



THE UNIVERSITY
OF QUEENSLAND
AUSTRALIA

AERO4470

High Temperature Gas Dynamics Lecture 2: Equilibrium Mixtures

C.M. James (using lectures written by S.W. Lewis with some changes)

Centre for Hypersonics, The School of Mechanical and Mining Engineering,
The University of Queensland, Brisbane, QLD, 4072, Australia

28th February 2024



Introduction

Learning Outcomes

- ▶ Today our end goal is to be able to calculate the composition and properties of an equilibrium reacting mixture, and apply this to hypersonic flow. Specifically we will:
 - ▶ Revisit classical thermodynamics and derive a thermodynamics-based understanding of what an equilibrium mixture is and how it behaves.
 - ▶ Outline a calculation procedure for finding the equilibrium composition.
 - ▶ Outline a procedure for solving across a shock under equilibrium conditions.
- ▶ Through this, I will try to strike a balance between showing the theoretical background needed for deep understanding, whilst not getting overly caught up in the mathematical details.

Learning Outcomes

- ▶ Recall from last lecture this plot which shows the equilibrium chemical composition of air for varying temperature at $p = 1 \text{ atm}$.
- ▶ In this lecture we will aim to teach you how to do these calculations yourself.

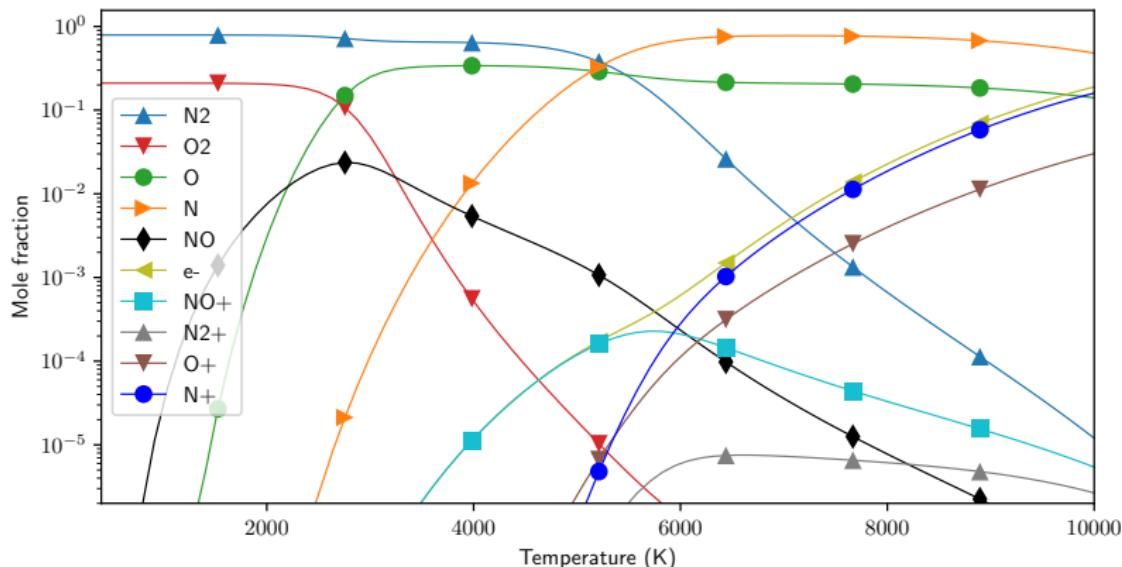


Figure: Equilibrium air composition at atmospheric pressure and varying temperature.

Some Recommended Resources

- ▶ Section 10.4 to the end of Chapter 10 from Anderson [1].
- ▶ Chapter 14 of Anderson [1] for the applications of equilibrium chemistry in hypersonic flows (if you want to go a bit deeper).
- ▶ The procedure to calculate the state behind an equilibrium normal shock which I present in this lecture is from Bertin [2].

Classical Thermodynamics

First Law of Thermodynamics

- Internal energy of a system can be changed either by heat transfer or by doing work:

$$\delta Q + \delta W = dE \quad (1)$$

- Assuming no shaft work, then work done by compression (-ve dV) or expansion (+ve dV):

$$\delta W = -pdV \quad (2)$$

$$\delta Q = dE + pdV$$

$$\delta q = de + pdv \quad (3)$$

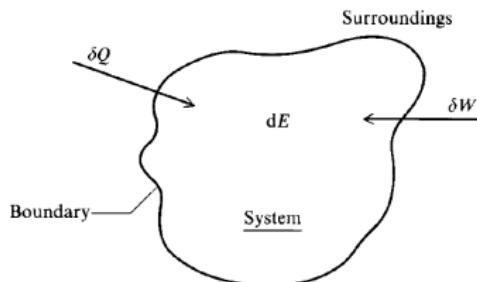


Figure: Thermodynamic system [3].

- From the definition of enthalpy ($h = e + pv$) we get:

$$dh = de + pdv + vdp$$

$$\delta q = dh - vdp \quad (4)$$

- So far, all relations are fundamental and applicable to any gas.

Perfect Gas Relationship Between C_p and C_v

- Now we will obtain a general expression relating C_p and C_v .
- Assuming an equilibrium system: $e = \text{internal energy}$

partial of internal energy $e = e(T, v)$

*over partial temp @
constant volume.* $de = \left(\frac{\partial e}{\partial T}\right)_v dT + \left(\frac{\partial e}{\partial v}\right)_T dv$ (5)

- The definition of C_v is:

$$C_v = \left(\frac{\partial e}{\partial T}\right)_v \quad (6)$$

$$\therefore de = C_v dT + \left(\frac{\partial e}{\partial v}\right)_T dv \quad (7)$$

- Subbing (7) into (3) we get: *small = specific*

$$\delta q = C_v dT + \left[\left(\frac{\partial e}{\partial v}\right)_T + p \right] dv \quad (8)$$

$\Delta \text{heat} = C_v \cdot dT + \left(\frac{\partial e}{\partial v} + \text{pressure}\right) d\text{volume}$

Perfect Gas Relationship Between C_p and C_v

specific heat @ constant temp = $\frac{\partial h}{\partial T}$

- From the definition of C_p :

= $\frac{\partial q}{\partial T}$
both at
constant
pressure
 C_p .

$$\underline{C_p} \equiv \left(\frac{\partial h}{\partial T} \right)_p \equiv \left(\frac{\partial q}{\partial T} \right)_p \quad (9)$$

- With constant pressure, Eq. (8) becomes:

$$\left(\frac{\partial q}{\partial T} \right)_p = C_v + \left[\left(\frac{\partial e}{\partial v} \right)_T + p \right] \left(\frac{\partial v}{\partial T} \right)_p \quad (10)$$

- We can now obtain a generalised expression relating C_p and C_v :

*

$$C_p - C_v = \left[\left(\frac{\partial e}{\partial v} \right)_T + p \right] \left(\frac{\partial v}{\partial T} \right)_p$$

(11)

- This relation applies to *any* gas, including all variations of perfect gas discussed in the last lecture *and* real gases.

Perfect Gas Relationship Between C_p and C_v

- If we use the perfect-gas equation of state (i.e. forget about real gas effects which we said were unimportant for hypersonic flows):

$$v = \frac{RT}{p}$$

$$\therefore \left(\frac{\partial v}{\partial T} \right)_p = \frac{R}{p} \quad (12)$$

- Subbing (12) into (11):

$$C_p - C_v = R + \frac{R}{p} \left(\frac{\partial e}{\partial v} \right)_T \quad (13)$$

- This works for any perfect gas, including chemically reacting mixtures where $e = e(T, v)$ and $(\delta e / \delta v)_T \neq 0$. For both calorically perfect gas AND thermally perfect gases we have $(\partial e / \partial v)_T = 0$, and obtain the familiar:

$$C_p - C_v = R \quad (14)$$

Second Law of Thermodynamics

- ▶ Introduces the *state variable* called entropy. The change in entropy for a system is given by:

$$ds = \frac{\delta q}{T} + ds_{irrev} \quad (15)$$

- ▶ Dissipative processes always increase entropy:

$$ds_{irrev} > 0$$

$$\therefore ds > \frac{\delta q}{T} \quad (16)$$

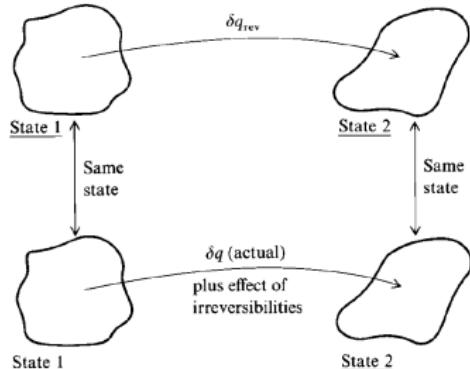


Figure: Illustration of second law [3].

- ▶ For an adiabatic process ($\delta q = 0$):

$$ds > 0 \quad (17)$$

Second Law of Thermodynamics

- Recall for a *calorically perfect gas only*:

$$s_2 - s_1 = C_p \ln \left(\frac{T_2}{T_1} \right) - R \ln \left(\frac{p_2}{p_1} \right) \quad (18)$$

$$s = C_p \ln \left(\frac{T}{T_{ref}} \right) - R \ln \left(\frac{p}{p_{ref}} \right) + s_{ref} \quad (19)$$

- For now we'll use Anderson's convention of lowercase being mass-based, and uppercase being mole-based. Some derivation yields an analogous expression for an equilibrium mixture:

$$S = \sum_i X_i \left[\int_{T_{ref}}^T C_{p,i} \left(\frac{dT}{T} \right) - R_u \ln \left(\frac{p_i}{p_{ref}} \right) \right] + S_{ref} \quad (20)$$

- Where $S_{ref} = \sum_i X_i S_{i,ref}$

Gibbs Free Energy

- Now we will introduce a “defined” thermodynamic quantity, the Gibbs free energy:

$$G \equiv H - TS \quad (21)$$

- Conceptually, this quantity is the maximum amount of reversible work that may be performed by a thermodynamic system at a constant temperature and pressure.
- Under thermochemical equilibrium, $G = G(p, T)$. However, for chemical nonequilibrium:

$$G = G(T, p, N_1, N_2, \dots, N_i, \dots, N_n) \quad (22)$$

- Where N is *particles per mole of mixture*. It can be shown that the entropy generation by nonequilibrium chemical reactions is:

$$-TdS_{irrev} = \sum_i \frac{\partial G}{\partial N_i} dN_i = 0 \text{ for EQ} \quad (23)$$

Gibbs Free Energy

- For a mixture, we can express G as:

$$G = \sum_i N_i g'_i = N_1 g'_1 + N_2 g'_2 + \cdots + N_i g'_i + \cdots + N_n g'_n \quad (24)$$

- where g'_i is Gibbs free energy of species i per particle.
- The derivative is:

$$\frac{\partial G}{\partial N_i} = g'_i \quad (25)$$

- Subbing (25) into (23):

$$dS_{irrev} = -\frac{1}{T} \sum_i g'_i dN_i \quad (26)$$

Gibbs Free Energy

- We can insert Avogadro's number into the previous equation (Eq. 26):

$$dS_{irrev} = -\frac{1}{T} \sum_i (N_A g'_i) \left(\frac{dN_i}{N_A} \right) \quad (27)$$

- Using $N_A g'_i = G_i$ (Gibbs free energy of species i per mole of i) and $\frac{dN_i}{N_A} = d\mathcal{N}_i$ (change in the number of moles of i) we get:

$$dS_{irrev} = -\frac{1}{T} \sum_i G_i d\mathcal{N}_i \quad (28)$$

- This now provides a tool to solve for an equilibrium system, where by definition $dS_{irrev} = 0$. We must simply find a way to satisfy:

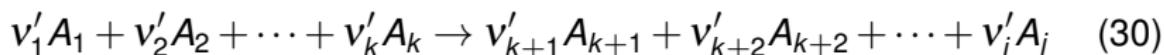
$$\sum_i G_i d\mathcal{N}_i = 0$$

(29)

The Equilibrium Constant

The Equilibrium Constant

- ▶ We have found a thermodynamic condition for chemical equilibrium. Now we will see how to take a set of chemical reactions and apply this criterion, resulting in what's known as the *equilibrium constant*.
- ▶ First, consider a generalised form for a chemical reaction:



- ▶ where A_i indicates species i , and v'_i is the stoichiometric mole number for species i . On the LHS are *reactants*, and on the RHS are *products*.
- ▶ This can be compactly expressed as:

$$0 = \sum_{i=1}^j v_i A_i \quad (31)$$

- ▶ where v_i is the stoichiometric mole number and it is *negative for reactants and positive for products*.

Equilibrium Constant Motivating Example

- ▶ Let us start by considering H_2 somehow turning into $2H$.
- ▶ The reaction is $H_2 \rightarrow 2H$.

$A_1 = H_2, v_1 = -1$ (negative as H_2 is a reactant)

$A_2 = H, v_2 = 2$ (positive as H is a product)

- ▶ We could also consider the equivalent $\frac{1}{2} H_2 \rightarrow H$:

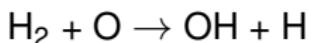
$A_1 = H_2, v_1 = -\frac{1}{2}$

$A_2 = H, v_2 = 1$

- ▶ (Which is still correct as it is in proportion, but generally whole numbers are preferred with this stuff.)

