 \cdot 10^{-4} \text{ K}$

b) 1J of heat is added to 1 kg of 50%/50% mixed ice/liquid water at $T=0^\circ\text{C}$.

- i. Which point in the Q vs T diagram does this correspond to initially?

C

- ii. How much does the temperature go up?

Temperature does not change during a phase transition, $\Delta T = 0$

- iii. How much does the entropy of the mixture increase?

$dS = \frac{dQ}{T} \rightarrow \Delta S = \frac{\Delta Q}{T}$ since, during the phase transition, the temperature is constant.

$$\Delta S = \frac{1J}{273.15 \text{ K}} = 3.66 \cdot 10^{-3} \frac{J}{K}$$

We are going to derive some important and general relationships between *macroscopic* changes in entropy and internal energy in terms of heat capacity and temperature.

- a) Using the first law of thermodynamics, $dU = dQ - pdV$, and the definition of constant volume heat capacity, $C_V = \left(\frac{dQ}{dT}\right)_V$, write down a general expression for ΔU in terms of C_V and T (hint: an integral is involved).

Since the volume is constant, $dV = 0$, we have:

$$C_V = \left(\frac{dQ}{dT}\right)_V = \left(\frac{dU + pdV}{dT}\right)_V = \left(\frac{dU}{dT}\right)_V$$

$$dU = C_V dT \rightarrow \Delta U = \int C_V dT$$

This expression is always valid for a fixed volume process. To solve the integral, we must know how C_V changes with temperature.

- b) Use your solution from part a) and the definition of temperature defined $\frac{1}{T} = \left(\frac{dS}{dU}\right)_V$, write down a general expression for ΔS in terms of C_V and T .

$$dS = \frac{dU}{T} = \frac{C_V dT}{T} \rightarrow \Delta S = \int \frac{C_V dT}{T}$$

This expression is always valid for a fixed volume process.

Now we will use the general relationships to solve a specific problem: One mole of helium gas, with constant volume heat capacity of 12.5 J/K, is in a sealed copper container (constant volume) made of 1 mole of copper, constant volume heat capacity 25 J/K. Initially the helium is at 20°C and the Cu is at 23°C.

- c) After He and Cu equilibrate, what are their temperatures? (hint: conservation of energy)

Conservation of energy dictates that $\Delta U_{He} = -\Delta U_{Cu}$

Further the since the heat capacities given above are constants, i.e. temperature independent, the integral in part (a) is easy to evaluate:

$$\Delta U_{He} = -\Delta U_{Cu} \rightarrow \int C_{V,He} dT = - \int C_{V,Cu} dT \rightarrow C_{V,He}(T_f - T_{i,He}) = -C_{V,Cu}(T_f - T_{i,Cu})$$

Solving for final temperature we get: $T_f = \frac{C_{V,He}T_{i,He} + C_{V,Cu}T_{i,Cu}}{C_{V,He} + C_{V,Cu}} = 295.15 \text{ K}$

- d) How much does the entropy S of the whole system change in this equilibration process?

$$\Delta S = \Delta S_{He} + \Delta S_{Cu}$$

$$\Delta S_{He} = \int_{T_{i,He}}^{T_f} \frac{C_{V,He}}{T} dT = C_{V,He} \ln\left(\frac{T_f}{T_{i,He}}\right) = C_{V,He} \ln\left(\frac{295.15K}{293.15K}\right) = +8.499 \cdot 10^{-2} \frac{J}{K}$$

$$\Delta S_{Cu} = \int_{T_{i,Cu}}^{T_f} \frac{C_{V,Cu}}{T} dT = C_{V,Cu} \ln\left(\frac{T_f}{T_{i,Cu}}\right) = C_{V,Cu} \ln\left(\frac{295.15K}{293.15K}\right) = -8.456 \cdot 10^{-2} \frac{J}{K}$$

$$\Delta S = 4.31 \cdot 10^{-4} \frac{J}{K}$$

- e) By what factor was the initial macrostate (with T's differing by 3°C) less likely than the equilibrium macrostate?

$$\Delta S = k \ln \frac{\Omega_f}{\Omega_i} \quad \frac{\Delta S}{k} = \ln \frac{\Omega_f}{\Omega_i} = 3.126 \cdot 10^{19}$$

$$\frac{P_f}{P_i} \propto \frac{\Omega_f}{\Omega_i} = e^{\frac{\Delta S}{k_B}} = e^{3.12 \cdot 10^{19}}$$

In air, roughly 20% of the molecules are O₂ and 80% are N₂. Each of these types of molecules can, of course, move in three dimensions, and each can have energy due to rotations about two axes.

- a) What fraction of the translation kinetic energy in air resides in the O₂, on the average?

The average kinetic energy of a molecule in an ideal diatomic gas is given by:

$$\langle KE \rangle = \frac{5}{2} kT.$$

Of this, $\frac{3}{2} kT$ is in translational kinetic energy, and $\frac{2}{2} kT$ is in rotational kinetic energy. Since oxygen and nitrogen are both diatomic, the average kinetic energy of an oxygen molecule is the same as the average kinetic energy of a nitrogen molecule. Thus **20%** of the kinetic energy is in the oxygen. The fact that O₂ and N₂ have different masses does not come into play.

- b) If you heat some air in a box from 22°C to 52°C, the molecules will move faster. By what factor will the typical translational molecular speed increase?

We take the rms (root-mean-squared) speed, $v_{\text{rms}} = \sqrt{\langle v^2 \rangle}$ as the typical translational molecular speed. In three dimension there are three DOFs for the translational kinetic energy. By equipartition:

$$\frac{1}{2} m \langle v^2 \rangle = \frac{3}{2} kT, \text{ so } \frac{v_{\text{rms}}(T_1)}{v_{\text{rms}}(T_2)} = \sqrt{\frac{T_1}{T_2}} = \sqrt{\frac{325 \text{ K}}{295 \text{ K}}} = 1.0496.$$

Thus, the typical speed increases by 4.96%.

- c) To what temperature would you have to heat air to get the typical translational speed of the molecules to be twice as fast as it is at room temperature, 22°C?

Since the speed is proportional to the square root of temperature, you need to multiply the temperature by a factor of 4 to double the speed: $T = 4 \times (273.15 + 22) \text{ K} = 1180.6 \text{ K}$

- d) To what temperature would you have to heat the air to double its pressure, assuming constant density?

We start from the ideal gas law: $p \cdot V = N \cdot k \cdot T \Rightarrow p = \frac{N}{V} kT$

The density is just N/V , so at fixed density, $p \sim T$, and to double the pressure we need to double the temperature to $T = 590.3 \text{ K}$.

- e) Consider a gas of pure oxygen with an rms translational molecular speed of 300 m/s. What is the temperature of this gas? The molecular weight of O₂ is 32 (*i.e.*, 32g/mole).

