IV. Facts about heat capacities

Heat capacity $C = \frac{\partial Q}{\partial T}$. We need an expression for ∂Q.

Recall the First Law: $dE = dQ - dW + m dN$.

Solve for dQ.

Let dW be represented generally by pdV

Recall $E_{\substack{total\\ internal}} = N\left(\frac{n}{2}kT + m\right)$

$n =$ #dof per molecule

$N =$ #molecules

Consider an isolated system, so $m = 0$.

Then $dE = \frac{Nn}{2}kdT$

so $dQ = \frac{Nn}{2}kdT + pdV$.

Divide through by # moles:

$$\frac{dQ}{mole} = \frac{Nk}{mole} \cdot \frac{\nu}{2} dT + p\frac{dV}{mole}$$

$$\frac{dV}{mole} \equiv dv, \text{ the molar volume}$$

$$\frac{Nk}{mole} = R, \text{ the gas constant}$$

$$\frac{dQ}{mole} = dq, \text{ the heat added per mole}$$

So $dq = R\frac{\nu}{2}dT + pdv$ 'Eq 1'

Recall $C_V = \left.\frac{\partial Q}{\partial T}\right|_V$ is the heat capacity @ constant volume

So $c_V = \left.\frac{\partial q}{\partial T}\right|_V$ is the molar heat capacity @ constant volume

Plug in q from Eq 1 to get:

$c_V = \frac{R\nu}{2}$. This is IMPORTANT because it means:

measuring c_V gives us ν, the #dof per molecule.

Also recall $C_P = \left.\frac{\partial Q}{\partial T}\right|_p$, so $c_P = \left.\frac{\partial q}{\partial T}\right|_p$

Recall $dq = R\frac{\nu}{2}dT + pdv,$ so

$$c_P = R\frac{\nu}{2} + p\left.\frac{\partial v}{\partial T}\right|_p = c_V + p\left.\frac{\partial v}{\partial T}\right|_p$$

Thus $c_P - c_V = p\left.\frac{\partial v}{\partial T}\right|_p$

Based on empirical data (most things expand when heated), c_P is almost always > c_V.

These equations are true for ANY system.

Now apply them to the special case of an ideal gas.

Begin with the ideal gas law, $pv = RT$, so

$$v = \frac{R}{p} T$$

$$\left. \frac{dv}{dT} \right|_p = \frac{R}{p}$$

$$p \left. \frac{dv}{dT} \right|_p = R$$

So for an ideal gas,

$$c_P - c_V = p \left. \frac{\partial v}{\partial T} \right|_p = R$$

I. Applications of the laws of thermodynamics

II. Maxwell's Relations

III. Definitions of types of constraints

IV. Facts about ideal gases

Please read Stowe Chapter 16 and Appendix 21A.

I. Applications of the laws of thermodynamics

This is Chapters 13 and 14.

Begin with the First Law: $dE = dQ - pdV + \mu dN$

Substitute $dQ = TdS$, solve for it, and rewrite

$TdS = dE + pdV - \mu dN$

All 4 differentials are exact. They concern functions (properties) of the system that can be known unambiguously at any moment in the quasi-static evolution of the system.

This equation says that not all 4 are independent. Any 3 are independent: for example, we can separately vary volume V, number N, and heat Q.

These 2 chapters work out the consequences of their interdependence.

II. Maxwell's Relations

Compare the physics equation: $dE = TdS - pdV + \mu dN$

to the math equation: $dE = \left.\frac{\partial E}{\partial S}\right|_{V,N} dS + \left.\frac{\partial E}{\partial V}\right|_{S,N} dV + \left.\frac{\partial E}{\partial N}\right|_{V,S} dN$

We notice 2 things:

1) We can compare terms to find that

$$\left.\frac{\partial E}{\partial S}\right|_{V,N} = T$$

$$\left.\frac{\partial E}{\partial V}\right|_{S,N} = -p$$

$$\left.\frac{\partial E}{\partial N}\right|_{V,S} = \mu$$

2) Since dE is an exact differential, the path in $S-V-N$ space to any particular value of (S,V,N) does not affect the energy $E(S,V,N)$. We can display this path explicitly through the ordering of partial differentials:

$$\frac{\partial^2 E}{\partial S \partial V} = \frac{\partial^2 E}{\partial V \partial S} \qquad \frac{\partial^2 E}{\partial S \partial N} = \frac{\partial^2 E}{\partial N \partial S} \qquad \frac{\partial^2 E}{\partial V \partial N} = \frac{\partial^2 E}{\partial N \partial V}$$

$$\frac{\partial}{\partial S}(-p) = \frac{\partial}{\partial V}(T) \qquad \frac{\partial}{\partial S}(\mu) = \frac{\partial}{\partial N}(T) \qquad \frac{\partial}{\partial V}(\mu) = \frac{\partial}{\partial N}(-p)$$

$$\boxed{-\frac{\partial p}{\partial S} = \frac{\partial T}{\partial V} \qquad \frac{\partial \mu}{\partial S} = \frac{\partial T}{\partial N} \qquad \frac{\partial \mu}{\partial V} = -\frac{\partial p}{\partial N}}$$

These are the first 3 of Maxwell's Relations.

How to find the rest:

$T,\ S,\ p,\ V,\ \mu,$ and N are the external parameters we can control for a system.

Keep in mind that (p,V) represent all generalized contributions to work.

In the First Law, we see that they appear naturally paired as

(T,S)

(p,V)

(μ,N)

such that their product forms a physically meaningful exact differential: energy.

We keep one of each pair fixed while examining how the variation in the other one affects dE.

There are 8 unique ways to keep one of each pair fixed while varying the other.