Equilibrium Constant Motivating Example

- ▶ Now lets try something a bit more complicated:



$A_1 = \text{H}_2, v_1 = -1$ (negative as H_2 is a reactant)

$A_2 = \text{O}, v_2 = -1$ (negative as O is a reactant)

$A_3 = \text{OH}, v_3 = 1$ (positive as OH is a product)

$A_4 = \text{H}, v_4 = 1$ (positive as H is a product)

Equilibrium Constant Derivation

- ▶ Note that any change in $d\mathcal{N}_i$ must be proportional to v_i :

$$d\mathcal{N}_1 : d\mathcal{N}_2 : \cdots : d\mathcal{N}_j = v_1 : v_2 : \cdots : v_j \quad (32)$$

- ▶ Defining a proportionality constant $d\xi$:

$$\frac{d\mathcal{N}_1}{v_1} = \frac{d\mathcal{N}_2}{v_2} = \frac{d\mathcal{N}_j}{v_j} = d\xi \text{ or:} \quad (33)$$

$$d\mathcal{N}_1 = v_1 d\xi$$

$$d\mathcal{N}_2 = v_2 d\xi$$

⋮

$$d\mathcal{N}_j = v_j d\xi$$

Equilibrium Constant Derivation

- The quantity ξ is known as the “degree of advancement”, and is effectively a “dummy” variable to get us to a form we want. If we define a reference condition where $\xi = 0$ and $\mathcal{N}_i = \mathcal{N}_{i,\text{ref}}$:

$$\int_{\mathcal{N}_{i,\text{ref}}}^{\mathcal{N}_i} d\mathcal{N}_i = \int_0^\xi v_i d\xi$$

$$\mathcal{N}_i - \mathcal{N}_{i,\text{ref}} = v_i \xi \quad (34)$$

- From the previous slide we have $d\mathcal{N}_i = v_i d\xi$, we can now express Eq. (29) as:

$$\sum_i G_i v_i d\xi = 0 \quad (35)$$

- As $d\xi$ is the same for all species, it is a constant value, so:

$$d\xi \left(\sum_i G_i v_i \right) = 0 \quad (36)$$

$\sum_i G_i v_i = 0$

we are now close to a solution! (37)

Equilibrium Constant Derivation

- We have reached another form of the equilibrium condition:

$$\sum_i G_i v_i = 0$$

- Now consider G :

$$G_i = H_i - TS_i$$

$$G_i = H_i - T \left(\int_{T_{ref}}^T C_{pi} \frac{dT}{T} - R_u \ln \frac{p_i}{p_{ref}} + S_{i,ref} \right) \quad (38)$$

- If we contrive to use atm as the unit for pressure, and set $p_{ref} = 1$, we can take advantage of some mathematical trickery to reach:

$$\prod_i p_i^{v_i} = \exp \left(- \sum_i v_i \frac{G_i^{p_i=1}}{R_u T} \right) \quad (39)$$

Equilibrium Constant Derivation

- If we define:

$$\Delta G^{p=1} \equiv \sum_i v_i G_i^{p_i=1} = (G^{p=1} \text{ for products}) - (G^{p=1} \text{ for reactants}) \quad (40)$$

- Then we finally reach the end of our journey and the definition of the equilibrium constant (remembering that \prod is the product):

$$\prod_i p_i^{v_i} = e^{-\Delta G^{p=1}/R_u T} \equiv K_p(T) \quad (41)$$

- Note that $K_p(T)$ is a function of T only. This can either be obtained from experiment, data tables, or calculated from first principles by statistical mechanics.
- Various data tables exist. I find McBride [4] et al.'s the easiest to use:
<https://ntrs.nasa.gov/archive/nasa/casi.ntrs.nasa.gov/19630013835.pdf>
- Now we will see how to put this into practice!

Equilibrium Composition Example

- ▶ Now for a much more in depth example, let us consider how to find the equilibrium composition related to hydrogen combustion.

Equilibrium Composition Example

- ▶ Now for a much more in depth example, let us consider how to find the equilibrium composition related to hydrogen combustion.
- ▶ We have four reactions as hydrogen combustion actually occurs via several intermediate steps:

- 1 $\text{H}_2 \rightarrow 2\text{H}$
- 2 $\text{O}_2 \rightarrow 2\text{O}$
- 3 $\text{H}_2 + \text{O} \rightarrow \text{OH} + \text{H}$
- 4 $\text{OH} + \text{H} \rightarrow \text{H}_2\text{O}$

Equilibrium Composition Example

- ▶ Let us start by considering reaction 1:
 - ▶ $A_1 = \text{H}_2$, $v_1 = -1$ (negative as H_2 is a reactant)
 - ▶ $A_2 = \text{H}$, $v_2 = 2$ (positive as H is a product)

$$K_{p_1}(T) = \prod_i p_i^{v_i} = p_H^2 \cdot p_{\text{H}_2}^{-1} = \frac{p_H^2}{p_{\text{H}_2}} = e^{-\Delta G^{p=1}/R_u T} \quad (1)$$

- ▶ A quick note, if we used our equivalent $\frac{1}{2} \text{H}_2 \rightarrow \text{H}$:
 - ▶ $K_{p_1} = \frac{p_H}{\sqrt{p_{\text{H}_2}}} \neq \frac{p_H^2}{p_{\text{H}_2}}$ different value!
- ▶ It won't change the final answer though.

Equilibrium Composition Example

- ▶ For the other three reactions we have:

$$K_{p_2}(T) = \frac{p_O^2}{p_{O_2}} \quad (2)$$

$$K_{p_3}(T) = \frac{p_{OH}p_H}{p_{H_2}p_O} \quad (3)$$

$$K_{p_4}(T) = \frac{p_{H_2O}}{p_{OH}p_H} \quad (4)$$

- ▶ Thinking about what we have now, we have six unknowns:
 - ▶ p_{H_2} , p_{O_2} , p_H , p_O , p_{OH} , p_{H_2O}
- ▶ But we only have four equations from our equilibrium constants.
- ▶ We need two more to solve the problem.

Equilibrium Composition Example

- We know our starting pressure, and we assume that the process is isentropic, so Dalton's law of partial pressures from the last lecture is our fifth equation:

$$p = p_{H_2} + p_{O_2} + p_H + p_O + p_{OH} + p_{H_2O} \quad (5)$$

- Our final equation is the conversation of nuclei, which will be based on our initial conditions:

$$\frac{N_H}{N_O} = \frac{N_A(2\eta_{H_2} + \eta_H + \eta_{OH} + 2\eta_{H_2O})}{N_A(2\eta_{O_2} + \eta_O + \eta_{OH} + \eta_{H_2O})}$$

- which, if we note that $\eta_i = \frac{p_i v}{R_u T}$ and v , R_u and T are all constant for our system, becomes:

$$\frac{N_H}{N_O} = \frac{2p_{H_2} + p_H + p_{OH} + 2p_{H_2O}}{2p_{O_2} + p_O + p_{OH} + p_{H_2O}} \quad (6)$$

Equilibrium Composition Example

- ▶ Now that we have enough equations, we just need numbers for K_p .
- ▶ We will use the $\text{H}_2 \rightarrow 2\text{H}$ reaction and a temperature of 1,500 K for our example:

$$K_{p_1}(T) = \prod_i p_i^{v_i} = p_H^2 \cdot p_{H_2}^{-1} = \frac{p_H^2}{p_{H_2}} = e^{-\Delta G^{p=1}/R_u T}$$

Equilibrium Composition Example

- To get our Gibbs free energy terms we have to go looking in McBride et al. [4]:

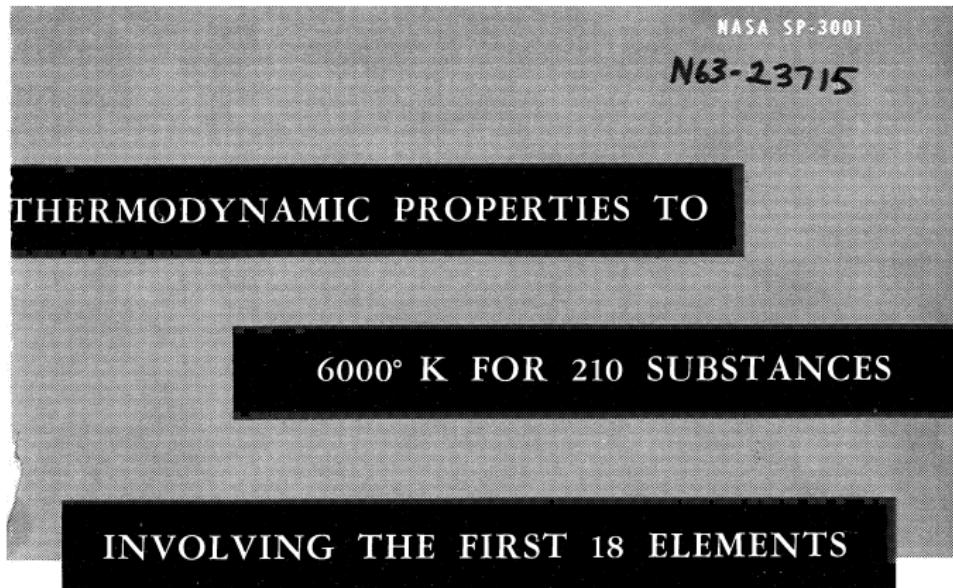


Figure: Cover of McBride et al. [4].

Equilibrium Composition Example

- To get our Gibbs free energy terms we have to go looking in McBride et al. [4]:

CONTENTS	
	Page
SUMMARY	1
INTRODUCTION	1
THERMODYNAMIC FUNCTIONS OF IDEAL GASES	2
Internal Partition Function for Diatomic and Polyatomic Molecules	3
General form	3
Closed form for rotation	4
Closed form for rotation and vibration	5
Contribution of higher electronic states	6
Internal Partition Function for Monatomic Gases	6
THERMODYNAMIC FUNCTIONS OF CONDENSED SUBSTANCES	8
DISCUSSION OF TABLES	9
Molecular Constants	9
Estimation techniques	9
Adjustment for isotopes	10
Moments of inertia	10
Thermodynamic Properties	11
Assigned reference elements	12
Assigned enthalpy values	12
Units of expression	12
Equilibrium constants	13
Physical constants	14
Temperature Coefficients for Thermodynamic Functions	14
APPENDICES	16
A - SYMBOLS	16
B - PARTITION FUNCTIONS AND THEIR DERIVATIVES FOR DIATOMIC AND POLYATOMIC MOLECULES	20
C - DISCUSSION OF PARTICULAR SUBSTANCES	27
REFERENCES	56
TABLES	
I - MOLECULAR CONSTANTS OF DIATOMIC GASES	64
II - MOLECULAR CONSTANTS OF POLYATOMIC GASES	68
III - THERMODYNAMIC PROPERTIES	91
IV - HEATS OF FORMATION	301
V - TEMPERATURE COEFFICIENTS FOR THERMODYNAMIC FUNCTIONS	308
INDEX TO SUBSTANCES	327

Figure: Contents of McBride et al. [4].

Equilibrium Composition Example

- ▶ Bonnie J. McBride worked at NASA Glenn Research Center for 48 years from 1957 until she passed away in 2005.
- ▶ Her life's work focused on the compilation and maintenance of NASA's physical constants for high-temperature gases and along with her colleague, Sanford Gordon, she wrote and maintained NASA's chemical equilibrium codes, such as the ubiquitous Chemical Equilibrium with Applications (CEA) program which we will use in this course and most of us in hypersonics use daily in our work lives.



Figure: Bonnie McBride at work in 1964 [5].



Figure: NASA Glenn Hall of Fame plaque for Sanford Gordon and Bonnie J. McBride [5].