Using equipartition again, $\frac{1}{2} m \langle v^2 \rangle = \frac{3}{2} kT$ we have $T = \frac{m \langle v^2 \rangle}{3k}$

The mass of a single oxygen molecule is $m = 0.032 \text{ kg/mol} \cdot (\text{mol}/6.022 \times 10^{23} \text{ molecules}) = 5.31 \times 10^{-26} \text{ kg}$. Hence the temperature is $T = 5.31 \times 10^{-26} \text{ kg} \times (300 \text{ m/s})^2 / (3k) = 115 \text{ K}$

Consider oxygen gas O_2 which we will treat as a diatomic ideal gas with three translational and two rotational degrees of freedom initially at pressure 1 atm, temperature 22°C , and occupying a volume of 1m^3 . Suppose the gas can push on a piston.

We hold the temperature of the gas fixed and allow it to expand to a volume of 2m^3 pushing against the piston. This is known as isothermal expansion.

- a) How much work is done by the gas on the piston?

We start with $W_{by} = \int p dV$ to calculate the work, and use the ideal gas law, $p = NkT/V$ to write the pressure in terms of volume. Since N (number of molecules) and T (temperature) are fixed, they can be moved outside the integral, yielding:

$$W_{by} = NkT \int \frac{1}{V} dV = NkT \ln \frac{V_f}{V_i} = NkT \ln(2)$$

Using the ideal gas law again, we obtain NkT from the initial conditions given above:
 $NkT = p_i V_i = 1.01 \times 10^5 \text{ Pa} \times 1\text{m}^3 = 1.01 \times 10^5 \text{ J}$, so $W_{by} = 7.02 \times 10^4 \text{ J}$.

- b) How much does the internal energy of the gas change?

For equipartition $U \propto T$, so if T is fixed, U doesn't change.

- c) How much heat must flow into the system in order to keep the temperature fixed?

Using the first law, $\Delta U = Q_{in} + W_{on} = Q_{in} - W_{by}$, together with $\Delta U = 0$, we have:
 $Q_{in} = W_{by} = 7 \times 10^4 \text{ J}$.

Now we hold the volume fixed and the temperature of the gas is raised to 30°C . This is known as isochoric heating.

- d) How much work is done by the gas on the environment in this process?

We have $W_{by} = \int p dV$, and since the volume doesn't change, $W_{by} = 0 \text{ J}$.

- e) How much does the internal energy of the gas change?

For a gas with five degrees of freedom, $U = \left(\frac{5}{2}\right) NkT$, so $\Delta U = \left(\frac{5}{2}\right) Nk\Delta T$

We determine Nk from the initial conditions using the ideal gas law: $Nk = \frac{p_i V_i}{T_i}$

$$\Delta U = \frac{5}{2} \frac{p_i V_i}{T_i} (T_f - T_i) = \frac{5}{2} \left(\frac{1.01 \times 10^5 \text{ J}}{295.14 \text{ K}} \right) (8\text{K}) = 6.87 \times 10^3 \text{ J}.$$

- f) How much heat must flow into the system for this process?

Using the first law $\Delta U = Q_{in} - W_{by} = Q_{in}$, so $Q_{in} = \Delta U = 6.87 \times 10^3 \text{ J}$

- a) Calculate the “molar specific heat”, i.e., the heat capacity per *mole* of copper metal assuming equipartition of thermal energy for **three kinetic energy degrees of freedom** and **three potential energy degrees of freedom** for each atom.

$$U = \frac{6}{2} NkT = \frac{6}{2} nRT \text{ by equipartition. The heat capacity is then } C_V = \frac{\partial U}{\partial T} = 3nR.$$

$$\text{The molar specific heat is then: } c_{V,mol} = \frac{C_V}{n} = 3R = 25 \frac{\text{J}}{\text{K}\cdot\text{mol}}$$

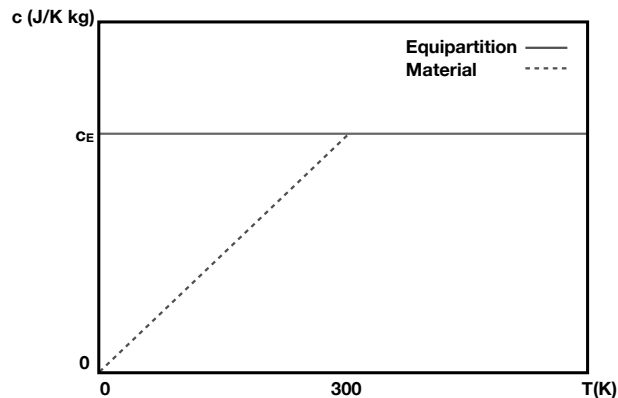
- b) Convert your answer to the mass specific heat, i.e. the heat capacity per kg. The atomic weight of copper is 63.5 g/mol. (Compare your answer to the measured value of 386 J/ K·kg at room temperature.)

The mass specific heat predicted by equipartition, $c_{V,m} = 3R \frac{1 \text{ mol}}{0.0635 \text{ kg}} = 393 \frac{\text{J}}{\text{K}\cdot\text{kg}}$, is quite close to the measured value.

At low enough temperatures, all materials have *lower* specific heats than predicted by equipartition. Suppose that some material has a non-equipartition molar specific heat

$$c(T) = \begin{cases} c_E \frac{T}{300K} & T \leq 300K \\ c_E & T > 300K \end{cases}$$

where c_E is the equipartition molar specific heat calculated in part b).



- c) Calculate the change in internal energy $U(300K) - U(0K)$ using $c(T)$ above and compare to the change $U_E(300K) - U_E(0K)$ using the equipartition specific heat from b).

In general $\frac{\partial U}{\partial T} = C_V \rightarrow \Delta U = \int C_V dT$. For the temperature dependent $c(T)$, the integral gives $U(300K) - U(0K)$

$$= \int_{0K}^{300K} c(T) n dT = \int_{0K}^{300K} c_E n \frac{T}{300K} dT = c_E n \cdot \frac{1}{2} T^2 \Big|_{0K}^{300K} = c_E n \cdot 150 \text{ K}.$$

For the temperature independent case (as predicted by equipartition), the integral gives

$$U_E(300K) - U_E(0K) = \int_{0K}^{300K} c_E n dT = c_E n \cdot 300 \text{ K}.$$

Hence equipartition predicts a change that is larger by a factor of 2.

- d) For that same material with specific heat $c(T)$, what is S at 300K?

For a quasi-static process $dS = dQ/T$, using the first law at fixed volume (the solid doesn't expand much under heating) $dS = dU/T = C_V dT/T$.

$$S(300K) - S(0K) = \int_{0K}^{300K} c(T)n \frac{dT}{T} = \frac{c_E n}{300K} \int_{0K}^{300K} dT = c_E n$$

- e) What are thermal U and S at 400K for the material with specific heat $c(T)$?