Combination #			
1	TdS	pdV	mdN
2	TdS	dpV	mdN
3	TdS	pdV	dmN
4	TdS	dpV	dmN
5	dTS	pdV	mdN
6	dTS	dpV	mdN
7	dTS	pdV	dmN
8	dTS	dpV	dmN

Among the 6 parameters, m cannot be independently changed for an isolated system, so we will ignore combinations that include a dm

Rewrite the list, excluding combinations 3, 4, 7, and 8:

Combination #

1 $TdS \quad pdV \quad m dN$

2 $TdS \quad dpV \quad m dN$

5 $dTS \quad pdV \quad m dN$

6 $dTS \quad dpV \quad m dN$

Add plus and minus signs to combine these, and name the combinations:

Combination #

1 $+TdS - pdV + m dN = dE$ internal energy

2 $+TdS + Vdp + m dN$ º dH "enthalpy"

5 $-SdT - pdV + m dN$ º dF "Helmholtz free energy"

6 $-SdT + Vdp + m dN$ º dG "Gibbs free energy"

Each of these 4 combinations is an exact differential, so we repeat on Combinations 2, 5, and 6 the procedure we used on Combination 1 (compare "physics equation" with "math equation") to get 3 more Maxwell's Relations for each.

4 Combinations × 3 Maxwell's Relations per combination = 12 Maxwell's Relations total
They are listed in Table 13.1 in the Stowe book.

Facts about Maxwell's Relations:

1) They are useful because they:

relate [quantities that are difficult to measure] to [quantities that are easier to measure]

For example, Relation #10:

$$\text{difficult: } \left.\frac{\partial S}{\partial p}\right|_{T} \quad = \quad \text{easier: } -\left.\frac{\partial V}{\partial T}\right|_{p}$$

2) They are true for any isolated equilibrium system

3) We will see later how the +'s and -'s were chosen for the combinations. It turns out that these combinations are preserved during certain processes (for example phase changes) and under certain constraints (for example constant-temperature/isothermal).

4) Notice that none of the "official" Relations include $\dfrac{\partial E}{\partial something}$. If we need a relation involving that term, we begin again with the First Law. We rewrite it in a way that moves the dE to the righthand side, and moves to the lefthand side one of the other differentials that we don't need. Then we repeat the procedure.

III. Definitions of types of constraints

Non-diffusive	$dN = 0$
Isovolumic, isochoric	$dV = 0$
Adiabatic	$dQ = 0$
Isobaric	$dp = 0$
Isothermal	$dT = 0$

IV. Facts about ideal gases

Fact 1: for an ideal gas in an adiabatic process,

$p \times V^{g} =$ constant,

where $g = \frac{n+2}{n} = \frac{C_p}{C_V}$

and $n = \#$ dof per mole

C_p, C_V are specific heats

Proof: Consider an isolated system, so $dN = 0$. Write down everything (i.e., 3 things) we know about it. Begin with:

(1) The equation of state, $pV = NkT$

Take differentials of both sides: $d(pV) = d(NkT)$

Because $dN = 0$, this simplifies to $pdV + Vdp = NkdT$

¸ by Nk to get: $\frac{p}{Nk}dV + \frac{V}{Nk}dp = dT$ "Eq 1"

(2) The energy $E = \# dof \times \frac{\frac{1}{2}kT}{dof}$.

A truly ideal gas has 3 dof (from p_x, p_y, p_z) per molecule.

Generalize this: just say it has ν dof per molecule.

If it has N molecules,

$$E = \frac{1}{2} N\nu kT$$

Take the differential of both sides:

$$dE = \frac{1}{2} N\nu k dT \qquad \text{"Eq 2"}$$

(3) The First Law: $dE = dQ - pdV + \mu dN$.

Isolated system: $dN = 0$

Adiabatic process: $dQ = 0$

$$dE = -pdV \qquad \text{"Eq 3"}$$

Combine Eq 2 and Eq 3 to eliminate dE:

$$\frac{1}{2}N\nu k dT = -pdV$$

$$dT = \frac{-2p}{N\nu k}dV \qquad \text{"Eq 4"}$$

Combine Eq 1 and Eq 4 to eliminate dT:

$$\frac{p}{Nk}dV + \frac{V}{Nk}dp = \frac{-2p}{N\nu k}dV$$

$$pdV + Vdp = \frac{-2p}{\nu}dV$$

÷ through by pV:

$$\frac{dV}{V} + \frac{dp}{p} = -\frac{2}{\nu}\frac{dV}{V}$$

$$\left(1+\frac{2}{n}\right)\frac{dV}{V} = -\frac{dp}{p}$$

$$\left(\frac{n+2}{n}\right)\frac{dV}{V} = -\frac{dp}{p}$$

Integrate both sides.

$$\left(\frac{n+2}{n}\right)\ln V = -\ln p + const$$

$$\underbrace{\left(\frac{n+2}{n}\right)}_{\Downarrow}\ln V + \ln p = const$$

Call this "g"

$$g \ln V + \ln p = const$$

Exponentiate both sides.

$$pV^{g} = const$$

We have the right form of the equation, but we still must now show that $g=\frac{C_p}{C_V}$:

Begin again with (3) the First Law: $dE = dQ - pdV + \mu dN$.

For isolated systems, $dN = 0$.

Then $dQ = dE + pdV$. "Eq 5"

(4) Recall definition: $C_V \equiv \left.\frac{\partial Q}{\partial T}\right|_V$

Plug in Eq 5:

$$C_V \equiv \left.\frac{\partial E}{\partial T}\right|_V$$

(5) Recall definition: $C_p \equiv \left.\frac{\partial Q}{\partial T}\right|_p$

Plug in Eq 5:

$$C_p \equiv \left.\frac{\partial E}{\partial T}\right|_p + p\left.\frac{\partial V}{\partial T}\right|_p$$

So $\dfrac{C_p}{C_V} = \dfrac{\left.\frac{\partial E}{\partial T}\right|_p + p\left.\frac{\partial V}{\partial T}\right|_p}{\left.\frac{\partial E}{\partial T}\right|_V}$ "Eq 6"

Recall (1) the equation of state: pV=NkT.

So $p\left.\frac{\partial V}{\partial T}\right|_p = Nk$. Plug this into Eq. 6.

Recall (2) the energy equation: $E = \frac{N\nu kT}{2}$.

So $\left.\frac{\partial E}{\partial T}\right|_p = \frac{N\nu k}{2}$

and $\left.\frac{\partial E}{\partial T}\right|_V = \frac{N\nu k}{2}$ Plug these into Eq 6.