Equilibrium Composition Example

- Here F_T is ‘free energy’ i.e. Gibbs free energy and everything is in American units:

184

 TABLE III. - Continued. THERMODYNAMIC PROPERTIES
(194) Σ (gas); molecular weight, 1.000

$T,$ $^{\circ}\text{K}$	$C_p^0,$ cal/mole $^{\circ}\text{K}$	$H_f^0 - H_f^0_{\text{ref}},$ cal/mole	$S_f^0,$ cal/mole $^{\circ}\text{K}$	$-HF_f^0 - H_f^0,$ cal/mole	$H_f^0,$ cal/mole	Formation from assigned reference elements	Formation from gaseous atoms		
						$(\Delta H_f^0)^0,$ cal/mole	$\log_{10} K_f$	$\Delta H_f^0,$ cal/mole	$\log_{10} K$
0		0	0	0	0	0	0	0	0
100	4.951×1	4.951 $\times 1$	21.963×1	1494.7	10041.5	21478.6	0	0	0
200	4.951×1	9.902 $\times 1$	25.458×1	4098.1	11121.5	21478.6	-11.939	0	0
300	4.951×1	14.853 $\times 1$	27.423×1	4809.4	13160.1	21478.6	-5.415	0	0
400	4.951×1	19.794 $\times 1$	27.423×1	4756.9	23210.9	21478.6	-3.8	0	0
500	4.951×1	24.735 $\times 1$	27.423×1	4222.2	32100.9	21478.6	-2.17	0	0
600	4.951×1	29.676 $\times 1$	27.423×1	3790.9	41290.6	21478.6	-0.917	0	0
700	4.951×1	34.617 $\times 1$	27.423×1	3269.2	50480.4	21478.6	-0.198	0	0
800	4.951×1	39.558 $\times 1$	27.423×1	2747.5	59670.2	21478.6	0.538	0	0
900	4.951×1	44.499 $\times 1$	27.423×1	2225.7	68860.0	21478.6	1.178	0	0
1000	4.951×1	49.439 $\times 1$	27.423×1	1704.0	78050.8	21478.6	1.817	0	0
1100	4.951×1	54.379 $\times 1$	27.423×1	1182.3	87240.6	21478.6	2.456	0	0
1200	4.951×1	59.319 $\times 1$	27.423×1	660.6	96430.4	21478.6	3.095	0	0
1300	4.951×1	64.259 $\times 1$	27.423×1	16.3	105620.2	21478.6	3.734	0	0
1400	4.951×1	69.199 $\times 1$	27.423×1	-44.7	114810.0	21478.6	4.373	0	0
1500	4.951×1	74.139 $\times 1$	27.423×1	-97.4	124000.8	21478.6	5.012	0	0
1600	4.951×1	79.079 $\times 1$	27.423×1	-150.1	133190.6	21478.6	5.651	0	0
1700	4.951×1	83.019 $\times 1$	27.423×1	-202.8	142380.4	21478.6	6.289	0	0
1800	4.951×1	87.959 $\times 1$	27.423×1	-255.5	151570.2	21478.6	6.928	0	0
1900	4.951×1	92.899 $\times 1$	27.423×1	-308.2	160760.0	21478.6	7.567	0	0
2000	4.951×1	97.839 $\times 1$	27.423×1	-360.9	169950.8	21478.6	8.206	0	0
2100	4.951×1	102.779 $\times 1$	27.423×1	-413.6	179140.6	21478.6	8.845	0	0
2200	4.951×1	107.719 $\times 1$	27.423×1	-466.3	188330.4	21478.6	9.484	0	0
2300	4.951×1	112.659 $\times 1$	27.423×1	-519.0	197520.2	21478.6	10.123	0	0
2400	4.951×1	117.599 $\times 1$	27.423×1	-571.7	206710.0	21478.6	10.762	0	0
2500	4.951×1	122.539 $\times 1$	27.423×1	-624.4	215900.8	21478.6	11.401	0	0
2600	4.951×1	127.479 $\times 1$	27.423×1	-677.1	225090.6	21478.6	12.039	0	0
2700	4.951×1	132.419 $\times 1$	27.423×1	-729.8	234280.4	21478.6	12.678	0	0
2800	4.951×1	137.359 $\times 1$	27.423×1	-782.5	243470.2	21478.6	13.317	0	0
2900	4.951×1	142.299 $\times 1$	27.423×1	-835.2	252660.0	21478.6	13.956	0	0
3000	4.951×1	147.239 $\times 1$	27.423×1	-887.9	261850.8	21478.6	14.595	0	0
3100	4.951×1	152.179 $\times 1$	27.423×1	-940.6	271040.6	21478.6	15.234	0	0
3200	4.951×1	157.119 $\times 1$	27.423×1	-993.3	280230.4	21478.6	15.873	0	0
3300	4.951×1	161.959 $\times 1$	27.423×1	-1046.0	289420.2	21478.6	16.512	0	0
3400	4.951×1	166.899 $\times 1$	27.423×1	-1098.7	298610.0	21478.6	17.151	0	0
3500	4.951×1	171.839 $\times 1$	27.423×1	-1151.4	307800.8	21478.6	17.789	0	0
3600	4.951×1	176.779 $\times 1$	27.423×1	-1204.1	317000.6	21478.6	18.428	0	0
3700	4.951×1	181.719 $\times 1$	27.423×1	-1256.8	326190.4	21478.6	19.067	0	0
3800	4.951×1	186.659 $\times 1$	27.423×1	-1309.5	335380.2	21478.6	19.706	0	0
3900	4.951×1	191.599 $\times 1$	27.423×1	-1362.2	344570.0	21478.6	20.345	0	0
4000	4.951×1	196.539 $\times 1$	27.423×1	-1414.9	353760.8	21478.6	20.984	0	0
4100	4.951×1	201.479 $\times 1$	27.423×1	-1467.6	362950.6	21478.6	21.623	0	0
4200	4.951×1	206.419 $\times 1$	27.423×1	-1520.3	372140.4	21478.6	22.262	0	0
4300	4.951×1	211.359 $\times 1$	27.423×1	-1573.0	381330.2	21478.6	22.899	0	0
4400	4.951×1	216.299 $\times 1$	27.423×1	-1625.7	390520.0	21478.6	23.538	0	0
4500	4.951×1	221.239 $\times 1$	27.423×1	-1678.4	409710.8	21478.6	24.177	0	0
4600	4.951×1	226.179 $\times 1$	27.423×1	-1731.1	418900.6	21478.6	24.816	0	0
4700	4.951×1	231.119 $\times 1$	27.423×1	-1783.8	428090.4	21478.6	25.455	0	0
4800	4.951×1	236.059 $\times 1$	27.423×1	-1836.5	437280.2	21478.6	26.094	0	0
4900	4.951×1	240.999 $\times 1$	27.423×1	-1889.2	446470.0	21478.6	26.733	0	0
5000	4.951×1	245.939 $\times 1$	27.423×1	-1941.9	455660.8	21478.6	27.372	0	0
5100	4.951×1	250.879 $\times 1$	27.423×1	-1994.6	464850.6	21478.6	28.011	0	0
5200	4.951×1	255.819 $\times 1$	27.423×1	-2047.3	474040.4	21478.6	28.649	0	0
5300	4.951×1	260.759 $\times 1$	27.423×1	-2099.9	483230.2	21478.6	29.288	0	0
5400	4.951×1	265.699 $\times 1$	27.423×1	-2152.6	492420.0	21478.6	29.927	0	0
5500	4.951×1	270.639 $\times 1$	27.423×1	-2205.3	501610.8	21478.6	30.566	0	0
5600	4.951×1	275.579 $\times 1$	27.423×1	-2258.0	510800.6	21478.6	31.205	0	0
5700	4.951×1	280.519 $\times 1$	27.423×1	-2310.7	519990.4	21478.6	31.844	0	0
5800	4.951×1	285.459 $\times 1$	27.423×1	-2363.4	529180.2	21478.6	32.483	0	0
5900	4.951×1	290.399 $\times 1$	27.423×1	-2416.1	538370.0	21478.6	33.122	0	0
6000	4.951×1	295.339 $\times 1$	27.423×1	-2468.8	547560.8	21478.6	33.761	0	0
6100	4.951×1	300.279 $\times 1$	27.423×1	-2521.5	556750.6	21478.6	34.399	0	0
6200	4.951×1	305.219 $\times 1$	27.423×1	-2574.2	565940.4	21478.6	35.038	0	0
6300	4.951×1	310.159 $\times 1$	27.423×1	-2626.9	575130.2	21478.6	35.677	0	0
6400	4.951×1	315.099 $\times 1$	27.423×1	-2679.6	584320.0	21478.6	36.316	0	0
6500	4.951×1	320.039 $\times 1$	27.423×1	-2732.3	593510.8	21478.6	36.955	0	0
6600	4.951×1	324.979 $\times 1$	27.423×1	-2785.0	602700.6	21478.6	37.594	0	0
6700	4.951×1	329.919 $\times 1$	27.423×1	-2837.7	611890.4	21478.6	38.233	0	0
6800	4.951×1	334.859 $\times 1$	27.423×1	-2890.4	621080.2	21478.6	38.872	0	0
6900	4.951×1	339.799 $\times 1$	27.423×1	-2943.1	630270.0	21478.6	39.511	0	0
7000	4.951×1	344.739 $\times 1$	27.423×1	-2995.8	639460.8	21478.6	40.150	0	0
7100	4.951×1	349.679 $\times 1$	27.423×1	-3048.5	648650.6	21478.6	40.789	0	0
7200	4.951×1	354.619 $\times 1$	27.423×1	-3101.2	657840.4	21478.6	41.428	0	0
7300	4.951×1	359.559 $\times 1$	27.423×1	-3153.9	667030.2	21478.6	42.067	0	0
7400	4.951×1	364.499 $\times 1$	27.423×1	-3206.6	676220.0	21478.6	42.706	0	0
7500	4.951×1	369.439 $\times 1$	27.423×1	-3259.3	685410.8	21478.6	43.345	0	0
7600	4.951×1	374.379 $\times 1$	27.423×1	-3312.0	694600.6	21478.6	43.984	0	0
7700	4.951×1	379.319 $\times 1$	27.423×1	-3364.7	703790.4	21478.6	44.623	0	0
7800	4.951×1	384.259 $\times 1$	27.423×1	-3417.4	712980.2	21478.6	45.262	0	0
7900	4.951×1	389.199 $\times 1$	27.423×1	-3470.1	722170.0	21478.6	45.901	0	0
8000	4.951×1	394.139 $\times 1$	27.423×1	-3522.8	731360.8	21478.6	46.539	0	0
8100	4.951×1	399.079 $\times 1$	27.423×1	-3575.5	740550.6	21478.6	47.178	0	0
8200	4.951×1	404.019 $\times 1$	27.423×1	-3628.2	749740.4	21478.6	47.817	0	0
8300	4.951×1	408.959 $\times 1$	27.423×1	-3680.9	758930.2	21478.6	48.456	0	0
8400	4.951×1	413.899 $\times 1$	27.423×1	-3733.6	768120.0	21478.6	49.095	0	0
8500	4.951×1	418.839 $\times 1$	27.423×1	-3786.3	777310.8	21478.6	49.734	0	0
8600	4.951×1	423.779 $\times 1$	27.423×1	-3839.0	786500.6	21478.6	50.373	0	0
8700	4.951×1	428.719 $\times 1$	27.423×1	-3891.7	795690.4	21478.6	51.012	0	0
8800	4.951×1	433.659 $\times 1$	27.423×1	-3944.4	804880.2	21478.6</td			

Equilibrium Composition Example

- Here F_T is ‘free energy’ i.e. Gibbs free energy and everything is in American units:

184

TABLE III. - Continued. THERMODYNAMIC PROPERTIES
(94) H (gas); molecular weight, 1.008

T , °K	C_p^o , cal/mole °K	$H_T^o - H_O^o$, cal/mole	S_T^o , cal/mole °K	$-(F_T^o - H_O^o)$, cal/mole	H_T^o , cal/mole	Formation from assigned reference elements		Formation from gaseous atoms	
						$(\Delta H_f^o)_f$, cal/mole	$\log_{10} K_f$	ΔH_f^o , cal/mole	$\log_{10} K$
0	-----	0	-----	0	50616.5	51628.4	-----	0	-----
100	4.9681	496.8	21.9650	1699.7	51113.3	51745.7	-110.4946	0	0
200	4.9681	993.6	25.4087	4088.1	51610.1	51941.2	-54.3196	0	0
298.15	4.9681	1481.3	27.3324	6685.8	52097.7	52097.7	-35.6106	0	0
300	4.9681	1490.4	27.4231	6736.5	52100.6	52100.6	-35.3752	0	0
400	4.9681	1987.3	26.8523	9553.7	52603.8	52250.1	-25.8747	0	0
500	4.9681	2484.1	29.9609	12496.4	53100.6	52397.6	-20.1578	0	0
600	4.9681	2980.9	30.8667	15539.2	53597.4	52544.4	-16.3357	0	0
700	4.9681	3477.7	31.6326	18665.1	54094.2	52690.1	-13.5982	0	0
800	4.9681	3974.5	32.2960	21862.3	54591.0	52834.2	-11.5392	0	0
900	4.9681	4471.3	32.8812	25121.7	55087.8	52975.4	-9.9334	0	0
1000	4.9681	4968.1	33.4046	28436.5	55584.6	53113.2	-8.6453	0	0
1100	4.9681	5465.0	33.8781	31801.0	56081.5	53246.8	-7.5889	0	0
1200	4.9681	5961.8	34.3104	35210.7	56578.3	53375.8	-6.7063	0	0
1300	4.9681	6458.6	34.7081	38661.9	57075.1	53499.7	-5.9576	0	0
1400	4.9681	6955.4	35.0762	42151.3	57571.9	53618.5	-5.3147	0	0
1500	4.9681	7452.2	35.4190	45676.3	58068.7	53731.7	-4.7561	0	0

Figure: Atomic hydrogen thermodynamic properties from McBride et al. [4].