Using the integrals from above:

$$U(400K) - U(0K) = U(400K) - U(300K) + U(300K) - U(0K) = \int_{300K}^{400K} c(T)n dT + c_E n \cdot 150K = c_E n \cdot 150K + \int_{300K}^{400K} c_E n dT = c_E n \cdot 250K$$

$$S(400K) - S(0K) = S(400K) - S(300K) + S(300K) - S(0K) = c_E n + \int_{300K}^{400K} \frac{c(T)n dT}{T} = c_E n + c_E n \int_{300K}^{400K} dT/T = c_E n \left(1 + \ln \frac{4}{3} \right) = 1.29 c_E n.$$

0.1m^3 of an ideal gas of CO_2 at $T=295\text{K}$ and $p=10^6\text{ Pa}$ is in a container that springs a leak, allowing very rapid expansion into a previously empty space, ending up with 1m^3 volume. This process is too fast for heat to leak in or out of the gas.

- a) How much work does the gas do in the expansion?

No work is done in free expansion.

- b) How much does the internal energy U change?

There is no heat flowing into the system since it is thermally isolated, so according to the first law, we have: $\Delta U = Q + W_{on} = 0$

- c) What is the final temperature?

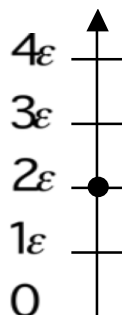
The temperature doesn't change since equipartition says that U is proportional to T .

- d) How much work would it take to slowly squash the gas back down to 0.1 m^3 , keeping the temperature fixed?

$$\begin{aligned} W_{on} &= - \int_{1\text{m}^3}^{0.1\text{m}^3} p \, dV = -NkT \int_{1\text{m}^3}^{0.1\text{m}^3} \frac{1}{V} \, dV = NkT \cdot \ln 10 = p_i V_i \cdot \ln 10 \\ &= 2.30 \times 10^5 \text{J}. \end{aligned}$$

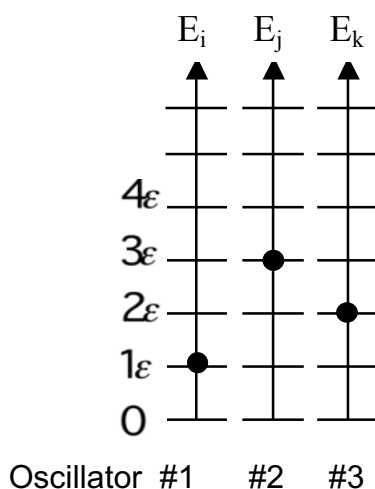
Thermodynamic processes almost always involve the exchange of energy between subsystems. To begin our study of energy exchange, we consider the simplest possible system: a **harmonic oscillator** such as a vibrating diatomic molecule. The molecule can absorb or emit only an integral number of energy packets. We write the energy levels of an oscillator as a ladder of equally spaced energy levels, where epsilon (ϵ) is the quantum of energy:

$$\text{Energy} = n\epsilon$$



Convention:
 E = single-particle energy
 U = energy of a many-particle system

The oscillator shown has an energy of 2ϵ ; that is, it possesses two quanta (or packets) of energy. Now imagine three such oscillators which are able to exchange energy. One possible **microstate** of the 3-particle system is the following:



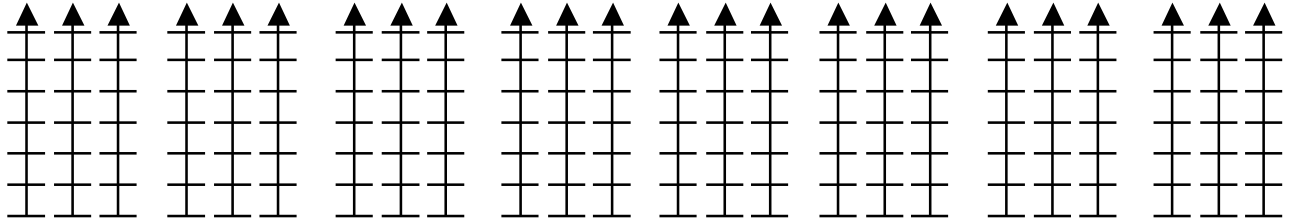
- a) What is the total energy U of the situation depicted above, in terms of ϵ ? $U = \underline{\hspace{2cm}}$. In general we will write $U = q\epsilon$, where q is the total number of energy quanta in the system.

- b) Determine the number of microstates for the three-oscillator system with a total energy of $U = 6\epsilon$.

[Hint: Start with $E_i = 0$ and count the # of ways you could arrange 6ϵ in oscillators 2 and 3.

Next set $E_i = \epsilon$ and count the # of ways you could arrange 5ϵ in oscillators 2 and 3.

Continue, and add up all the possibilities. Ω = total # microstates. Here is some workspace:



- c) Now fill out the table below by counting the number of microstates Ω_q for the three-oscillator system for the total energies shown. To save time, notice how the 6ϵ answer is changed when you go to 5ϵ , etc. Check your answer with the formula given below, a derivation of which will be given in the posted solutions.

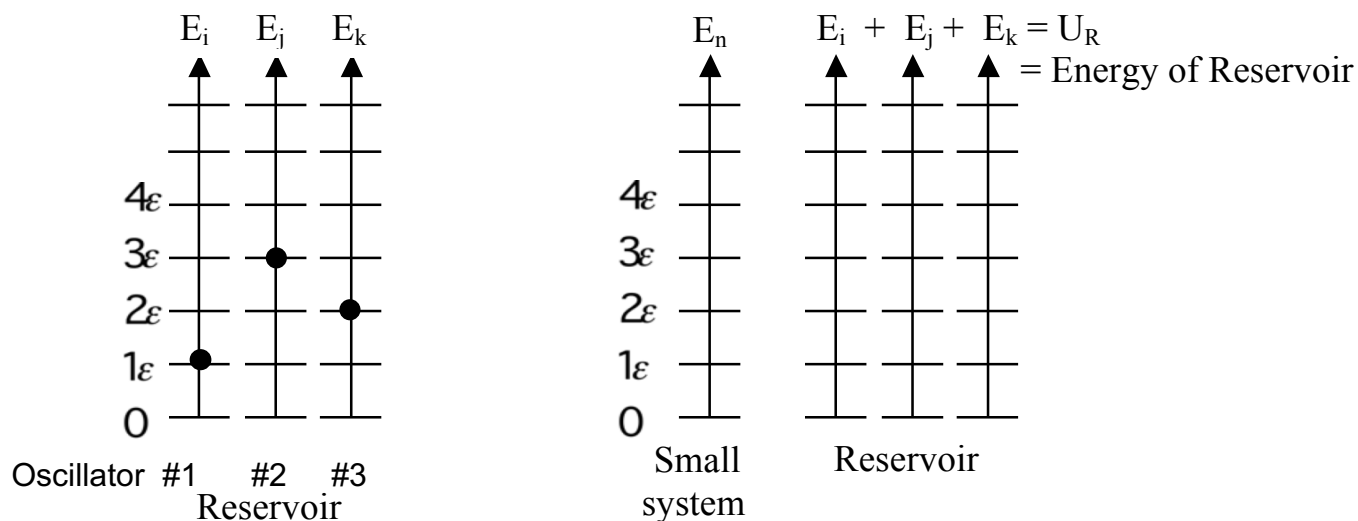
$U=q\epsilon$	Ω_q
0	
1ϵ	
2ϵ	
3ϵ	
4ϵ	
5ϵ	
6ϵ	

$$\Omega_q = \frac{(q + N - 1)!}{(N - 1)!q!}$$

q = # quanta

N = # oscillators

Let us now consider the 3-oscillator system with $U = 6\epsilon$ as a “thermal reservoir”. We ask how this system will share its energy with another “**small system**”. This problem mimics many problems in real life, as we shall soon see. Our thermal reservoir is shown on the left, in a particular microstate:



Now we bring a single oscillator (the small system) into thermal contact with the reservoir (see the figure on the right).

The small system initially has no energy, therefore $E_n + U_R = 6\epsilon$. We wish to know the probability P_n that the **small system** is in **one particular state n**, which has energy $E_n = n\epsilon$.

$\Omega(n) = \Omega_R(n)$ where Ω_R stands for the number of states of the reservoir (3-oscillators).

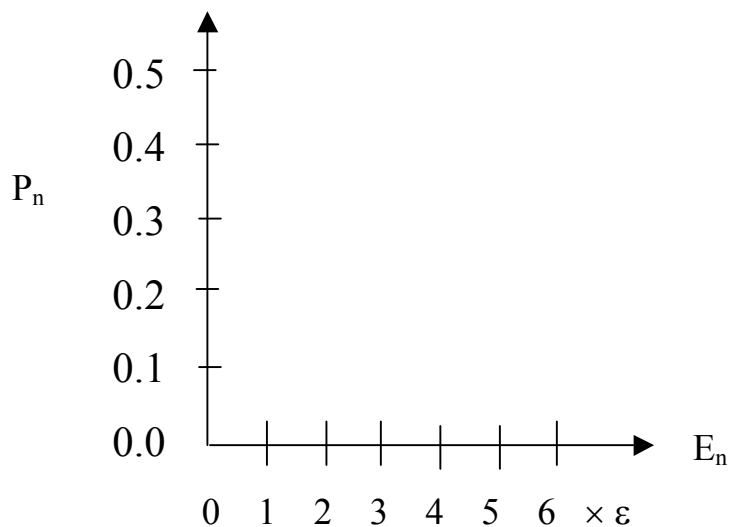
$P_n = \Omega_R(n)/\Omega_{\text{tot}}$, where Ω_{tot} is the total number of microstates for all possible E_n .

That's what we are going to calculate.

- a) Fill out the table below. You have already determined the Ω_R 's in the previous problem. Remember, $E_n + U_R = 6\varepsilon$. (Check your numbers with the sums given.)

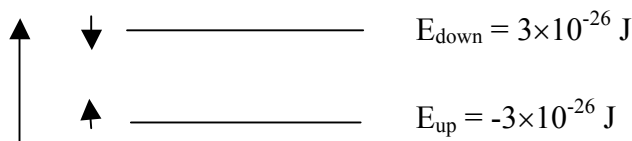
E_n	U_R	Ω_R	P_n
0			
ε			
2ε			
3ε			
4ε			
5ε			
6ε			
		$\Omega_{\text{tot}} = \Sigma \Omega_R = 84$	$\Sigma P_n = 1$

- b) Plot your result on the graph below.



- c) Compute the average energy of the oscillator using the formula, $\langle E \rangle = \Sigma P_n E_n$, and mark the average energy with a vertical line. Does the answer agree with what you know it has to be for 4 oscillators sharing 6ε ?

Magnetic Resonance Imaging (MRI) detects the spins of protons (hydrogen nuclei) in organic matter and water. A proton in a magnetic field of 2 Tesla has two spin states with energies $E = \pm 3 \times 10^{-26}$ J.



- a) At body temperature (310 K), what fraction of the spins are in the low-energy (up) state? The definition of the ‘fraction of up-spins’ f is given below. [Hint: You can calculate the ratio $r = N_{\text{up}}/N_{\text{down}}$ using the Boltzmann factor, and f can be written as a function of r .]

$$f = N_{\text{up}} / (N_{\text{up}} + N_{\text{down}})$$

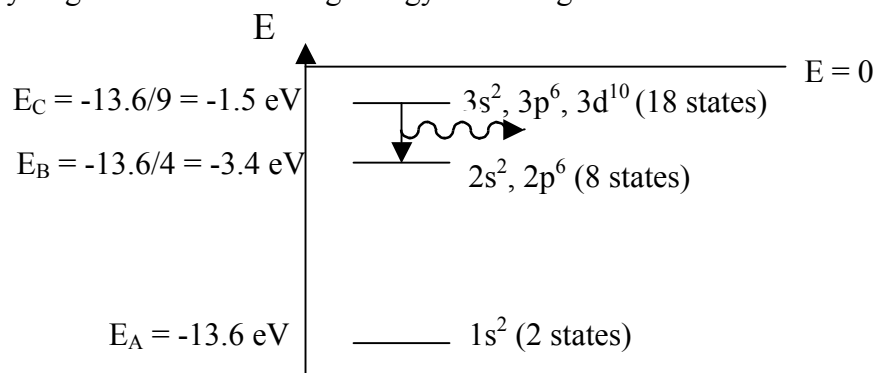
- b) At what temperature are 3/4 of the spins up?

- c) Calculate the entropy of this two state system in the two limits $T \rightarrow 0$ and $T \rightarrow \infty$.

- d) The MRI signal is proportional to $N_{\text{up}} - N_{\text{down}}$, which is relatively small at $T = 300$ K but increases significantly as the temperature is lowered. Is it practical to improve the signal of a medical MRI device by cooling the sample to line up more of the spins?
Yes__ No__

It's often useful to remotely sense the temperature of objects. Fortunately the Boltzmann distribution of the occupancy of atomic states manifests itself in the spectrum of light emitted from hot objects, so the light can be used as a thermometer.