Then $\frac{C_p}{C_V} = \frac{\frac{N\nu k}{2} + Nk}{\frac{N\nu k}{2}} = \frac{\nu + 2}{\nu}$

Fact 2 about ideal gases: $E = E(T)$ only, no volume dependence.

Proof:

Recall for any system, $dE = dQ - pdV + \mu dN$

Plug in $dQ = TdS$

Then $dE = TdS - pdV + \mu dN$

This would lead us to expect E to depend on T and V.

But: for ideal gases, because V and T are connected through $pV = NkT$, we can write $E = E(T)$ only.

Fact 3 about ideal gases: $TV^{\gamma-1} = constant$

Proof: begin with $pV^{\gamma} = constant$ "Eq 1"

Equation of state: $pV = NkT$, so $p = \dfrac{NkT}{V}$.

Then Eq 1 becomes:

$$\frac{NkT}{V} \cdot V^{\gamma} = constant$$

$$TV^{\gamma-1} = \frac{constant}{Nk} = constant2$$

I. Free expansion of a non-ideal gas
II. Reversibility
III. Behavior of a system in equilibrium with a reservoir

Please read Stowe Chapter 17 and the Feynman slides linked to the course webpage.

I. Free expansion of a non-ideal gas

Consider a gas isolated in a container. Allow its volume to change by ΔV. How does its temperature change?

This problem serves as an example to illustrate use of Maxwell's Relations and definitions of various thermodynamic quantities.

Method	Actions
"Where to begin? Write the First Law."	$dE = dQ - pdV + \mu dN$ Let $dQ = TdS$ $dE = TdS - pdV + \mu dN$
"See what we can set = 0 based on constraint info given in the statement of the problem."	"isolated": $dE = 0,\ dN = 0$ Thus $0 = TdS - pdV + 0$ Rewrite this as $dS = \frac{p}{T}dV$ "Eq 1"

Method	Actions
"This relates dS to dV, but the problem asks for a relation between dV and dT. Use Maxwell's Relations to convert dS to dV and dT."	Eq 1 is the "physics statement". Need also a "math statement": $dS = \left.\frac{\partial S}{\partial T}\right\|_V dT + \left.\frac{\partial S}{\partial V}\right\|_T dV$ "Eq 2" Compare Eq 1 to Eq 2. LHS's are equal so RHS's must also be equal: $\left.\frac{\partial S}{\partial T}\right\|_V dT + \left.\frac{\partial S}{\partial V}\right\|_T dV = \frac{p}{T} dV$
"Substitute for the partial derivatives by using Maxwell's Relations or definitions of heat capacity, compressibility, etc. (measureable properties)."	$\left.\frac{\partial S}{\partial T}\right\|_V \equiv \frac{1}{T} C_V$ $\left.\frac{\partial S}{\partial V}\right\|_T = \left.\frac{\partial p}{\partial T}\right\|_V$ Compute $\left.\frac{\partial p}{\partial T}\right\|_V$ from the equation of state.

Substitute:

$$\frac{1}{T}C_V dT + \left.\frac{\partial p}{\partial T}\right|_V dV = \frac{p}{T}dV$$

$$dT = \frac{T}{C_V}\left[\frac{p}{T}dV - \left.\frac{\partial p}{\partial T}\right|_V dV\right]$$

$$dT = \frac{1}{C_V}\left[p - T\left.\frac{\partial p}{\partial T}\right|_V\right]dV$$

II. Reversibility

Consider a thermodynamic system and its local surroundings.

Ex: a glass of water, piston in cylinder, etc.

These are any other systems that may provide energy to it or absorb energy from it, such as heat reservoirs, springs, weights on pulleys.

Suppose the thermodynamic system undergoes a process: it receives or loses heat, compresses or expands, etc.

Use this context to define Reversibility in two ways:

Definition 1: The process is called reversible if, at its conclusion, both the system and its local surroundings may be restored to their initial states without producing any changes (i.e., any increase in the number of accessible states) in the rest of the universe.

Definition 2: Call the thermodynamic system + the local surroundings + the rest of the universe "the combined system A_0" which has entropy S_0. Recall that for any process, $\Delta S_0 \geq 0$. A process is reversible only if its $\Delta S_0 = 0$.

If the forward process were to cause $\Delta S_0 > 0$, then the initial conditions could only be recovered by a reverse process that yielded $\Delta S_0 < 0$, and this is forbidden by the Second Law.

Example of an irreversible process: free expansion of a real gas in a volume. To return it to its original compressed state requires adding work from the local surroundings. The work heats the gas. The heat must be exhausted to a reservoir. So returning the gas to its original $\left(T_i, V_i\right)$ requires the external environment to provide work and absorb heat. In this case $\Delta S_{gas} + \Delta S_{environment} > 0$.

No natural process is truly reversible, because all natural processes involve dissipative effects (friction, viscosity, electrical resistance, etc.) which cause work to be converted to heat. There is no way to "organize" the heat in a way that will reconvert 100% of it to work.

Any reversible process is a theoretical approximation to a real system in which dissipation has been minimized. A dissipative process takes coherent collective motion (e.g. a book sliding on a table) and transforms it into heat (random motion of the stalled book's molecules).

Coherent motion can be achieved in fewer ways $\left(W_i\right)$ than random motion $\left(W_f\right)$, so friction increases the entropy $\left(S = k \ln W\right)$ of a system.

III. Behavior of a system in equilibrium with a reservoir

The issue is: we typically want to write questions like

$$\text{"What is the state of } \left\{\begin{matrix}\text{an electron}\\ \text{an atom}\end{matrix}\right\} \text{ in } \left\{\begin{matrix}\text{a metal}\\ \text{a stellar atmosphere}\end{matrix}\right\}?$$

We mean: what is the probability that it is in a specific state, which is characterized by particular values of energy, angular momentum, etc.

Example: if the system is at temperature T, what is the probability that the electrons are in energy level L and will radiate correspondingly?