Equilibrium Composition Example

- Here F_T is ‘free energy’ i.e. Gibbs free energy and everything is in American units:

185

 TABLE III - Continued. THERMODYNAMIC PROPERTIES
(in) \bar{M}_T (g/mol); molecular weight, 2.016

T_c °K	$\frac{\partial P}{\partial T}$ cal/mole °K	$M_T - \bar{M}_T$ cal/mole	S_T^0 cal/mole °K	$-(F_T^0 - \bar{H}_T^0)$ cal/mole	H_T^0 cal/mole	Formation from assigned reference elements		Formation from gasless atoms	
						$\Delta H_{f,0}^0$ cal/mole	$\log_{10} K_f$ cal/mole	$\Delta H_{f,0}^0$ cal/mole	$\log_{10} K$
0	0	0	0	0	0	0	0	0	0
200	6.5162	1.01617	204.347	-1074.9	-1074.9	0	-1.0749	0	0
208.15	6.4914	202.616	211.279	-2093.0	-2093.0	0	-1.0931	0	0
210	6.4887	202.517	211.277	-2093.0	-2093.0	0	-1.0931	0	0
208	6.4752	211.1	211.275	-1959.1	-1959.1	0	-1.0930	0	0
206	6.4627	214.71	211.273	-1901.9	-1901.9	0	-1.0929	0	0
204	6.4492	218.31	211.271	-1834.7	-1834.7	0	-1.0928	0	0
202	6.4356	221.91	211.269	-1767.5	-1767.5	0	-1.0927	0	0
200	6.4219	225.51	211.267	-1700.3	-1700.3	0	-1.0926	0	0
198	6.4083	229.11	211.265	-1633.1	-1633.1	0	-1.0925	0	0
196	6.3946	232.71	211.263	-1565.9	-1565.9	0	-1.0924	0	0
194	6.3809	236.31	211.261	-1500.7	-1500.7	0	-1.0923	0	0
192	6.3672	239.91	211.259	-1433.5	-1433.5	0	-1.0922	0	0
190	6.3535	243.51	211.257	-1366.3	-1366.3	0	-1.0921	0	0
188	6.3398	247.11	211.255	-1300.1	-1300.1	0	-1.0920	0	0
186	6.3261	250.71	211.253	-1232.9	-1232.9	0	-1.0919	0	0
184	6.3124	254.31	211.251	-1165.7	-1165.7	0	-1.0918	0	0
182	6.2987	257.91	211.249	-1100.5	-1100.5	0	-1.0917	0	0
180	6.2850	261.51	211.247	-1033.3	-1033.3	0	-1.0916	0	0
178	6.2713	265.11	211.245	-966.1	-966.1	0	-1.0915	0	0
176	6.2576	268.71	211.243	-900.9	-900.9	0	-1.0914	0	0
174	6.2439	272.31	211.241	-834.7	-834.7	0	-1.0913	0	0
172	6.2302	275.91	211.239	-768.5	-768.5	0	-1.0912	0	0
170	6.2165	279.51	211.237	-702.3	-702.3	0	-1.0911	0	0
168	6.2028	283.11	211.235	-636.1	-636.1	0	-1.0910	0	0
166	6.1891	286.71	211.233	-570.9	-570.9	0	-1.0909	0	0
164	6.1754	290.31	211.231	-504.7	-504.7	0	-1.0908	0	0
162	6.1617	293.91	211.229	-438.5	-438.5	0	-1.0907	0	0
160	6.1480	297.51	211.227	-372.3	-372.3	0	-1.0906	0	0
158	6.1343	301.11	211.225	-306.1	-306.1	0	-1.0905	0	0
156	6.1206	304.71	211.223	-240.9	-240.9	0	-1.0904	0	0
154	6.0969	308.31	211.221	-174.7	-174.7	0	-1.0903	0	0
152	6.0832	311.91	211.219	-108.5	-108.5	0	-1.0902	0	0
150	6.0695	315.51	211.217	-42.3	-42.3	0	-1.0901	0	0
148	6.0558	319.11	211.215	18.7	18.7	0	-1.0900	0	0
146	6.0421	322.71	211.213	82.9	82.9	0	-1.0899	0	0
144	6.0284	326.31	211.211	147.1	147.1	0	-1.0898	0	0
142	6.0147	329.91	211.209	211.3	211.3	0	-1.0897	0	0
140	5.9910	333.51	211.207	275.5	275.5	0	-1.0896	0	0
138	5.9773	337.11	211.205	339.7	339.7	0	-1.0895	0	0
136	5.9636	340.71	211.203	403.9	403.9	0	-1.0894	0	0
134	5.9499	344.31	211.201	468.1	468.1	0	-1.0893	0	0
132	5.9362	347.91	211.199	532.3	532.3	0	-1.0892	0	0
130	5.9225	351.51	211.197	596.5	596.5	0	-1.0891	0	0
128	5.9088	355.11	211.195	660.7	660.7	0	-1.0890	0	0
126	5.8951	358.71	211.193	724.9	724.9	0	-1.0889	0	0
124	5.8814	362.31	211.191	789.1	789.1	0	-1.0888	0	0
122	5.8677	365.91	211.189	853.3	853.3	0	-1.0887	0	0
120	5.8540	369.51	211.187	917.5	917.5	0	-1.0886	0	0
118	5.8403	373.11	211.185	981.7	981.7	0	-1.0885	0	0
116	5.8266	376.71	211.183	1045.9	1045.9	0	-1.0884	0	0
114	5.8129	380.31	211.181	1110.1	1110.1	0	-1.0883	0	0
112	5.8092	383.91	211.179	1174.3	1174.3	0	-1.0882	0	0
110	5.7955	387.51	211.177	1238.5	1238.5	0	-1.0881	0	0
108	5.7818	391.11	211.175	1302.7	1302.7	0	-1.0880	0	0
106	5.7681	394.71	211.173	1366.9	1366.9	0	-1.0879	0	0
104	5.7544	398.31	211.171	1431.1	1431.1	0	-1.0878	0	0
102	5.7407	401.91	211.169	1495.3	1495.3	0	-1.0877	0	0
100	5.7270	405.51	211.167	1559.5	1559.5	0	-1.0876	0	0
98	5.7133	409.11	211.165	1623.7	1623.7	0	-1.0875	0	0
96	5.6996	412.71	211.163	1687.9	1687.9	0	-1.0874	0	0
94	5.6859	416.31	211.161	1752.1	1752.1	0	-1.0873	0	0
92	5.6722	419.91	211.159	1816.3	1816.3	0	-1.0872	0	0
90	5.6585	423.51	211.157	1880.5	1880.5	0	-1.0871	0	0
88	5.6448	427.11	211.155	1944.7	1944.7	0	-1.0870	0	0
86	5.6311	430.71	211.153	2008.9	2008.9	0	-1.0869	0	0
84	5.6174	434.31	211.151	2073.1	2073.1	0	-1.0868	0	0
82	5.6037	437.91	211.149	2137.3	2137.3	0	-1.0867	0	0
80	5.5899	441.51	211.147	2201.5	2201.5	0	-1.0866	0	0
78	5.5762	445.11	211.145	2265.7	2265.7	0	-1.0865	0	0
76	5.5625	448.71	211.143	2329.9	2329.9	0	-1.0864	0	0
74	5.5488	452.31	211.141	2394.1	2394.1	0	-1.0863	0	0
72	5.5351	455.91	211.139	2458.3	2458.3	0	-1.0862	0	0
70	5.5214	459.51	211.137	2522.5	2522.5	0	-1.0861	0	0
68	5.5077	463.11	211.135	2586.7	2586.7	0	-1.0860	0	0
66	5.4940	466.71	211.133	2650.9	2650.9	0	-1.0859	0	0
64	5.4793	470.31	211.131	2715.1	2715.1	0	-1.0858	0	0
62	5.4656	473.91	211.129	2779.3	2779.3	0	-1.0857	0	0
60	5.4519	477.51	211.127	2843.5	2843.5	0	-1.0856	0	0
58	5.4382	481.11	211.125	2907.7	2907.7	0	-1.0855	0	0
56	5.4245	484.71	211.123	2971.9	2971.9	0	-1.0854	0	0
54	5.4108	488.31	211.121	3036.1	3036.1	0	-1.0853	0	0
52	5.3971	491.91	211.119	3100.3	3100.3	0	-1.0852	0	0
50	5.3834	495.51	211.117	3164.5	3164.5	0	-1.0851	0	0
48	5.3697	499.11	211.115	3228.7	3228.7	0	-1.0850	0	0
46	5.3560	502.71	211.113	3292.9	3292.9	0	-1.0849	0	0
44	5.3423	506.31	211.111	3357.1	3357.1	0	-1.0848	0	0
42	5.3286	510.91	211.109	3421.3	3421.3	0	-1.0847	0	0
40	5.3149	514.51	211.107	3485.5	3485.5	0	-1.0846	0	0
38	5.3012	518.11	211.105	3549.7	3549.7	0	-1.0845	0	0
36	5.2875	521.71	211.103	3613.9	3613.9	0	-1.0844	0	0
34	5.2738	525.31	211.101	3678.1	3678.1	0	-1.0843	0	0
32	5.2601	528.91	211.099	3742.3	3742.3	0	-1.0842	0	0
30	5.2464	532.51	211.097	3806.5	3806.5	0	-1.0841	0	0
28	5.2327	536.11	211.095	3870.7	3870.7	0	-1.0840	0	0
26	5.2190	539.71	211.093	3934.9	3934.9	0	-1.0839	0	0
24	5.1953	543.31	211.091	4000.1	4000.1	0	-1.0838	0	0
22	5.1816	546.91	211.089	4064.3	4064.3	0	-1.0837	0	0
20	5.1679	550.51	211.087	4128.5	4128.5	0	-1.0836	0	0
18	5.1542	554.11	211.085	4192.7	4192.7	0	-1.0835	0	0
16	5.1405	557.71	211.083	4256.9	4256.9	0	-1.0834	0	0
14	5.1268	561.31	211.081	4321.1	4321.1	0	-1.0833	0	0
12	5.1131	564.91	211.079	4385.3	4385.3	0	-1.0832	0	0
10	5.0994	568.51	211.077	4449.5	4449.5	0	-1.0831	0	0
8	5.0857	572.11	211.075	4513.7	4513.7	0	-1.0830	0	0
6	5.0720	575.71	211.073	4577.9	4577.9	0	-1.0829	0	0
4	5.0583	579.31	211.071	4642.1	4642.1	0	-1.0828	0	0
2	5.0446	582.91	211.069	4706.3	4706.3	0	-1.0827	0	0
0	5.0309	586.51	211.067	4770.5	4770.5	0	-1.0826	0	0

Figure: Molecular hydrogen thermodynamic properties from McBride et al. [4].

Equilibrium Composition Example

- Here F_T is 'free energy' i.e. Gibbs free energy and everything is in American units:

185

TABLE III. - Continued. THERMODYNAMIC PROPERTIES

 (95) H₂ (gas); molecular weight, 2.016

T , °K	C_p^o , cal/mole °K	$H_T^o - H_0^o$, cal/mole	S_T^o , cal/mole °K	$-(F_T^o - H_0^o)$, cal/mole	H_T^o , cal/mole	Formation from assigned reference elements		Formation from gaseous atoms	
						$(\Delta H_f^o)_r$, cal/mole	$\log_{10} K_f$	ΔH_f^o , cal/mole	$\log_{10} K$
0	-----	0	-----	0	-2023.8	0	-----	-103256.8	-----
100	5.3934	758.9	24.3677	1679.8	-1264.9	0	0	-103491.5	221.8988
200	6.5182	1361.7	28.5212	4342.5	-662.1	0	0	-103882.3	108.6393
298.15	6.8918	2023.8	31.2079	7280.8	0	0	0	-104195.5	71.2212
300	6.8938	2036.5	31.2517	7339.0	12.7	0	0	-104201.1	70.7505
400	6.9753	2731.1	33.2508	10569.2	707.3	0	0	-104500.2	51.7494
500	6.9932	3429.7	34.8088	13974.7	1405.9	0	0	-104795.2	40.3156
600	7.0091	4129.7	36.0647	17521.1	2105.9	0	0	-105088.9	32.6715
700	7.0369	4831.9	37.1677	21189.5	2808.1	0	0	-105380.3	27.1963
800	7.0806	5537.5	38.1097	24950.3	3513.7	0	0	-105668.4	23.0784
900	7.1422	6248.6	39.9663	28803.1	4224.8	0	0	-105950.9	19.8668
1000	7.2197	6966.7	39.7015	32734.7	4922.9	0	0	-106226.4	17.2905
1100	7.3091	7693.1	40.3950	36741.4	5669.3	0	0	-106493.6	15.1778
1200	7.4065	8428.8	41.0349	40813.2	6405.0	0	0	-106751.6	13.4126
1300	7.5118	9174.6	41.6311	44945.9	7150.8	0	0	-106999.4	11.9153
1400	7.6172	9930.7	42.1935	49140.2	7906.9	0	0	-107237.0	10.6295
1500	7.7205	10697.8	42.7221	53389.4	8674.0	0	0	-107463.4	9.5122

Figure: Molecular hydrogen thermodynamic properties from McBride et al. [4].