Atomic hydrogen has the following energy-level diagram:

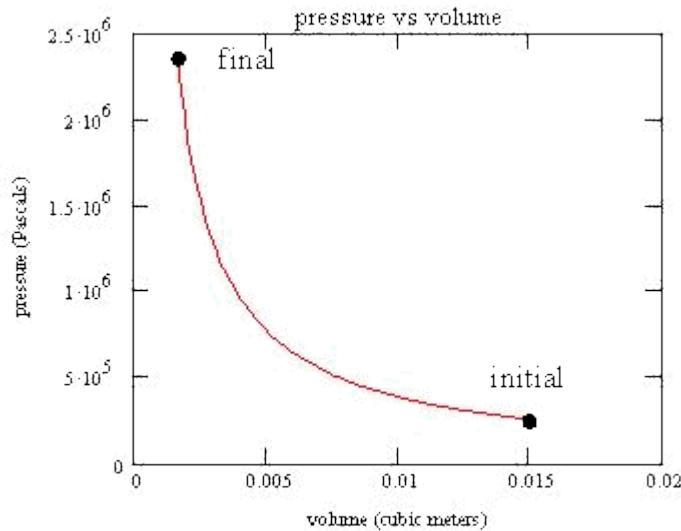


The atom emits light when it falls from a higher-energy state to a lower one. The frequency of light depends on the energy of the photons, the same as the difference between the energies of the states. For example, in the transition indicated above, a photon of wavelength 653 nm will be emitted. So the colors of light emitted by atoms falling from states with E_C are different from the light from atoms falling from E_B . The ratio of the amounts of the different colors of light then depends on how many atoms are in different excited states. (The ground state can't emit anything.)

- a) Calculate the ratio of the number of atoms with $E = E_C$ to the number with $E = E_B$ for $T = 2000 \text{ K}$. Don't forget to take into account that different numbers of states have E_C and E_B . You should see that most of the atoms are in their ground state.

- b) What is that same ratio at $T=2020 \text{ K}$ (1% higher)?

- a) One and one-half moles of a diatomic gas at temperature 35°C are compressed quasistatically isothermally from a volume of 0.015 m³ to a volume of 0.0015 m³. Sketch the process on a p-V diagram and show what corresponds to the work done **on** the gas. Calculate the work done **on** the gas. (Note: ignore vibrational energy of the molecules.)



The figure above shows the path along which the gas is compressed from the initial state to the final state. The path is an isotherm, meaning T is constant, and the $1/V$ shape of the path follows from the ideal gas law:

$$p = \frac{nRT}{V}$$

The differential of the work done by the gas is $dW_{by} = p dV$, and the work done is given by the area underneath the curve. Substituting for p , we obtain:

$$W_{on} = -W_{by} = -\int_{V_i}^{V_f} p dV = -nRT \int_{V_i}^{V_f} \frac{1}{V} dV = nRT \ln \frac{V_i}{V_f} = 8844 \text{ J}$$

Note that the work done **on** the gas is positive, and the work done **by** the gas is negative. Also note that the above expression for the work done by (or on) the gas, i.e. $W_{by} = nRT \ln(V_f/V_i)$ is specific to an isothermal ($T=\text{const}$) process.

- b) How much heat flowed into the gas during the compression?

Use the First Law and the fact that $U = U(T)$, for ideal gases, i.e. that the internal energy depends only on the temperature of the gas. Hence, for an isothermal process, $U = \text{const.}$ or $\Delta U = 0$:

$$\Delta U = Q_{\text{in}} + W_{\text{on}} = Q_{\text{in}} - W_{\text{by}}$$

$$Q_{\text{in}} = -W_{\text{on}} = -8844 \text{ J}$$

- c) What is the final pressure of the gas?

$$p_f V_f = p_i V_i = nRT$$

so

$$p_f = \frac{nRT}{V_f} = 10 \times \frac{nRT}{V_i} = 2.56 \times 10^6 \text{ Pa}$$

$$\text{And } p_i = \frac{nRT}{V_i} = 2.56 \times 10^5 \text{ Pa.}$$

So, the pressure has increased by a factor of ten while the volume has decreased by a factor of ten. The product pressure times volume is constant, since T is constant.

- d) What was the entropy change of the gas?

There are two ways for finding the entropy change:

i) Since an isothermal (quasistatic) process is reversible, we can use the relation between entropy and heat, $dS = \frac{\delta Q_{\text{in}}}{T}$. Since T is constant, we have:

$$\Delta S = \frac{Q_{\text{in}}}{T} = -28.7 \frac{\text{J}}{\text{K}}$$

ii) Determine the change in the number of states:

The gas was held at fixed temperature, so there was no change to the range of accessible / typical velocities of the gas particles – i.e. no change to the number of velocity states per particle. However, the gas was compressed. This reduction in the volume of the gas leads to a proportional reduction in the number of places in space that the gas particles can be. Thus, the number of available states per particle is reduced by a factor (V_f/V_i) , and the total number of states for N particles is reduced by a factor $(V_f/V_i)^N$.

The change in entropy of the gas is given by:

$$\Delta S = k[\ln(\Omega_f) - \ln(\Omega_i)] = k \ln(\Omega_f/\Omega_i) = k \ln\left((V_f/V_i)^N\right) = Nk \ln(V_f/V_i)$$

$$\Delta S = nR \ln(V_f/V_i) = (1.5 \text{ mol}) \left(8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}}\right) \ln(0.1) = -28.7 \text{ J/K}$$

- e) What was the entropy change of the total system (gas *plus* the thermal surroundings)?

This process is reversible, so by the Second Law, the change in entropy of the total system must be zero:

$$\Delta S = \Delta S_{env} + \Delta S_{gas} = 0.$$

Suppose that 5 m^3 of argon, an ideal monatomic gas initially at $p = 10^5 \text{ Pa}$ and $T = 300 \text{ K}$ is adiabatically compressed 1%, to 4.95 m^3 . During this process p obviously goes up, but not very much.

- a) What is the constant-volume heat capacity of this gas, in J/K?

For an ideal gas, the constant-volume heat capacity is given by: $C_V = \alpha nR$

Using the ideal gas law, we can find n from the initial conditions given above: $n = \frac{p_i V_i}{RT_i}$

Hence,

$$C_V = \alpha \left(\frac{p_i V_i}{RT_i} \right) R = \frac{\alpha p V}{T} = 2500 \text{ J/K}$$

- b) Calculate the work done on the gas. The pressure only changes a small amount, so you can assume that it's constant.

$$W_{\text{on}} \approx -p \Delta V = 5000 \text{ J}$$

Note that this answer relies on the approximation that $p \approx \text{constant}$, which is only a good approximation for **small** adiabatic changes.

- c) What is the increase in T caused by this compression?

$$\text{No heat flow } (Q_{\text{in}} = 0), \text{ so } \Delta T = \frac{W_{\text{on}}}{C_V} = 2 \text{ K}$$

- d) What percent change in p is caused by this compression? Compare this result to the result for an isothermal compression at $T = 300 \text{ K}$ from 5 m^3 to 4.95 m^3 .

Using the ideal gas law, we can relate changes in V and T to changes in p . In the adiabatic case, both V and T change:

$$\Delta p = -\frac{nRT \Delta V}{V^2} + \frac{nR \Delta T}{V}$$

or

$$\frac{\Delta p}{p} = -\frac{\Delta V}{V} + \frac{\Delta T}{T} = 1\% + 0.7\% = 1.7\%$$

In the isothermal case, $\Delta T = 0$, so

$$\frac{\Delta p}{p} = -\frac{\Delta V}{V} = 1\%$$

- e) What is the entropy change due to this adiabatic compression?