To answer, we calculate the probability, compare to experiment, and if we find a disagreement, this may signal that the theory that predicted these levels is wrong. Then the theory develops further....

To describe these probabilities, consider a small system named D, in equilibrium with a reservoir R. Call the combined system of $\left(\mathsf{D}+R\right)=A_0$.

We cannot consider D alone. It cannot do anything alone.

If it makes a transition, that is because it gets energy from R or gives up energy to R.

So the two systems are coupled.

Let the # of accessible states for D be called W_D.

and the # of accessible states for R be called W_R.

Thus the # of accessible states for A_0 is $W_0 = W_R \cdot W_D$.

Recall that the probability for $\begin{pmatrix} \text{D is in a particular configuration AND} \\ \text{R is in a particular configuration} \end{pmatrix} = \dfrac{W_R \cdot W_D}{W_{tot}}$

(Recall an example computation of this in Stowe Table 8.1 and page 76 of these lectures.)

Suppose we want to ask, "what is the probability that D is in one particular state (call that state "s")?

Thus by the formulation of the question, $W_D = 1$.

Then $\text{Prob}_{\text{D is in state } s} = \dfrac{W_R \cdot 1}{W_{tot}} \propto W_R$

Now recall the entropy of R:

$S_R = k \ln W_R$

So $W_R = e^{S_R/k}$

So $\text{Prob}_{\text{D is in state } s} \propto e^{S_R/k}$ "Eq 1"

Notice that the probability for the configuration of D depends upon information from R because the two systems are coupled.

To find S_R :

Suppose that R begins with entropy S_R^0.

Recall with the First Law: $dE = TdS - pdV + \mu dN$,

so $dS = \frac{1}{T}dE + \frac{p}{T}dV - \frac{\mu}{T}dN$

Notice that in order to reach the state s, Δ must take from R:

energy dE

volume dV

particles dN.

When this happens, the entropy of R is reduced by

$$dS_R = \frac{1}{T}dE + \frac{p}{T}dV - \frac{\mu}{T}dN$$

So the entropy of R becomes

$$S_R = S_R^0 - dS_R = S_R^0 - \frac{1}{T}\left(dE + pdV - \mu dN\right)$$

Plug this into Eq. 1:

$$\text{Prob}_{\text{D is in state s}} \propto e^{S_R/k} \propto \exp\left[\frac{S_R^0}{k} - \frac{1}{kT}\left(dE + pdV - \mu dN\right)\right]$$

$$\propto \exp\left[\frac{S_R^0}{k}\right]\exp\left[-\frac{1}{kT}\left(dE + pdV - \mu dN\right)\right]$$

Define $\beta = \dfrac{1}{kT}$

absorb this term into the proportionality

$$\text{Prob}_{\text{D is in state s}} = C\exp\left[-\beta\left(dE + pdV - \mu dN\right)\right]$$

Constant of proportionality "C" is not determined yet.

I. Classical versus quantum statistics

II. Example problem using quantum statistics

III. Example problem using classical statistics

IV. Degeneracy and multistate systems

V. Equipartition

Please read Stowe Chapter 18.

I. Classical versus quantum statistics

We must distinguish STATES from SYSTEMS.

STATE: a unique set (or range) of parameters (x,p) in phase space

SYSTEM: not yet clearly defined in this course! We will now develop the meaning of "system".

Consider 2 ways of thinking about a microscopic system:

Way #1

A group of particles that can occupy any of several different states

Here $\Delta N = 0$ (number of particles is fixed)

So for this point of view, the probability that the system is in state "s" is

$$P_s = C_1 \exp\left[-\beta\left(\Delta E + p\Delta V - \mu\cancel{\Delta N}\right)\right]$$

Way #2

A state that can be occupied by various numbers of particles.

Here $\Delta V = 0$ (volume is fixed)

And for this point of view, the probability that the system is in state "s" is

$$P_s = C_2 \exp\left[-\beta\left(\Delta E + p\cancel{\Delta V} - \mu\Delta N\right)\right]$$

Need to know ΔE necessary to get to E_s

Do we need to know ΔV?

(Way #1, continued)

When a system changes state, its $\Delta E >> p\Delta V$. For example, when an electron changes energy levels in an atom, the volume of the atom changes very little. So $p\Delta V$ is negligible compared to ΔE.

Then $P_s \propto C_1 e^{-\beta \Delta E}$

Consider a system for which $E_{ground} = 0$. In this case the ΔE necessary to reach state "s" is E_s.

Then $P_s = C_1 e^{-\beta E_s}$

This point of view is called Classical Statistics.

(Way#2, continued)

No approximations yet here, so we still have:

$P_s = e^{-\beta(\Delta E - \mu\Delta N)}$. Factor out the ΔN in the exp to get:

$$P_s = e^{-\beta\Delta N\left(\frac{\Delta E}{\Delta N} - \mu\right)}.$$

Define $n = \Delta N =$ #particles in a state

Define $\varepsilon_s = \dfrac{\Delta E}{\Delta N} =$ energy per particle in the state.

$$P_s = C_2 e^{-\beta n(\varepsilon_s - \mu)}$$

This point of view is called Quantum Statistics.

Facts about both kinds of statistics:

i) Since $P \propto e^{E_s \text{ or } \varepsilon_s}$, the higher the energy of the state, the less probable it is that the system will populate it.

ii) Normalize to find the constants C_1 and C_2 :

(Classical)

Prob(system is in some state) = 1

$$\sum_s P_s = 1$$

$$\sum_s C_1 e^{-\beta E_s} = 1$$

$$C_1 = \frac{1}{\sum_s e^{-\beta E_s}}$$

(Quantum)

Prob(system has some number of particles in it) = 1

$$\sum_n P_s = 1$$

summation indices are different!

$$\sum_n C_2 e^{-\beta n(\varepsilon_s - \mu)} = 1$$

$$C_2 = \frac{1}{\sum_n e^{-\beta n(\varepsilon_s - \mu)}}$$

II. Example problem using quantum statistics

Consider photons in an oven.

$T = 500K$

m per photon = 0 (This means: "photons don't interact with each other.")