Equilibrium Composition Example

- ▶ From McBride et al. [4] (remembering that F_T is ‘free energy’ i.e. Gibbs free energy):
- ▶ For H :

$$H_0^0 = H_T @ 0\text{K} = 50,616.5 \frac{\text{cal}}{\text{mol}}$$

$$-(F_T - H_0^0) = 45,676.3 \frac{\text{cal}}{\text{mol}}$$

$$F_T = -45,676.3 \frac{\text{cal}}{\text{mol}} + H_0^0$$

$$F_T^0 = G_H^{p=1} = [-45,676.3 + 50,616.5] \frac{\text{cal}}{\text{mol}} \cdot 4.18 \frac{\text{J}}{\text{cal}}$$

$$G_H^{p=1} = 20,650 \frac{\text{J}}{\text{mol}}$$

Equilibrium Composition Example

- For H_2 :

$$H_0^0 = H_T @ 0\text{K} = -2,023.8 \frac{\text{cal}}{\text{mol}}$$

$$-(F_T - H_0^0) = 53,385.4 \frac{\text{cal}}{\text{mol}}$$

$$F_T = -53,385.4 \frac{\text{cal}}{\text{mol}} + H_0^0$$

$$F_T^0 = G_H^{p=1} = [-53,385.4 + -2,023.8] \frac{\text{cal}}{\text{mol}} \cdot 4.18 \frac{\text{J}}{\text{cal}}$$

$$G_{H_2}^{p=1} = -231,610 \frac{\text{J}}{\text{mol}}$$

Equilibrium Composition Example

- Now:

$$\Delta G^{p=1} = \sum_i v_i G_i^{p=1} = 2 \cdot 20,650 \frac{\text{J}}{\text{mol}} + -1 \cdot -231,610 \frac{\text{J}}{\text{mol}}$$

$$\Delta G^{p=1} = 272,910 \frac{\text{J}}{\text{mol}}$$

- From here:

$$K_{p_1} = e^{-\Delta G^{p=1}/R_u T} = \exp\left(\frac{-272,910 \frac{\text{J}}{\text{mol}}}{8.314 \frac{\text{J}}{\text{molK}} \cdot 1,500 \text{K}}\right)$$

$$K_{p_1} = \frac{p_H^2}{p_{H_2}} = 3.13 \times 10^{-10} \text{ atm}$$

- (Note that units will not always be the same, could be atmospheres squared, or dimensionless, for example.)

Equilibrium Composition Example

- ▶ Now, for a given p and T :
 - ▶ One can find each $K_p(T)$.
 - ▶ One has the pressure relationship from Dalton's Law.
 - ▶ One has nuclei conversation based on how much of each species we start with at the initial conditions.
- ▶ Then one can solve the simultaneous equations to obtain the composition.
- ▶ (You will have to do this for air [N₂/O₂] in the assignment.)

Equilibrium Composition Example

- ▶ Some subtle details:
 - ▶ For n unknown partial pressures, require $n - 2$ chemical reactions.
 - ▶ These must be independent (i.e. one cannot be obtained by adding or subtracting the others)
 - ▶ The remaining 2 equations are Dalton's Law and conservation of nuclei.
 - ▶ The choice of reactions is somewhat arbitrary, and requires an educated guess.
- ▶ More advanced equilibrium solvers use numerical algorithms which do not have such restrictions, but these methods are not amenable to solution by hand. You can try NASA's CEA code:
- ▶ <https://software.nasa.gov/software/LEW-17687-1>
or run online <https://cearun.grc.nasa.gov/>
- ▶ (We will use CEA in the assignment too.)

Equilibrium Normal Shock

- Recall normal shock conservation equations for mass, momentum, and energy:

$$\rho_1 u_1 = \rho_2 u_2 \quad (7)$$

$$p_1 + \rho_1 u_1^2 = p_2 + \rho_2 u_2^2 \quad (8)$$

$$h_1 + \frac{u_1^2}{2} = h_2 + \frac{u_2^2}{2} \quad (9)$$

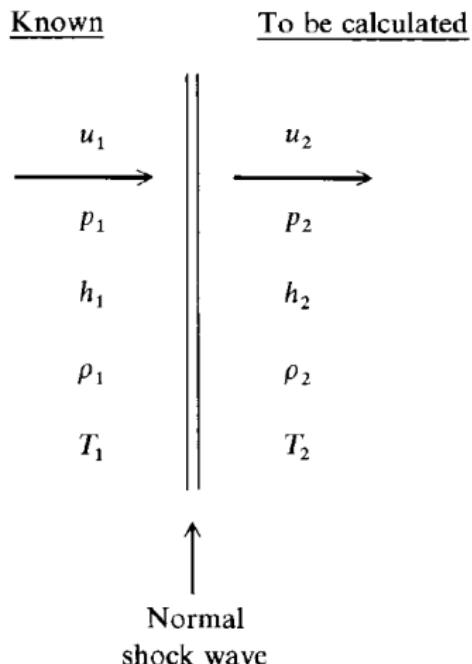


Figure: EQ normal shock [3].

Equilibrium Normal Shock

- ▶ Without post-shock chemistry, there is an analytical solution which we are all familiar with.
- ▶ With equilibrium chemistry, we need an iterative procedure to get the post-shock state.
- ▶ First, rearrange (7):

$$u_2 = \frac{\rho_1 u_1}{\rho_2} \quad (10)$$

Now, substituting (10) into (8) and (9) gives:

$$p_2 = p_1 + \rho_1 u_1^2 \left(1 - \frac{\rho_1}{\rho_2} \right) \quad (11)$$

$$h_2 = h_1 + \frac{u_1^2}{2} \left[1 - \left(\frac{\rho_1}{\rho_2} \right)^2 \right] \quad (12)$$

Equilibrium Normal Shock

- ▶ The iterative solution procedure is as follows:
 - 1 Guess ρ_1/ρ_2 (Anderson suggests 0.1)
 - 2 Use guess to calculate p_2 and h_2 from (11) and (12)
 - 3 Use p_2 and h_2 to find new ρ_2
 - 4 Iterate until converged (typically in 5 or so steps)
- ▶ This sounds easy, BUT in practice ρ_2 is calculated from p , T rather than p , h , and there is no straightforward way of getting T from h .

Equilibrium Normal Shock

(1) Assumed $\rho_2^{(k)}$ leads, with the aid of equations (1) to (3), to $p_2^{(k)}, H_2^{(k)}$. In principle, these two thermodynamic properties allow the evaluation of $\rho_2^{(k+1)}$ which is used once again in equations (1) to (3). This procedure, which shall be referred to as the major iteration, is repeated to convergence, solving the problem. In practice, however, the equilibrium program requires a p, T input making necessary the Newton-Raphson iterative procedure (hereinafter called the minor iteration) in order to determine a value of $T_{(n)}^{(k)}$ compatible with the pressure and enthalpy solved for in the major iteration. With this temperature, or an approximation to it, $\rho_2^{(k+1)}$ is determined and the procedure repeated until the desired convergence between $\rho_2^{(k)}$ and $\rho_2^{(k+1)}$ is achieved. The superscript (k) refers to the kth major iteration and the subscript (n) is associated with the minor iterations.

(2) The recursive equations used in the minor iteration are

$$T_{(n+1)}^{(k)} = T_{(n)}^{(k)} + \frac{H_2^{(k)} - H_{(n)}^{(k)}}{S_{(n)}^{(k)}} \quad (4)$$

where

$$S_{(n)}^{(k)} = \frac{H_{(n)}^{(k)} - H_{(n-1)}^{(k)}}{T_{(n)}^{(k)} - T_{(n-1)}^{(k)}} \quad (5)$$

Figure: Procedure outline by Callis and Kemper [6].

Equilibrium Normal Shock

- ▶ So we need a sub-iteration to find T_2 . An updated procedure:
 - 1 Guess ρ_1/ρ_2 (Anderson suggests 0.1 [3]) Use guess to calculate p_2 and h_2 from (11) and (12)
 - 1 Make two initial guesses for T_2 , and evaluate h_2
 - 2 Use results to obtain better guess for T_2
 - 3 Repeat until h_2 for given T_2 matches that of step 2 (to within reasonable accuracy)
 - 2 Use p_2 and T_2 to find new ρ_2
 - 3 Iterate until converged (typically in 5 or so steps)
- ▶ Callis and Kemper [6] suggest only doing a few temperature sub-iterations per full iteration, as the extra effort does not result in much more accuracy. For each new full iteration, use the best two T_2 guesses from the previous round to start off the next sub-iterations.
- ▶ Looking in Anderson [3], it is actually assumed that there exists some function $T(\rho, h)$ which allows us to get the temperature from the enthalpy and the density.
- ▶ This is kind of what we do in the solution procedure outlined in the next slide.

- ▶ Another similar way to do this is to follow the procedure of Chapter 1 and Example 1.1 of Bertin [2].
- ▶ After guessing for p_2 and h_2 starting with $u_2 = 0$ (which removes the need to guess the density ratio as well), it uses a figure with both p_2 and h_2 on it to find an equilibrium T_2 value, as well as a 'compressibility factor' (z_2) which takes into account how the chemistry changes R in the ideal gas law.
- ▶ z_2 can then be used to find ρ_2 :

$$\rho_2 = \frac{p_2}{z_2 RT_2} \quad (13)$$

- ▶ ρ_2 can then be used to find a new u_2 value:

$$u_2 = \frac{\rho_1 u_1}{\rho_2}$$

- ▶ u_2 and ρ_2 can then be fed into the next iteration until ρ_2 stops changing between iterations.

Equilibrium Normal Shock

- ▶ The compressibility factor (z) is the ratio of the mean molecular weight of the undissociated air to the mean molecular weight at the equilibrium conditions of interest.
- ▶ A figure from Bertin [2] showing how it changes with temperature and pressure can be seen below:

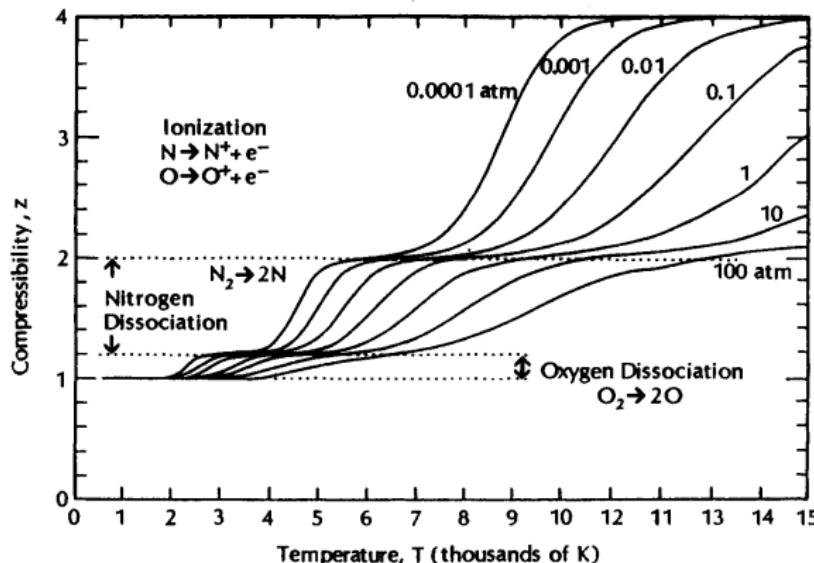


Figure: How the compressibility factor changes from Bertin [2].

Equilibrium Normal Shock

- ▶ I also think that this method is quite neat as it uses $u_2 = 0$ as an initial guess, which really simplifies the first iteration (as the u_2 terms drop right out).
- ▶ For a really rough calculation, even just assuming that $u_2 = 0$ and doing one iteration would give a reasonable value for at least T_2 .

Equilibrium Normal Shock

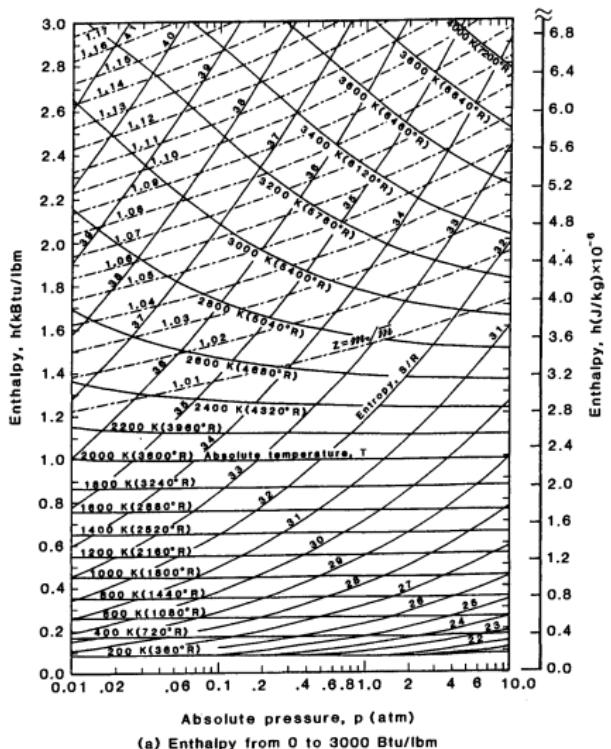


Fig. 1.17 Detailed charts for thermodynamic properties of air in chemical equilibrium, as taken from Ref. 18.

Figure: Fig 1.17a from Bertin [2].