For an adiabatic process, $Q = 0$ (thermal isolation means no heat in or out). And, since in general, $dS = \frac{\delta Q}{T}$, $\Delta S_{\text{gas}} = 0$.

Since the process is reversible, the change in total entropy is also zero, $\Delta S_{\text{tot}} = 0$.

- f) Which of the answers (a to e) would be the same if the argon were replaced with N_2 ?

Only the answers to (b) and (e) would remain the same, as there is no dependence on α .
However, the answer to (b) without the approximation ($p \approx \text{constant}$) does depend on α .
The answers to (d) depend on α , since ΔT depends on it.

- g) Which answers would be the same if the argon were replaced with a non-ideal gas?

The answer to (e) would remain the same [and also to part (b) if one still ignores any change in the pressure, as is instructed].

For part (e), our conclusion did not rely at all on the details of what was in the container – this result flowed simply from the logic that the process was reversible, and that no heat flowed into or out of the environment.

Nitrogen gas initially at 300K and atmospheric pressure in a volume of 1 liter (state a) is adiabatically expanded to 2 liters (state b), then isothermally returned to 1 liter (state c), then heated at constant volume back to the initial temperature by contact with a 300K bath.

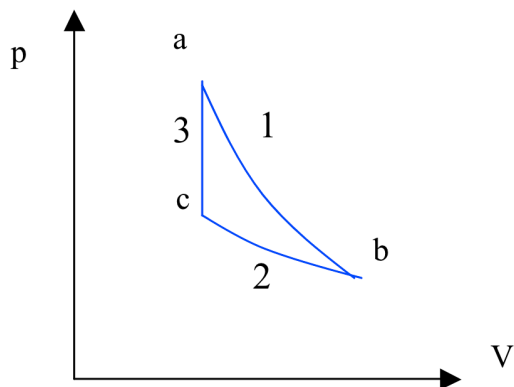
- a) How much did the entropy S of the N_2 change in this cycle?

Entropy is a state function. Because this cycle returns the gas back to its initial state (same volume, temperature, pressure, particle number), the entropy of the gas at the end of the cycle is the same as at the beginning.

- b) How much heat is required to restore the gas to its initial conditions? Draw and label a pV diagram and complete the following tables.

The heat required to bring the gas back to its initial state is
 $Q = (-0.52 + 0.60) \ell \cdot \text{atm} = 0.08 \ell \cdot \text{atm}$. See table below.

Hints: Start by using the ideal gas law $pV = nRT$ and the known initial values of p , V and T to find nR . Remember the relationships for isothermal work and adiabatic work.



Recall that for a diatomic gas, $\alpha = \frac{5}{2}$ and $\gamma = \frac{\alpha+1}{\alpha} = \frac{7}{5}$.

First, for nR : $nR = \frac{p_a V_a}{T_a} = 0.00333 \frac{\ell \cdot \text{atm}}{\text{K}}$. Then the calculations:

Process 1 ($a \rightarrow b$): $Q = 0$

$$V_b T_b^\alpha = V_a T_a^\alpha \rightarrow T_b = T_a \left(\frac{V_a}{V_b} \right)^{1/\alpha} = 227.4 \text{ K}$$

$$W_{by} = -\Delta U = \alpha nR(T_a - T_b) = 0.61 \ell \cdot \text{atm}$$

We can also use:

$$p_a V_a^\gamma = p_b V_b^\gamma \rightarrow p_b = p_a \left(\frac{V_a}{V_b} \right)^\gamma = 0.379 \text{ atm}$$

$$W_{by} = \alpha(p_a V_a - p_b V_b) = 0.61 \ell \cdot \text{atm}$$

The result for W_{by} is of course the same.

Process 2 ($b \rightarrow c$): $\Delta U = 0$

$$\frac{p_b V_b}{T_b} = \frac{p_c V_c}{T_c} \rightarrow p_c = \frac{p_b V_b}{V_c} = 0.758 \text{ atm, since } T_b = T_c.$$

$$W_{by} = nRT_b \ln \frac{V_c}{V_b} = -0.52 \ell \cdot \text{atm} = Q$$

Process 3 ($c \rightarrow a$): $W = 0$

$$Q = \Delta U = \alpha nR(T_a - T_c) = 0.61 \ell \cdot \text{atm}$$

So, in the final step 0.61 liter-atmospheres = 61 J of heat is required to return the gas to its initial state. In total, $0.08 \ell \cdot \text{atm} = 8.2 \text{ J}$ of heat enters the gas during the cycle, because some heat is released during the isothermal step.

state	p (atm)	V (ℓ)	T	process	Q ($\ell \cdot \text{atm}$)	$W_{by}(\ell \cdot \text{atm})$
a	1 atm	1 ℓ	300 K	1 ($a \rightarrow b$)	0	0.61
b	0.38	2 ℓ	227.4	2 ($b \rightarrow c$)	-0.52	-0.52
c	0.76	1 ℓ	227.4	3 ($c \rightarrow a$)	0.61	0

c) How much did the total entropy of the system and environment change in this process?

The change of the entropy of the system (gas) is zero, $\Delta S_{\text{sys}} = 0$. The change of the entropy of the in each process is:

Process 1: $Q_{\text{env}} = 0, \Delta S_{\text{env}} = 0$

Process 2: $\Delta S_{\text{env}} = \frac{Q_{\text{env}}}{T_{\text{env}}} \rightarrow \Delta S_{\text{env}} = \frac{Q_{\text{env}}}{T_{\text{env}}} = \frac{0.52 \ell \cdot \text{atm}}{227.4 \text{ K}} = 0.0023 \frac{\ell \cdot \text{atm}}{\text{K}}$, since T_{env} is fixed

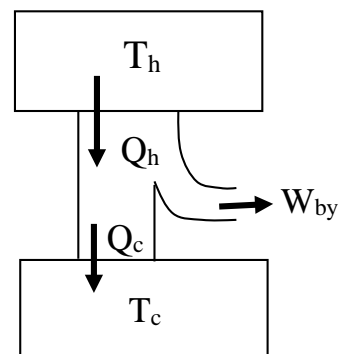
Process 3: $\Delta S_{\text{env}} = \frac{Q_{\text{env}}}{T_{\text{env}}} = \frac{-0.61 \ell \cdot \text{atm}}{300 \text{ K}} = -0.0020 \frac{\ell \cdot \text{atm}}{\text{K}}$, since T_{env} is fixed

$$\text{Hence } \Delta S_{\text{env}} + \Delta S_{\text{sys}} = 0.0003 \frac{\ell \cdot \text{atm}}{\text{K}} = 0.03 \frac{\text{J}}{\text{K}}$$

A power plant burns coal to heat a boiler to 450 °C. The waste heat leaves via a cooling tower at 60 °C.