Consider a state that has energy 0.1 eV.

(a) What is the relative probability that the state is occupied by 1 photon, compared to the probability that it is unoccupied?

Note: the subject of the question is the state itself, so we use quantum statistics.

Interpret the question mathematically:

What is $\dfrac{P(n=1)}{P(n=0)}$?

In general, with quantum statistics, $P(n) = Ce^{-n\beta(\varepsilon_s - \mu)}$.

Recall $\beta \equiv \dfrac{1}{kT}$.

Recall $C = C_2 = \dfrac{1}{\sum\limits_n e^{-\beta n(\varepsilon_s - \mu)}}$

So $\dfrac{P(n=1)}{P(n=0)} = \dfrac{Ce^{-1\cdot\beta(\varepsilon_s - 0)}}{Ce^{-0\cdot\beta(\varepsilon_s - 0)}} = \dfrac{e^{-\beta\varepsilon_s}}{1}$

$$= \exp\left[-\frac{1}{\left(8.63\times10^{-5}\dfrac{eV}{K}\right)(500K)}\cdot(0.1eV)\right] = 0.1.$$

(b) What if the question were rephrased as "What is the absolute probability that the state is unoccupied?"

Interpret this to mean: What is $\mathrm{P}(n=0)$?

i.e., Since $\mathrm{P}(n=0) = Ce^{-0\cdot\beta(\varepsilon_s - 0)} = C$, what is C?

Recall $C = \left[\sum_{n=0}^{M} e^{-n\beta(\varepsilon_s - \mu)} \right]^{-1}$ where M = max # photons that can occupy the state.

An interesting feature of photons is that for them, M is ∞.

So we need

$$C = \left[\sum_{n=0}^{\infty} e^{-nx} \right]^{-1}$$

where $x = \beta\varepsilon_s$.

This sum is computed in Appendix 21A (Stowe page 372).

$$C = \left[\frac{1}{1 - e^{-x}} \right]^{-1}.$$

Plug in $x = \beta\varepsilon_s = \dfrac{\varepsilon_s}{kT}$

$$C = \left[\frac{1}{1 - 0.1} \right]^{-1} = 0.9$$

III. Example problem using classical statistics

Consider hydrogen atoms in an oven.

$T = 300K$

$m = 0$

Recall that for electrons in hydrogen, $E_0 = -13.6eV$

$E_1 = -3.4eV$

What is the probability that any particular hydrogen's electron will be in E_1, compared to the probability that it will be in E_0 ?

Note: the subject of the question is a particle: use classical statistics.

Interpret the question: $\dfrac{P(s=1)}{P(s=0)} = ?$

Recall $P(s)_{\substack{\text{classical}\\ \text{statistics}}} = Ce^{-\beta E_s}$

$$\text{where } \beta = \frac{1}{kT}$$

$$\text{and } C = \left[\sum_s e^{-\beta E_s}\right]^{-1}.$$

So $\dfrac{P(s=1)}{P(s=0)} = \dfrac{Ce^{-\beta E_1}}{Ce^{-\beta E_0}} = e^{-\beta(E_1 - E_0)}.$

Plug in:

$$\frac{P(s=1)}{P(s=0)} = \exp\left[-\frac{1}{\left(8.63\times 10^{-5}\,\dfrac{eV}{K}\right)(300K)}\left\{(-3.4eV)-(-13.6eV)\right\}\right] = e^{-394}.$$

SMALL!

We can conclude that $\dfrac{P(s=1)}{P(s=0)} = \exp\left[-\dfrac{(E_1 - E_0)}{kT}\right] \approx 0$ for $(E_1 - E_0) >> kT$.

That is: the probability for excitation is negligibly small if $T << \dfrac{(E_1 - E_0)}{k}$.

Define: the *excitation temperature* T_e of a system is defined by

$$T_e \equiv \frac{(E_1 - E_0)}{k}.$$

It is the temperature above which there is a non-negligible probability that the system's particles will populate levels above the ground state.

IV. Degeneracy and multi-state systems

Suppose n_s states all have the same energy E_s, "level E_s is n-fold degenerate."
Suppose that the probability for the system to be in any particular state "s" is P_s.
Then the probability P_{E_s} that the system has energy E_s is: $P_{E_s} = n_s P_s$.

If there are several *excited* states ("e") of similar energy,
and several *ground* states ("g") of similar energy,

$$\frac{P(\text{particle is in any excited state})}{P(\text{particle is in any ground state})} = \frac{\sum\limits_{\substack{\text{all excited}\\\text{states "e"}}} Ce^{-\beta E_e}}{\sum\limits_{\substack{\text{all ground}\\\text{states "g"}}} Ce^{-\beta E_g}} = \frac{\sum\limits_{\substack{\text{all excited}\\\text{states "e"}}} e^{-\beta E_e}}{\sum\limits_{\substack{\text{all ground}\\\text{states "g"}}} e^{-\beta E_g}}$$

Suppose all excited states "e" have nearly the same energy.

Then E_e is a constant uninfluenced by the summation: $\displaystyle\sum_{\substack{\text{all excited}\\ \text{states "e"}}} e^{-bE_e} \Rightarrow e^{-bE_e}\left(\sum_{\substack{\text{all excited}\\ \text{states "e"}}} 1\right) = e^{-bE_e}\cdot n_e$

Suppose all ground states "g" have the same energy.

Then E_g is a constant uninfluenced by the summation: $\displaystyle\sum_{\substack{\text{all ground}\\ \text{states "g"}}} e^{-bE_g} \Rightarrow e^{-bE_g}\left(\sum_{\substack{\text{all ground}\\ \text{states "g"}}} 1\right) = e^{-bE_g}\cdot n_g$

Then $\displaystyle\frac{P(\text{particle is in any excited state})}{P(\text{particle is in any ground state})} = \frac{e^{-bE_e}\cdot n_e}{e^{-bE_g}\cdot n_g} = \left(\frac{n_e}{n_g}\right)e^{-b(E_e - E_g)}.$

This $(E_e - E_g)$ is called the "band gap."