Equilibrium Normal Shock

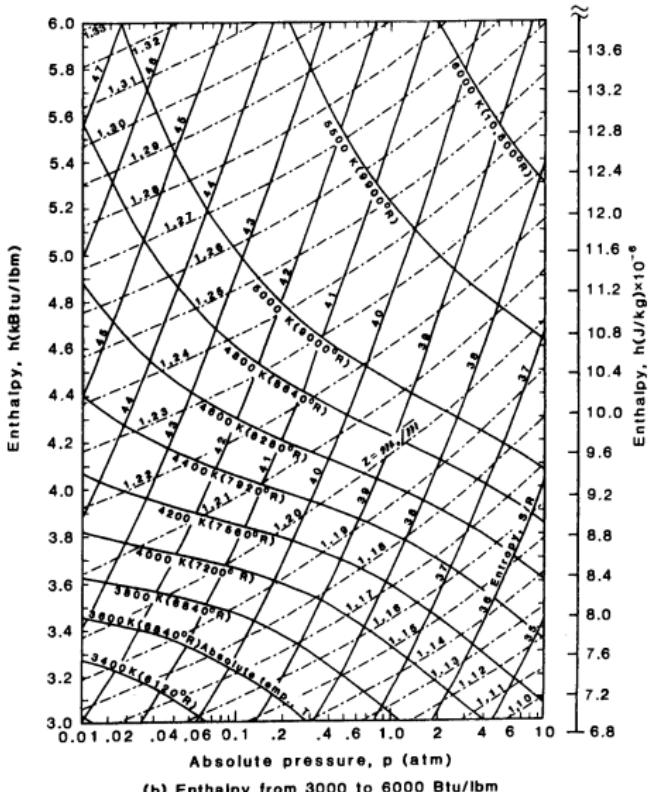


Fig. 1.17 Continued.

Figure: Fig 1.17b from Bertin [2].

Equilibrium Normal Shock

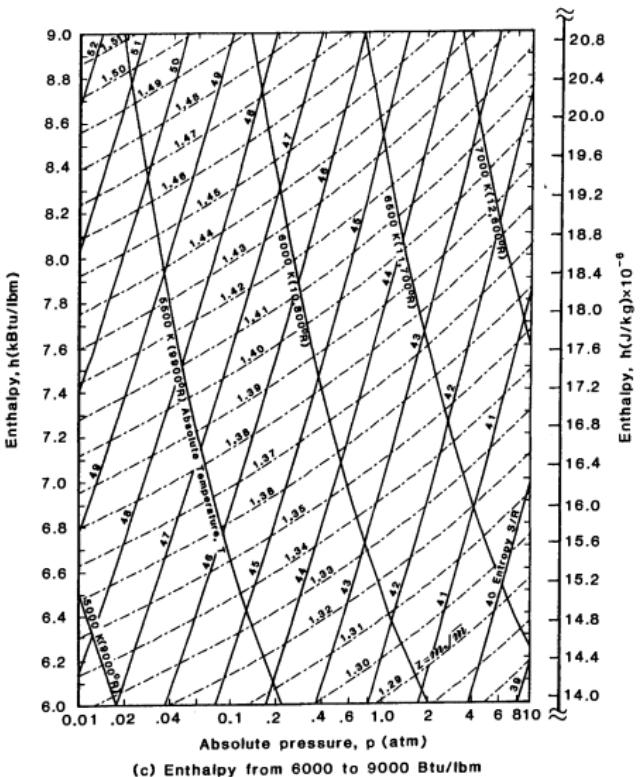
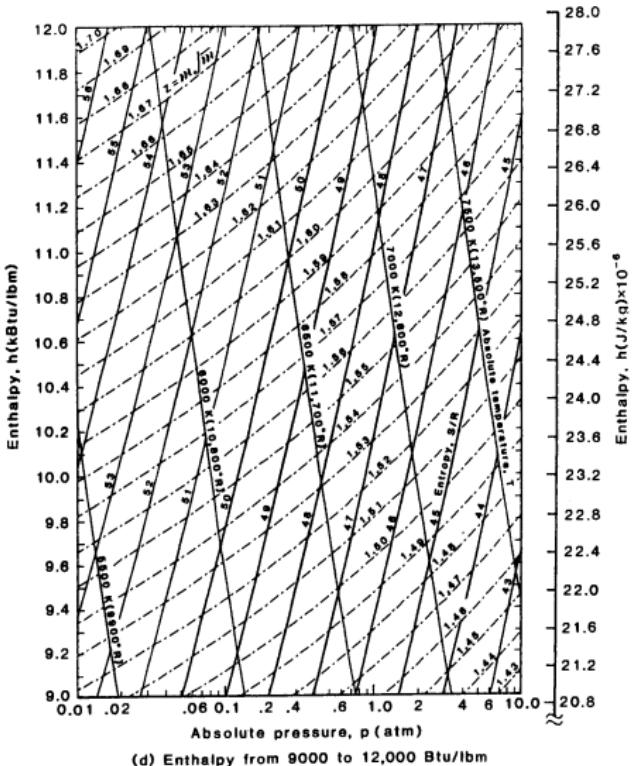


Fig. 1.17 Continued.

Figure: Fig 1.17c from Bertin [2].

Equilibrium Normal Shock



Equilibrium Normal Shock

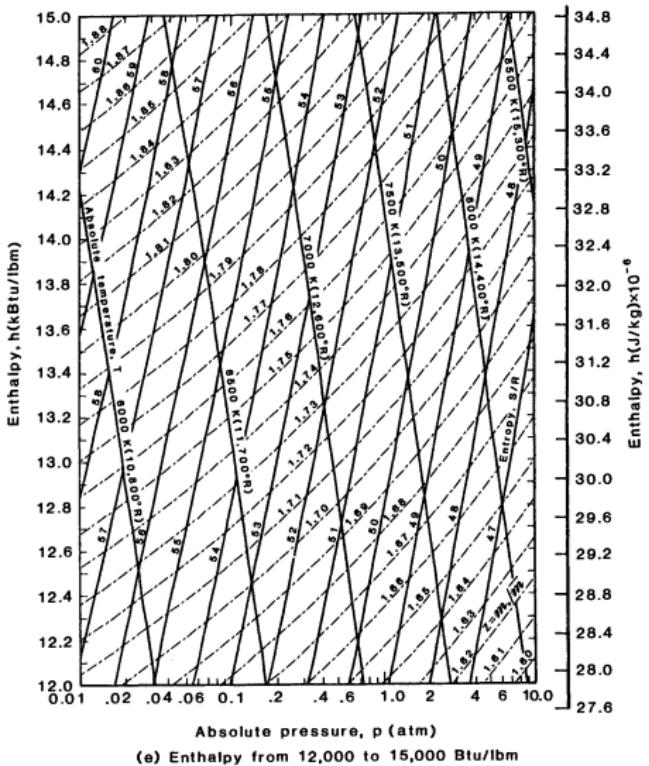


Fig. 1.17 Concluded.

Figure: Fig 1.17e from Bertin [2].

Equilibrium Normal Shock Example

- ▶ Calculate the equilibrium flow properties downstream of a normal shock wave, when $U_1 = 15,000 \text{ ft/s}$ at an altitude of 150,000 ft.
- ▶ (This is Example 1.1 from Bertin [2], which we will do in S.I units.)

Equilibrium Normal Shock Example

Summary

- ▶ In this lecture we covered:
 - ▶ A thermodynamics-based understanding of equilibrium mixtures.
 - ▶ A procedure for calculating equilibrium mixture composition and properties.
 - ▶ A procedure for solving across a normal shock with equilibrium chemistry.
- ▶ To be covered next lecture:
 - ▶ Statistical thermodynamics, which uses quantum mechanics as opposed to classical thermodynamics to develop an understanding of gas behaviour.

References |

- [1] Anderson, J. D., *Hypersonic and High-Temperature Gas Dynamics*, American Institute of Aeronautics and Astronautics, Inc., Reston, Virginia, USA, 3rd ed., 2019.
- [2] Bertin, J. J., *Hypersonic Aerothermodynamics*, American Institute of Aeronautics and Astronautics, Inc., 370 L'Enfant Promenade, SW, Washington, DC 20024-2518, 1st ed., 1994.
- [3] Anderson, J. D., *Hypersonic and High-Temperature Gas Dynamics*, American Institute of Aeronautics and Astronautics, Inc., 1801 Alexander Bell Drive, Reston, Virginia 20191-4344, 2nd ed., 2006.
- [4] McBride, B. J., Heimel, S., Ehlers, J. G., and Gordon, S., "Thermodynamic properties to 6000K for 210 substances involving the first 18 elements," Tech. Rep. NASA SP-3001 / N63-23715, National Aeronautics and Space Administration, 1963.

References II

- [5] National Aeronautics and Space Administration, "Bonnie J. McBride - Glenn Research Center — NASA,"
[https://www1.grc.nasa.gov/glenn-history/
hall-of-fame/biographies/bonnie-mcbride/](https://www1.grc.nasa.gov/glenn-history/hall-of-fame/biographies/bonnie-mcbride/), 2021,
Accessed April 12, 2022.
- [6] Callis, L. B. and Kemper, J. T., "A program for equilibrium normal
shock and stagnation point solutions for arbitrary gas mixtures," Tech.
Rep. NASA TN D-3215, National Aeronautics and Space
Administration, 1966.

Lecture 2 Notes

- We can now obtain a generalised expression relating C_p and C_v :

$$C_p - C_v = \left[\left(\frac{\partial e}{\partial v} \right)_T + p \right] \left(\frac{\partial v}{\partial T} \right)_p \quad (11)$$

$$C_p - C_v = R$$

- This works for any perfect gas, including chemically reacting mixtures where $e = e(T, v)$ and $(\delta e / \delta v)_T \neq 0$. For both calorically perfect gas AND thermally perfect gases we have $(\partial e / \partial v)_T = 0$, and obtain the familiar:

Second Law

$$C_p - C_v = R \quad (14)$$

Entropy is introduced to show how the energy of the system changes. Isentropic process is reversible as no heat is lost = adiabatic $\oint q = 0$ as $ds > 0$.

q = heat
 S = entropy

$$ds = \frac{\delta q}{T} + ds_{\text{irev.}}$$

$$s = C_p \ln \left(\frac{T}{T_{\text{ref}}} \right) - R \ln \left(\frac{p}{p_{\text{ref}}} \right) + s_{\text{ref}} \quad (19)$$

s_{ref} = starting entropy.

- For now we'll use Anderson's convention of lowercase being mass-based, and uppercase being mole-based. Some derivation yields an analogous expression for an equilibrium mixture:

\sum_i = for each species in the mixture.

$$s = \sum_i X_i \left[\int_{T_{\text{ref}}}^T C_{p,i} \left(\frac{dT}{T} \right) - R_u \ln \left(\frac{p_i}{p_{\text{ref}}} \right) \right] + s_{\text{ref}} \quad (20)$$

- Where $s_{\text{ref}} = \sum_i X_i s_{i,\text{ref}}$

lower = mass based UPPER = mole based.

Gibbs Free Energy (background)

$$G \equiv H - TS$$

The quantity is the maximum amount of reversible work that may be performed by a thermodynamic system at a constant temperature & pressure.

[For thermochemical equilibrium $G = G(p, T)$]
Is a function of pressure & Temperature.

However for chemical non-equilibrium

$$[G = G(p, T, N_1, N_2, N_n)]$$

Gibbs free energy is now a function of $N \Rightarrow$
Particles per mole of mixture.

Entropy Generation by Non-equilibrium chemical reactions.

$$-TdS_{irrev} = \sum_i \frac{\partial G}{\partial N_i} dN_i = 0 \text{ for EQ}$$

Eq. 23.

The negative of Temperature by irreversible entropy loss is equal to the sum of each species - partial Gibbs over partial particles per mole by the change in particles per mole is equal to 0.

For equilibrium mixtures,

The change in irreversible entropy is negative inverse Temperature by the sum of each species.

$$dS_{irrev} = -\frac{1}{T} \sum_i g'_i dN_i$$

► where g'_i is Gibbs free energy of species i per particle.

Basics of Gibbs free energy for upcoming work.