- a) What is the highest percentage of the chemical energy (released by burning the coal) that can be converted into electrical energy, if it all works as well as possible?

A power plant is a heat engine, generating work that is used at remote locations, such as your home. Thus, the electrical energy is the work, W_{by} , and the coal chemical energy is Q_H . The highest percentage of coal chemical energy that can be converted to work is the Carnot efficiency. (The symbols Q_C , Q_H and W_{by} are defined as positive.)



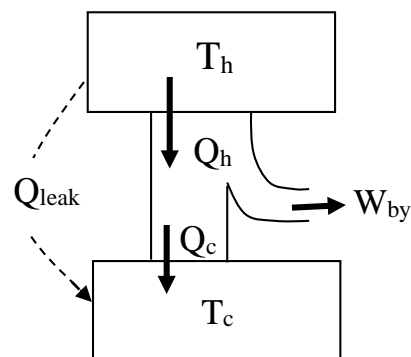
$$\begin{aligned} W_{by} / Q_H &= [Q_H - Q_C] / Q_H = 1 - (Q_C / Q_H) \\ &= 1 - (T_C / T_H) = 1 - ((60 + 273) / (450 + 273)) = \mathbf{0.539 = 53.9\%} \end{aligned}$$

Of course, the real efficiency [including other sources of heat loss, inefficiencies of the engine, etc.] is quite a bit less than this, typically about 30%.

- b) If 100 J of heat leaks directly from the boiler to the cooling system (i.e., lost energy), how much does the total entropy (engine plus reservoirs) increase?

The differential of the entropy in any quasistatic process is $dS = \delta Q / T$. The boiler and cooling system temperatures remain constant, so for each of them, the entropy change is $\Delta S = Q / T$, where Q is the total heat flow. (When the temperature changes, ΔS is found by replacing δQ with $C dT$, and then integrating.) For the boiler, $Q = -Q_H$ and for the cooler $Q = Q_C$. To find the total entropy change, add the changes in the boiler and in the cooling system.

$$\begin{aligned} \Delta S_{total} &= \Delta S_H + \Delta S_C = (-Q_H / T_H) + (Q_C / T_C) \\ &= (-100 \text{ J} / 723 \text{ K}) + (100 \text{ J} / 333 \text{ K}) = \mathbf{0.162 \text{ J} / \text{K}} \end{aligned}$$



Note that the total entropy change is positive. Heat flows from hot to cold, because that makes S increase.

- c) If for each 1 kJ of energy entering the boiler, 100 J leaks directly to the cooling system, but no other processes increase the net entropy, how much work can be obtained from the 1 kJ?

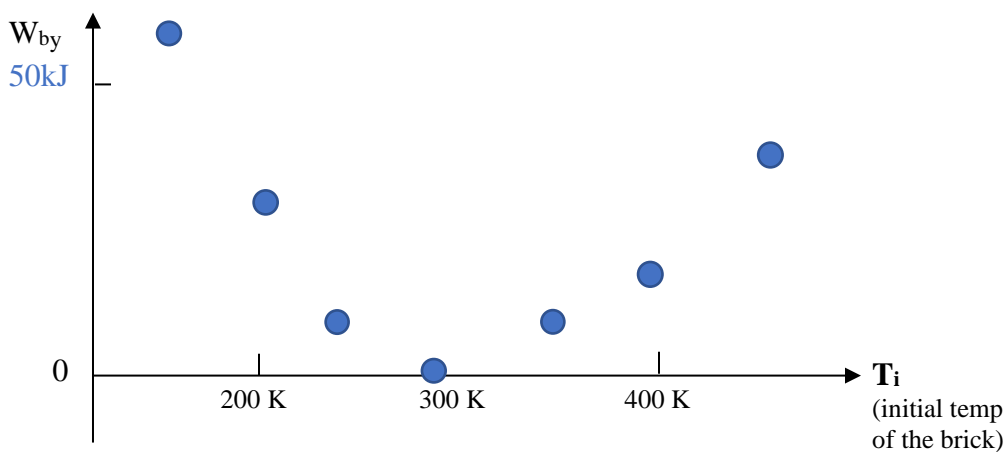
With 100 J leaking to the cooling system, 900 J remain to generate work. We saw in part a) that the Carnot efficiency is 0.539. Thus, the maximum work that can be extracted from 900 J is $\mathbf{900 \text{ J} \times 0.539 = 485 \text{ J}}$.

Consider our famous brick in an environment at $T=300\text{K}$. Let's say the brick has a heat capacity 1000J/K , independent of T over the range of T 's used here.

$$W_{by} = -\Delta F = \Delta U - T_{env}\Delta S$$

$$\Delta U = C(T_{env} - T_{brick}), \Delta S = C \int_{T_i}^{T_f} \frac{dT}{T} = C \ln \frac{T_{env}}{T_{brick}}$$

- a) Calculate and sketch the available work W_{by} for this set of initial brick temperatures: $T_i = \{150, 200, 250, 300, 350, 400, 450\}$ Kelvin



$T_{brick} \text{ (K)}$	$W_{by} \text{ (kJ)}$
450	28.4
400	13.7
350	3.8
300	0.0
250	4.7
200	21.6
150	57.9

- b) Consider an object in thermal contact with a reservoir at temperature T . Mark True or False:

- T F** a) The Energy U of the object is a minimum in equilibrium.
T F b) The free energy F of the object is a maximum in equilibrium.
T F c) The free energy F of the object is a minimum in equilibrium.
T F d) The entropy S of the object is a maximum in equilibrium.
T F e) The entropy of the object plus environment is a maximum in equilibrium.
T F f) The free energy of *liquid* N_2 in the room is greater than N_2 at room temperature.

Consider a container of fixed volume V split by an impermeable barrier into volumes V_A and V_B such that $V_A + V_B = V$. The volume V_A and V_B contain the same number of particles $N_A = N_B$. The volume V_A contains a monatomic ideal gas and the volume V_B contains a non-ideal monatomic gas. The container is in thermal contact with a reservoir of temperature T .

- a) Given that the entropy of an ideal gas is $S = Nk \ln V$ plus a term independent of volume (we will ignore this term), write down the free energy of the particles in volume V_A in terms of V_A and N_A .

$$F_A = \frac{3}{2} N_A kT - T N_A k \ln V_A$$

- b) The entropy of the non-ideal gas is $S = Nk \ln(V - Nb)$ where b is a constant with units m^3 . The internal energy is identical to that of an ideal monatomic gas. Write down the free energy of the particles in volume V_B in terms of V_A , N_A , b .

$$F_B = \frac{3}{2} N_B kT - T N_B k \ln(V_B - N_B b) = \frac{3}{2} N_A kT - T N_A k \ln(V - V_A - N_A b),$$

since $N_A = N_B$ and $V_B = V - V_A$.