V. Equipartition

Recall the Equipartition Theorem:

"If a system described by classical statistical mechanics is in equilibrium at the Kelvin temperature T, every independent quadratic term in its energy has a mean value equal to $\frac{1}{2}kT$."

We now prove this.

Consider a degree of freedom which is storing energy $E = bq^2$, where q is generalized x or p.

Recall the formula for the mean value of anything:

$$\bar{E} = \sum_{states\ s} P_s E_s$$

Here E_s is the energy of the system when in state "s"

Here P_s is the probability that the system is in state "s"

Plug in $P_s = Ce^{-\beta E_s} = \dfrac{e^{-\beta E_s}}{\sum_s e^{-\beta E_s}}$

$$\bar{E} = \frac{\sum_s e^{-\beta E_s} E_s}{\sum_s e^{-\beta E_s}}$$

Approximate $\sum$ by $\int dq$.

Plug in $E = bq^2$.

$$\bar{E} = \frac{\int dq e^{-\beta b q^2} b q^2}{\int dq e^{-\beta b q^2}}$$

$$= -\frac{\partial}{\partial \beta} \ln\left[\int dq e^{-\beta b q^2}\right]$$

Let $y = q\sqrt{\beta}$, so $q = \frac{y}{\sqrt{\beta}}$

Then $\beta b q^2 = b y^2$

and $dq = \frac{1}{\sqrt{\beta}} dy$

$$\bar{E} = -\frac{\partial}{\partial b}\ln\left[\int \frac{1}{\sqrt{b}}\, dy e^{-by^2}\right]$$

$$= -\frac{\partial}{\partial b}\ln\left[b^{-1/2}\int dy e^{-by^2}\right]$$

$$= -\frac{\partial}{\partial b}\left\{-\frac{1}{2}\ln b + \ln\left[\int dy e^{-by^2}\right]\right\}$$

Once this integral has been done, it will have no dependence on b,

so $\frac{\partial}{\partial b}$ acting on it will produce zero.

$$= -\frac{\partial}{\partial b}\left\{-\frac{1}{2}\ln b\right\}$$

$$= \frac{1}{2}\cdot\frac{1}{b}$$

But $b \equiv \frac{1}{kT}$

$$\bar{E} = \frac{1}{2}kT$$

per degree of freedom expressed as bq^2.

I. Heat capacities and dormant degrees of freedom
II. Brownian motion
III. Particle velocities in gases

Please read the slides on Transport Processes linked to the course webpage.

I. Heat capacities and dormant degrees of freedom

Plan for this section:

0) Recall that $g = \frac{C_V}{C_P} = \frac{u+2}{u}$ where u is number of dof of the species under consideration.

1) Calculate the theoretical g for a gas, using classical physics.

2) See that this prediction does not agree with data

3) Show how quantum mechanics explains the difference.

We now carry out the plan.

1) Recall the classical prediction for number of degrees of freedom (u) of a gas:

We used a table (*see page* 12 *of these lectures*) to count generalized coordinates, then assessed which of them contribute to degrees of freedom. For a system of molecules with N atoms per molecule:

 # generalized position coordinates $x_i = 3N$

3 are due to COM location

X are due to COM angular orientation

$$\text{where } X=\begin{cases} 0 \text{ for monatomic molecule} \\ 2 \text{ for linear molecule} \\ 3 \text{ for any other molecule} \end{cases}$$

Total needed to describe COM: 3+X

To make everything in this column sum to 3N, there must be 3N-(3+X) vibrational separations storing PE.

 # generalized momentum coordinates $p_i = 3N$

3 are due to COM momentum

X are due to COM angular momentum

$$\text{where } X=\begin{cases} 0 \text{ for monatomic molecule} \\ 2 \text{ for linear molecule} \\ 3 \text{ for any other molecule} \end{cases}$$

Total needed to describe COM: 3+X

Similarly, there must be 3N-(3+X) vibrational momenta storing KE.

Bear in mind that these coordinates do not contribute degrees of freedom in a field-free problem.

Let us use the table to make predictions for various gas species in a field-free environment.

Species	X	N	u=#dof	$g=\frac{u+2}{u}$
Monatomic gas (He, Kr, Ar)	0	1	3 [all due to COM KE]	$\frac{3+2}{3}=1.667$
diatomic (linear) gas (H_2,O_2)	2	2	7 [count: 3+2+2(3N-5)]	$\frac{7+2}{7}=1.286$
8-atomic gas (ethane, C_2H_6)	3	8	42[count: 3+3+2(3N-6)]	$\frac{42+2}{42}=1.05$

(We could translate these predictions from g to c_V, which is what is used by Stowe.)

2) Now compare to data, using Table 40-1 from the Feynman Lectures:

Species	Measured g (recorded at temperatures in the range 93-573 K)	
He	1.66	These match the prediction
Kr	1.68	
Ar	1.67	
H_2	1.40	These don't match the prediction, but they would if u were 5 instead of 7. Are there no vibrations?
O_2	1.40	
C_2H_6	1.22	These don't match, but would if u were 10 instead of 42.

Comparison to data, continued:

Classical theory predicts that u is not a function of temperature, but see Feynman Figure 40-6:

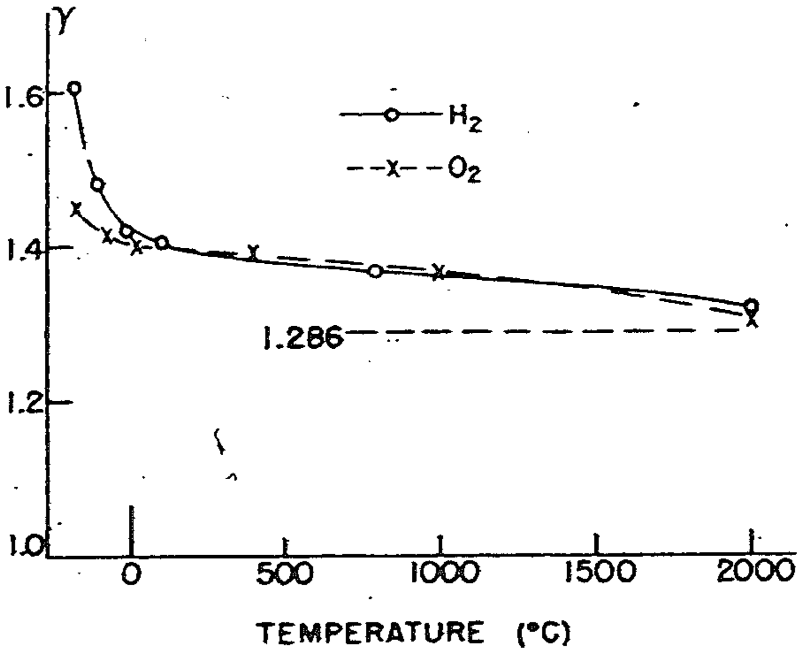
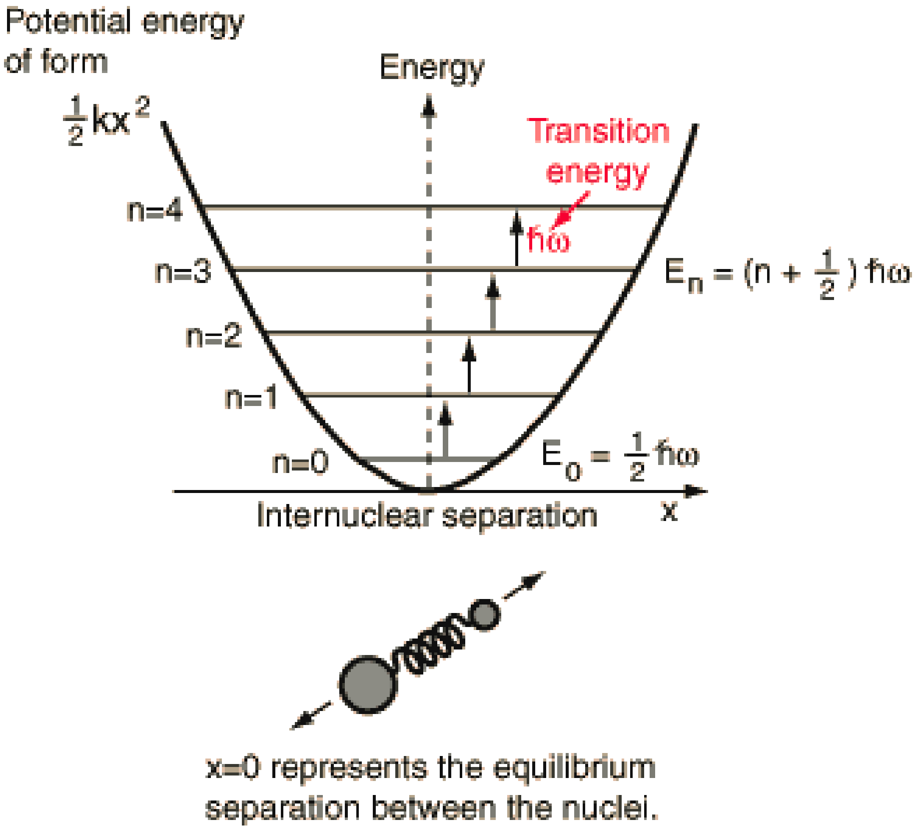


Fig. 40–6. Experimental values of γ as a function of temperature for hydrogen and oxygen. Classical theory predicts $\gamma = 1.286$, independent of temperature.

The theoretically predicted value for diatomic molecules, $\gamma=1.286$, does not onset until T=2273 K.

3) How quantum mechanics explains this

Recall from Physics 330 that both rotational and vibrational motion are quantized. Specifically,



$$E_{vib} = \left(n_{vib} + \tfrac{1}{2}\right)\hbar\omega_0$$

where $n_{vib} \in (0,\ 1,\ 2,\ \ldots)$

$$\hbar = 1.06\times10^{-34}\, J - \text{sec}$$

$$\omega_0 = \sqrt{\frac{k_{\text{"spring constant"}}}{m}}$$

$m =$ mass of bound particle

Similarly for angular momentum,

$$L = \sqrt{\ell(\ell+1)}\hbar \qquad\qquad \ell \in (0,\ 1,\ 2,\ldots)$$

so since $E = \dfrac{L^2}{2I}$,

$[I = \text{moment of inertia}]$

$$E_{rot} = \ell(\ell+1)\frac{\hbar^2}{2I}$$

Please accept for now that if a system is in its ground vibrational state ($n_{vib} = 0$), it doesn't vibrate (i.e., the $\frac{1}{2}$ doesn't contribute, to be explained later).

Similarly, for □ = 0, it doesn't rotate.

So $\mathrm{E}_{\substack{\min \\ \mathrm{vib}}} = 1.5\,\square\omega_0$

and $\mathrm{E}_{\substack{\min \\ \mathrm{rot}}} = \dfrac{2\square^2}{2I} = \dfrac{\square^2}{I}$.