- Using $N_A g'_i = G_i$ (Gibbs free energy of species i per mole of i) and $\frac{dN_i}{N_A} = d\mathcal{N}_i$ (change in the number of moles of i) we get:

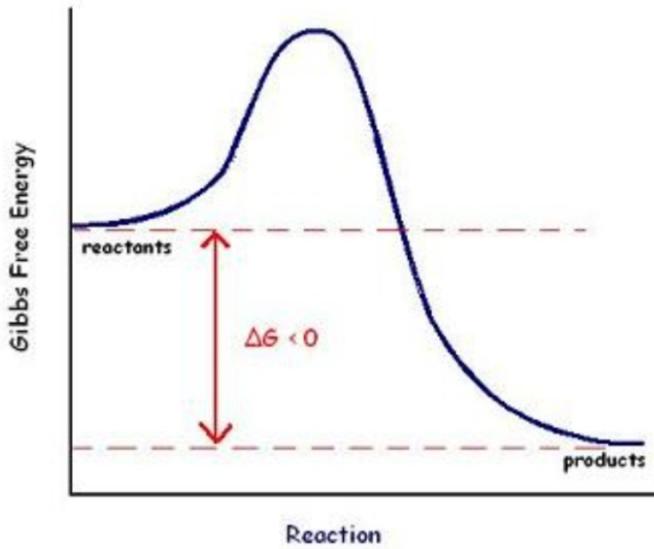
$$dS_{irrev} = -\frac{1}{T} \sum_i G_i d\mathcal{N}_i \quad (28)$$

- This now provides a tool to solve for an equilibrium system, where by definition $dS_{irrev} = 0$. We must simply find a way to satisfy:

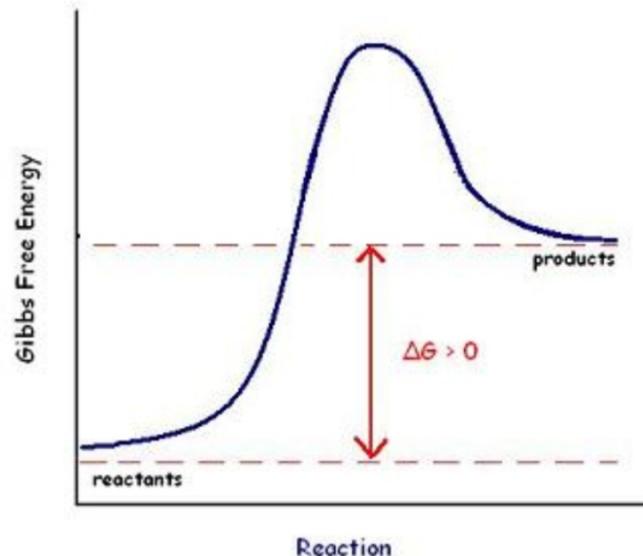
$$\sum_i G_i d\mathcal{N}_i = 0 \quad (29)$$

The Gibbs free energy graph shows whether or not a reaction is spontaneous—whether it is exergonic or endergonic. ΔG is the change in free energy. Generally, all reactions want to go to a lower energy state, thus a negative change is favored. Negative ΔG indicates that the reaction is exergonic and spontaneous.

Exergonic Reaction: $\Delta G < 0$
-Reaction is spontaneous.



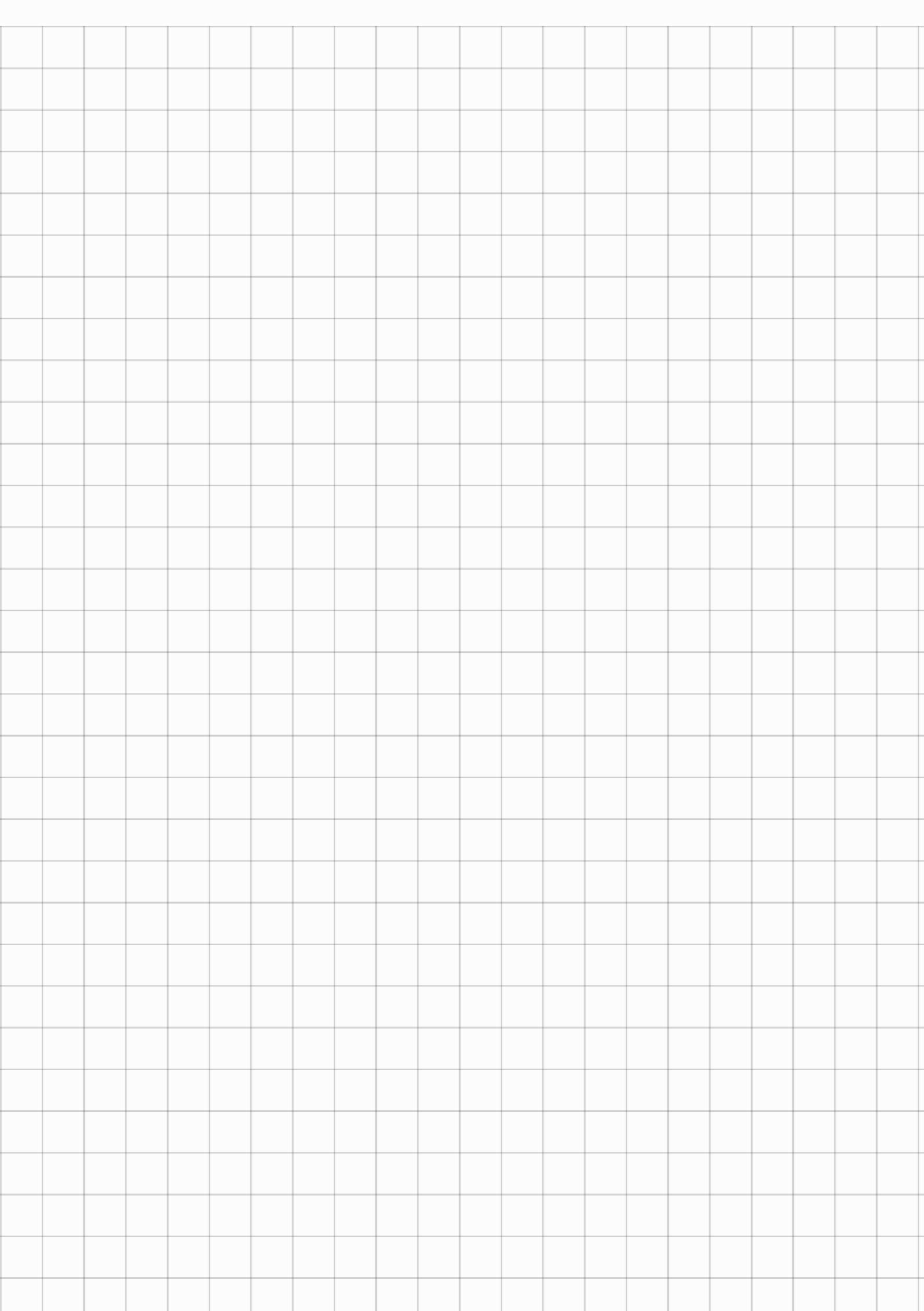
Endergonic Reaction: $\Delta G > 0$
-Reaction is not spontaneous.

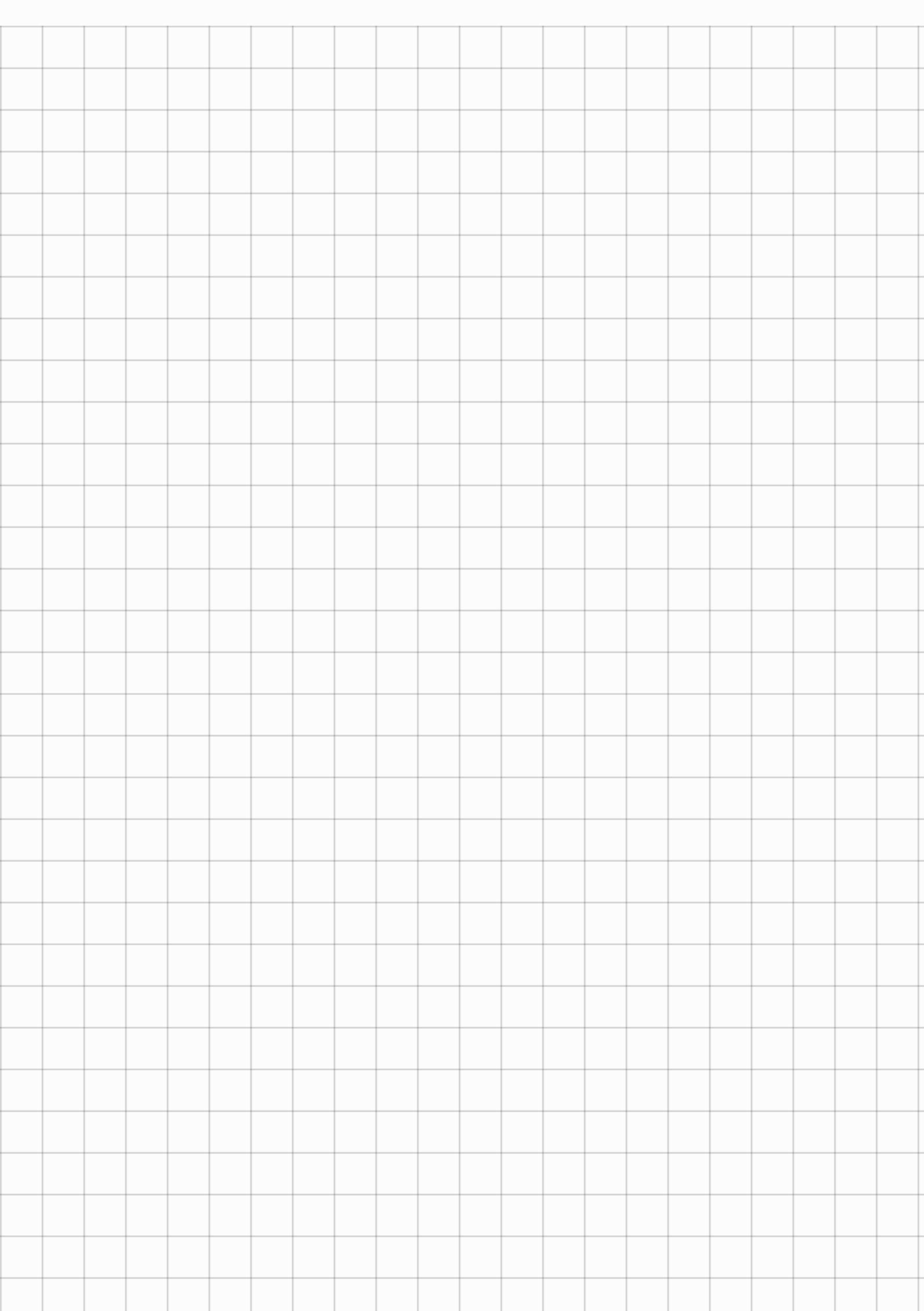


Slide 16 L2.

16 min left L2.

Equilibrium Constant







THE UNIVERSITY
OF QUEENSLAND
AUSTRALIA

AERO4470

High Temperature Gas Dynamics Lecture 3: Statistical Thermodynamics

C.M. James (using lectures written by S.W. Lewis with some changes)

Centre for Hypersonics, The School of Mechanical and Mining Engineering,
The University of Queensland, Brisbane, QLD, 4072, Australia

6th March 2024



Learning Outcomes

- ▶ Today we are going to learn about statistical thermodynamics, which allows for the calculation of a gas mixture's thermodynamic properties **from first principles.**
 - ▶ Discretisation of energy and energy macrostates / microstates.
 - ▶ The most probable macrostate (i.e. thermodynamic equilibrium)
 - ▶ The partition function, its evaluation from quantum mechanics, and the link to macroscopic properties.
 - ▶ Implications on high temperature gas behaviour.
- ▶ This content is very mathematics-intensive. You are not expected to memorise and wield all of these equations, but they are critical for conceptual understanding.

Some Recommended Resources

- ▶ Chapter 11 of Anderson [1] is where he discusses all about Statistical Thermodynamics.
- ▶ Vincenti and Kruger [2] was the book which Anderson was very influenced by in his High Temperature Gas Dynamics section. Chapter IV 'Statistical Mechanics' is very relevant for this lecture.

Energy States

Energy States

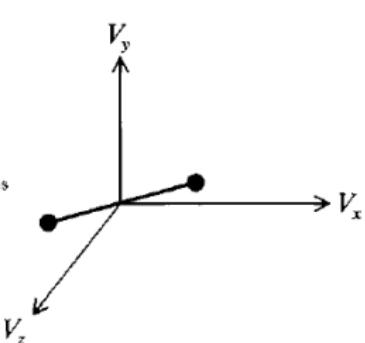
a) Diatomic molecule



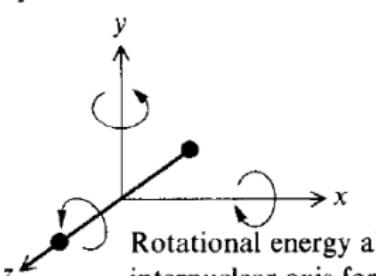
Source

Translational kinetic energy of the center of mass (thermal degrees of freedom—3)

b) Translational energy ϵ'_{trans}



c) Rotational energy ϵ'_{rot}



Rotational kinetic energy; (thermal degrees of freedom—2 for diatomic; 2 for linear polyatomic; and 3 for nonlinear polyatomic)

Rotational energy about the internuclear axis for a diatomic molecule is negligibly small

Figure: Modes of molecular energy [3].

Energy States

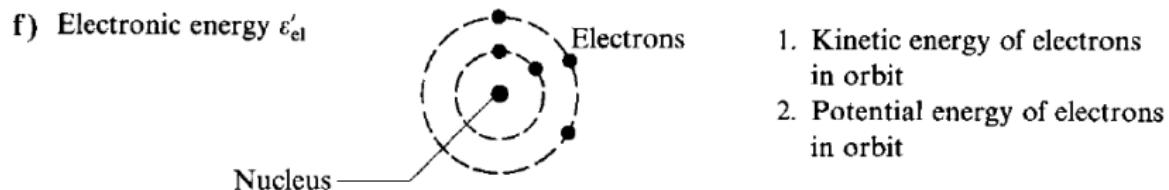
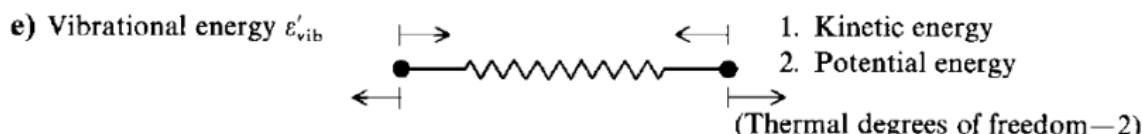
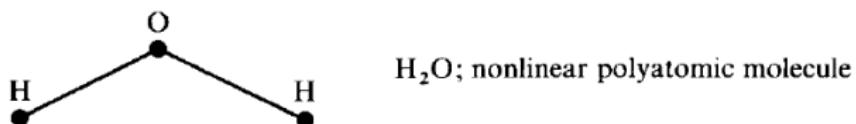


Figure: Modes of molecular energy [3].