- c) Write down the total free energy of the container and minimize to get the volume V_A at equilibrium. Compare this to the case when we had two *ideal* gases exchanging volume.

$$F = F_A + F_B = 3N_A kT - T N_A k (\ln V_A + \ln(V - V_A - N_A b))$$

$$\frac{dF}{dV_A} = 0 \text{ in equilibrium}$$

$$\frac{dF}{dV_A} = -N_A kT \left(\frac{1}{V_A} + \frac{1}{V - V_A - N_A b} * -1 \right) = 0$$

$$\frac{1}{V_A} = \frac{1}{V - V_A - N_A b} \rightarrow V_A = \frac{V - N_A b}{2}$$

For two ideal gases the solution would be $V_{A,\text{ideal}} = \frac{V}{2}$

Consider a monatomic ideal gas with $S = Nk \left(\ln \frac{n_T}{n} + \frac{5}{2} \right)$, where n_T is a constant that depends only on temperature and $n = N/V$ is the density of particles.

- a) Write down the free energy for a monatomic ideal gas.

$$F = U - TS = \frac{3}{2} NkT - NkT \left(\ln \left(\frac{n_T}{n} \right) + \frac{5}{2} \right) = NkT \left[\ln \frac{n}{n_T} - 1 \right]$$

- b) From your expression above calculate an expression for the chemical potential of a monatomic ideal gas.

Note, that it is easier to take the derivative after simplifying the expression for F in part (a):

$$\mu = \left(\frac{dF}{dN} \right)_{T,V} = kT \left[\ln \frac{n}{n_T} - 1 \right] + NkT \frac{1}{N} = kT \ln \frac{n}{n_T}$$

Suppose now we have a second container of monatomic ideal gas at height h off the ground so each atom feels an equal gravitational potential.

- c) Write down the internal energy for this ideal gas at height h . Does the entropy change if we lift the box to this height?

$$U = \frac{3}{2} NkT + Nmgh$$

Entropy does not change if we just move the center of mass to a different position.

- d) Write down an expression for the free energy of the container at height h .

Since only U changes by the addition of the $Nmgh$ term, the free energy is simply:

$$F = NkT \left[\ln \frac{n}{n_T} - 1 \right] + Nmgh = F_{ideal} + Nmgh$$

- e) From your expression above calculate the chemical potential of the lifted box. Compare the chemical potential to what you calculated in b).

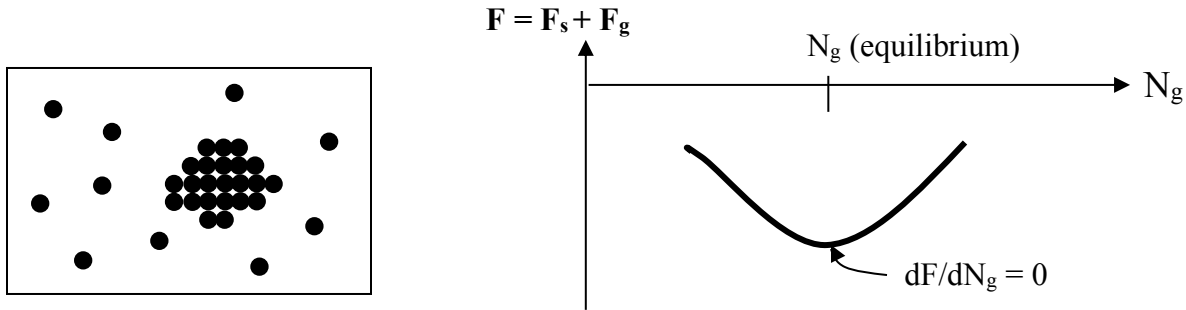
$F = F_{ideal} + Nmgh$, so

$$\mu = \mu_{ideal} + \frac{d}{dN} (Nmgh) \Rightarrow \mu = kT \ln \frac{n}{n_T} + mgh$$

The chemical potential is identical to the ideal gas plus a term that accounts for the increased potential energy per particle, mgh .

In general adding a potential energy to your system will result in an additional term in the chemical potential.

Consider the equilibrium between a simple solid and its gas phase. In equilibrium at temperature T , an average of N_s atoms are in the solid and N_g are in the gas. We will compute the vapor pressure in equilibrium with the solid, with a little approximation. Here's the picture:



The equilibrium condition $dF/dN_g = 0$ is equivalent to equalizing the chemical potentials of the solid and gas:

$$\mu_s = \mu_g$$

*Equilibrium condition
between phases*

Pretend that the solid is a perfect crystal with every atom held in place (only one microstate), so the entropy of the solid is zero. Also assume that the kinetic energy of the solid is zero. The binding energy of each atom in the solid is Δ , so its free energy is simply $F_s = U_s - TS_s = -N_s\Delta$.

a) Write out the chemical potentials for the solid and gas in terms of Δ , T , and number densities n and n_Q . (We need n_Q here because we're comparing state counts in the gas and in the solid.)

The chemical potential of the solid is just given by $\mu_s = \left(\frac{dF_s}{dN_s}\right) = -\Delta$.

For the chemical potential of the gas we can use the results from parts (a) and (b) of problem 3.

Starting with the entropy of an ideal gas, $S = Nk \left(\ln \frac{n_Q}{n} + \frac{5}{2} \right)$, where the n_T parameter used there is replaced by n_Q here, and where $n \equiv N_g/V_g$. The ideal gas free energy is

$F_g = U - TS = NkT \left[\ln \frac{n}{n_Q} - 1 \right]$. In summary we have:

$$\begin{aligned}\mu_s &= -\Delta \\ \mu_g &= kT \ln \frac{n}{n_Q}\end{aligned}$$

b) With the equilibrium condition, find the vapor pressure, p in terms of T , Δ , and n_Q .

$$\mu_s = \mu_g \Rightarrow -\frac{\Delta}{kT} = \ln \frac{n}{n_Q} \Rightarrow n = n_Q e^{-\Delta/kT}$$

$$\text{Now, } p = \frac{N_s kT}{V_s} = n kT = n_Q kT e^{-\Delta/kT}$$

- c) Evaluate the vapor pressure (in atm) at $T = 600\text{K}$ for atoms with an atomic weight of 28 that form a solid with binding energy $\Delta = 4.63\text{ eV}$. Interpret this.

The quantum density of the gas is $n_Q = 10^{30}\text{m}^{-3} \times (28)^{3/2} \times (600/300)^{3/2} = 4.2 \times 10^{32}\text{m}^{-3}$.

➤ These numbers (the atomic mass and the binding energy) describe silicon.

$$p = (4.2 \times 10^{32}\text{m}^{-3})(1.38 \times 10^{-23})(600\text{K})e^{-4.63/k600} = 4.6 \times 10^{-27}\text{ Pa} = 4.6 \times 10^{-32}\text{ atm}$$

The fact that this is so low means that at atmospheric pressure, silicon will basically never evaporate.