Now recall we just showed that in general,

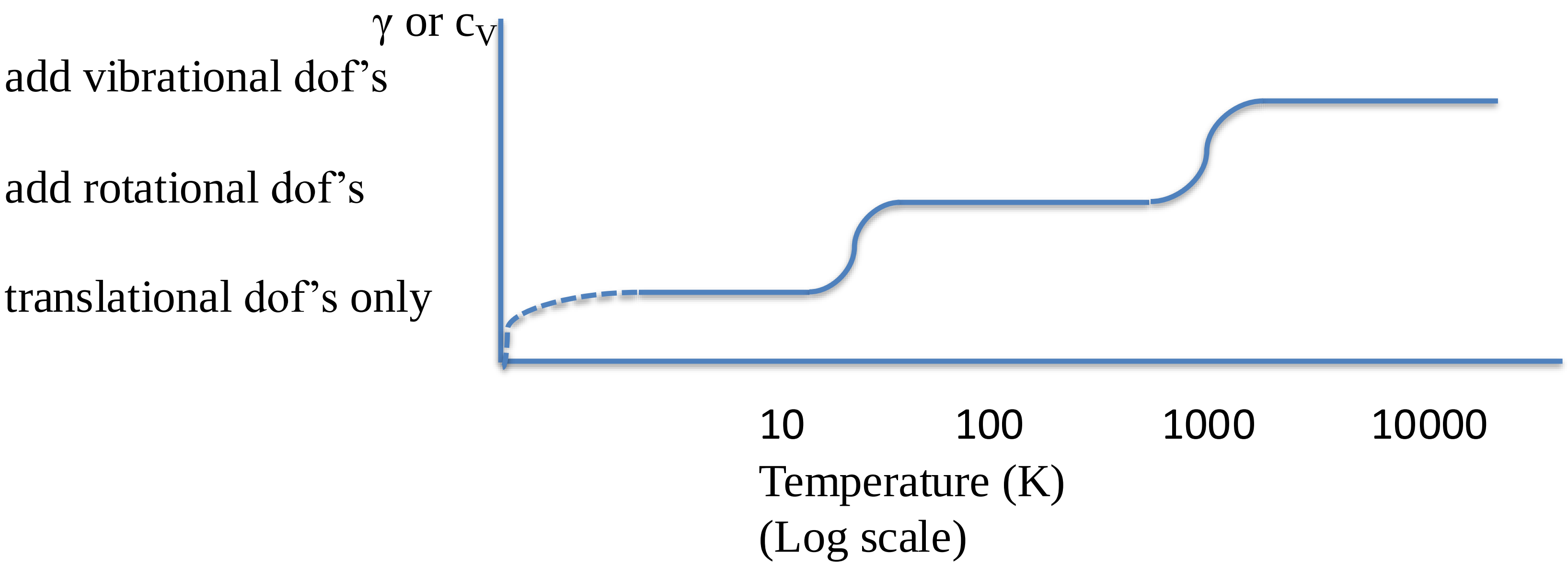
$$\frac{\text{Prob(excited)}}{\text{Prob(ground)}} = e^{-\beta\left(E_{\text{excited}} - E_{\text{ground}}\right)} = e^{-\left(E_{\text{excited}} - E_{\text{ground}}\right)/kT}.$$

So if $T \ll \dfrac{E_{excited} - E_{ground}}{k}$, the system has a low probability of being in its excited state.

For vibrational excitation, $\dfrac{E_{excited} - E_{ground}}{k} \approx \dfrac{\left(1.5\,\square\omega_0 - 0.5\,\square\omega_0\right)}{k} >_{typically} 2000K$

For rotational excitation, $\dfrac{E_{excited} - E_{ground}}{k} \approx \dfrac{\square^2}{I} >_{typically} 2K$

So we expect, for gases:



A similar effect occurs in solids. We observe it through their heat capacities:

Recall their $E = \dfrac{uNkT}{2}$

where $u =$ #dof per molecule

and $N =$ # molecules

But $Nk = nR$, for $n =$ #moles, $R =$ universal gas constant

Then $E = \dfrac{\upsilon nRT}{2}$

Consider a solid with N atoms.

$$\#\text{dof} = 6N - 12 \approx 6N$$

$$\frac{\#\text{dof}}{\text{atom}} = 6$$

Then $E = \dfrac{6nRT}{2}$

Recall $C_V = \left.\dfrac{\partial Q}{\partial T}\right|_V$

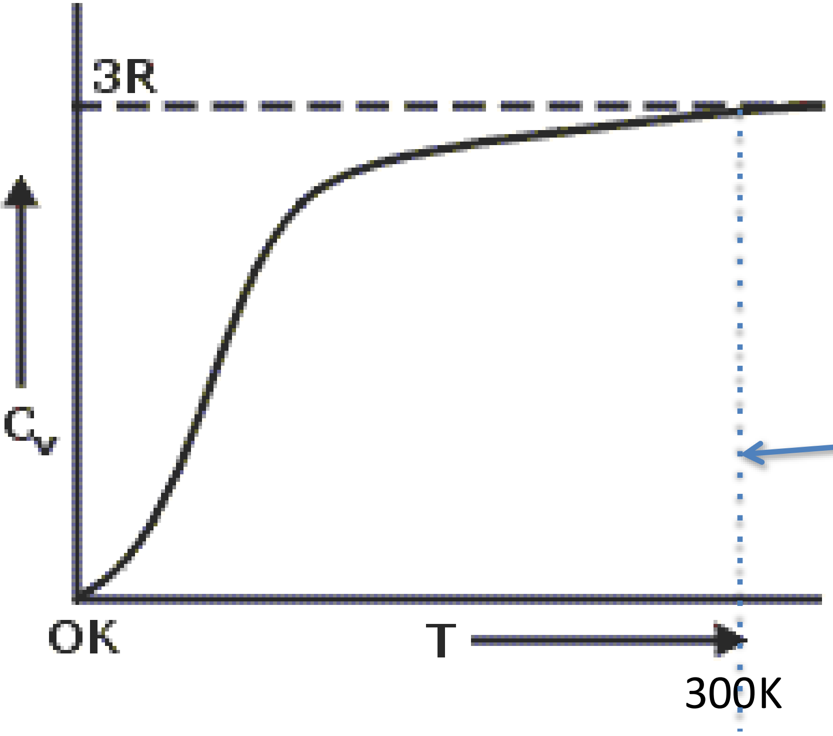
But $\Delta E = \Delta Q - p\Delta V + \mu\Delta N$, so

$$C_V = \left.\frac{\partial E}{\partial T}\right|_V \Rightarrow \frac{\partial\left(\frac{6nRT}{2}\right)}{\partial T} = 3nR$$

So *classically* we expect $c_V \equiv \dfrac{C_V}{n} = 3R$

So *classically* we expect $\dfrac{c_V}{R} = 3$ i.e., absolutely constant.

What is actually seen, experimentally:



Variation of C_V with T

Early experimenters could only measure at room temperature (here) so they did not see the fall-off at low temperature. Hence the so-called Dulong-Petit "Law" of 1819, that says $c_V = 3R$, is just a high-temperature approximation.