Energy States

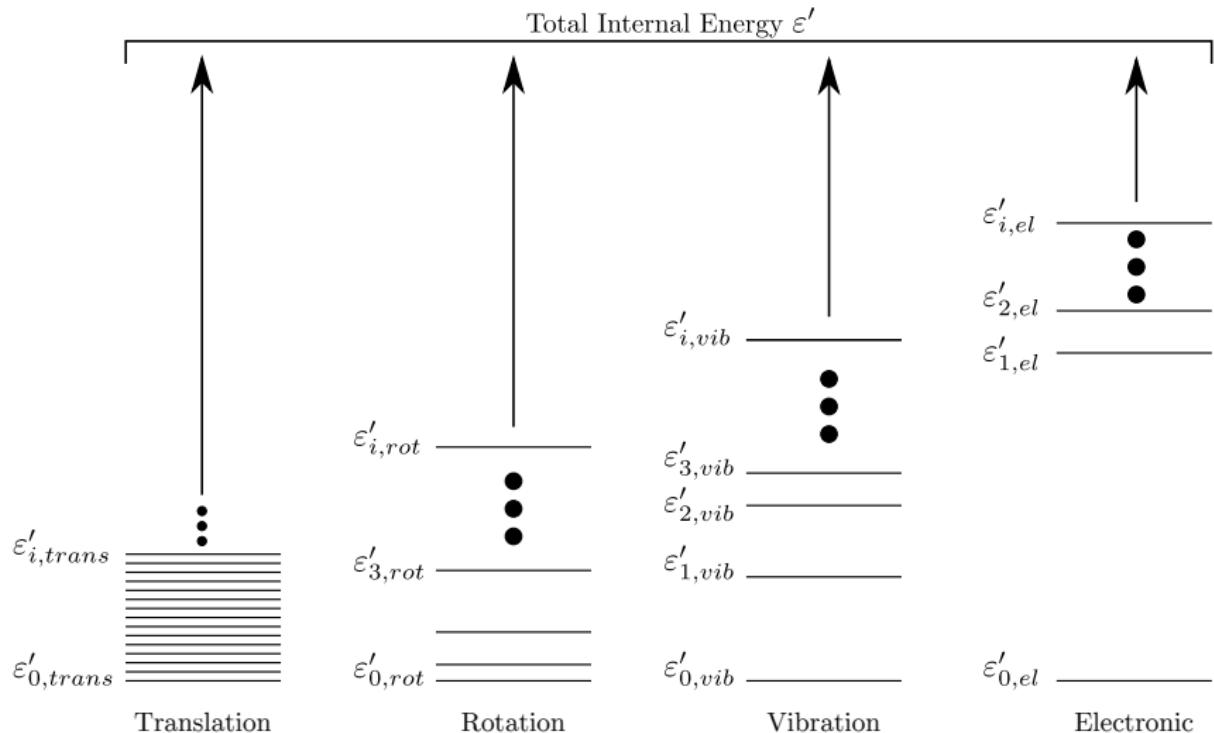


Figure: Molecular energy modes and discretisation (adapted from Anderson [3]).

Energy States

- ▶ For an atom:

$$\varepsilon' = \varepsilon'_{trans} + \varepsilon'_{el} \quad (1)$$

- ▶ For a molecule:

$$\varepsilon' = \varepsilon'_{trans} + \varepsilon'_{rot} + \varepsilon'_{vib} + \varepsilon'_{el} \quad (2)$$

- ▶ At absolute zero, there is still a finite amount of energy known as the “zero point energy”, which is fixed for a species:

$$\varepsilon'_0 = \varepsilon'_{0,trans} + \varepsilon'_{0,vib} + \varepsilon'_{0,el} \quad (3)$$

- ▶ Note that only $\varepsilon'_{0,rot} = 0$. It is common to consider energy as measured above the zero-point:

$$\varepsilon'_i = \varepsilon_{j,trans} + \varepsilon_{k,rot} + \varepsilon_{l,vib} + \varepsilon_{m,el} + \varepsilon'_0$$

$$\varepsilon_i = \varepsilon_{j,trans} + \varepsilon_{k,rot} + \varepsilon_{l,vib} + \varepsilon_{m,el} \quad (4)$$

Energy States

- ▶ For the same energy level ϵ'_i there may be multiple *states*. For example, same magnitude but different orientation of the angular momentum. The number of possible states for ϵ'_i is called the **degeneracy** g_i or the statistical weight.

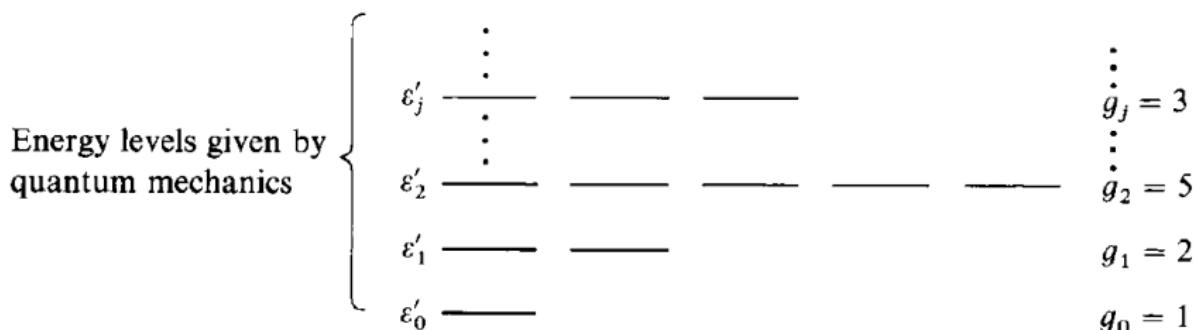


Figure: Illustration of degeneracy [3].

Energy States

- ▶ Consider a system of N molecules. Define N_j as the number of molecules in energy level ε'_j :

$$N = \sum_j N_j \quad (5)$$

- ▶ The set of N_j is the “macrostate” or “population distribution”. This may vary with time, due to collisions for example. The total system energy is:

$$E = \sum_j \varepsilon'_j N_j \quad (6)$$

- ▶ The particular macrostate will change with time; however, one specific macrostate will occur more frequently than any other. This is the “most probable macrostate” and **it is this macrostate which defines thermodynamic equilibrium.**

Energy States

Energy levels:	ε'_0	ε'_1	ε'_2	...	ε'_j	...
Statistical weights:	g_0	g_1	g_2	...	g_j	...
Populations at one instant:	$N_0 = 2$	$N_1 = 3$	$N_2 = 5$...	$N_j = 3$...
Populations at the next instant:	$N_0 = 3$	$N_1 = 1$	$N_2 = 3$...	$N_j = 6$...

One macrostate

Another macrostate

Figure: Illustration of macrostates [3].

Energy States

- To find the most probable macrostate, we must define the “microstate” which is the specific *arrangement* of occupied states.

$$\begin{array}{llll}
 \epsilon'_0 & \epsilon'_1 & \epsilon'_2 & \cdots \\
 N_0 = 2 & N_1 = 5 & N_2 = 3 \cdots & N_j = 2 \cdots \\
 g_0 = 5 & g_1 = 6 & g_2 = 5 \cdots & g_j = 3 \cdots
 \end{array}$$

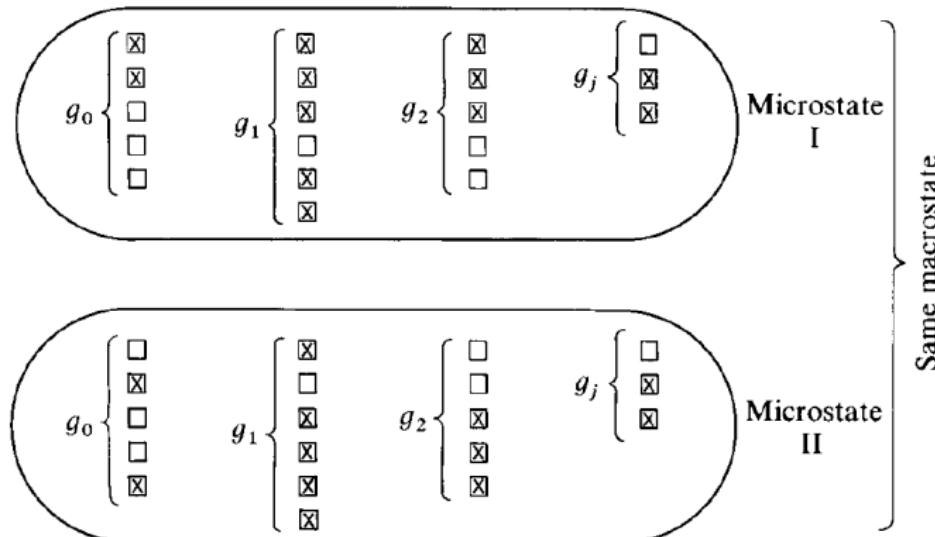


Figure: Illustration of microstates [3].

Energy States

- ▶ It is also interesting here to note the relationship to entropy:
 $S = k \ln W$.
- ▶ So maximum W is also the maximum entropy, which is the thermodynamic tendency.

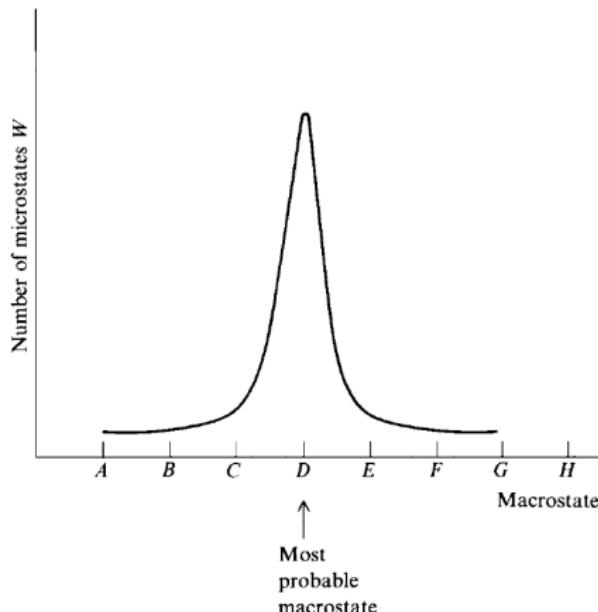


Figure: Most probable macrostate [3].

Thermodynamic Equilibrium

Thermodynamic Equilibrium

- ▶ One of the central assumptions is that each microstate is equally as likely as any other. Therefore, *the most probable macrostate is the one which has the maximum number of microstates.*
- ▶ Now, the exercise is reduced to counting the number of microstates for a given macrostate. Quantum mechanics makes a distinction between two different types of particles:
 - ▶ **Bosons** have an even number of elementary particles (protons, neutrons, electrons) and obey Bose-Einstein statistics. The number of particles which can be in any single degenerate state is unlimited.
 - ▶ **Fermions** have an odd number of elementary particles and obey Fermi-Dirac statistics. Only one molecule can be in any given degenerate state at any instant.

Thermodynamic Equilibrium

- ▶ By considering possible permutations, can find the total number of microstates W for a given macrostate N_j :

$$W_{bosons} = \prod_j \frac{(N_j + g_j - 1)!}{(g_j - 1)! N_j!} \quad (7)$$

$$W_{fermions} = \prod_j \frac{g_j!}{(g_j - N_j)! N_j!} \quad (8)$$

- ▶ If we force W to be maximum, can find the corresponding population distribution N_j^* :

$$N_{j,bosons}^* = \frac{g_j}{e^\alpha e^{\beta \varepsilon'_j} - 1} \quad (9)$$

$$N_{j,fermions}^* = \frac{g_j}{e^\alpha e^{\beta \varepsilon'_j} + 1} \quad (10)$$

- ▶ Where α and β are Lagrange multipliers introduced during the derivation.

Thermodynamic Equilibrium

- ▶ Differences between bosons and fermions are only significant at very low temperatures ($< 5\text{ K}$). Above this, have $N_j \ll g_j$, requiring a large denominator. In the high temperature limit:

$$N_j^* = \frac{g_j}{e^\alpha e^{\beta \varepsilon'_j}} \quad (11)$$

$N_j^* = g_j e^{-\alpha} e^{\beta \varepsilon'_j}$

The Boltzmann distribution! (12)

- ▶ Where $\beta = \frac{1}{kT}$ and $e^{-\alpha} = \frac{N}{\sum_j g_j e^{-\varepsilon'_j/kT}}$:

$$N_j^* = N \frac{g_j e^{-\varepsilon'_j/kT}}{\sum_j g_j e^{-\varepsilon'_j/kT}} \quad (13)$$

Thermodynamic Equilibrium

- Our most probable energy state moves to the right as the temperature goes up:

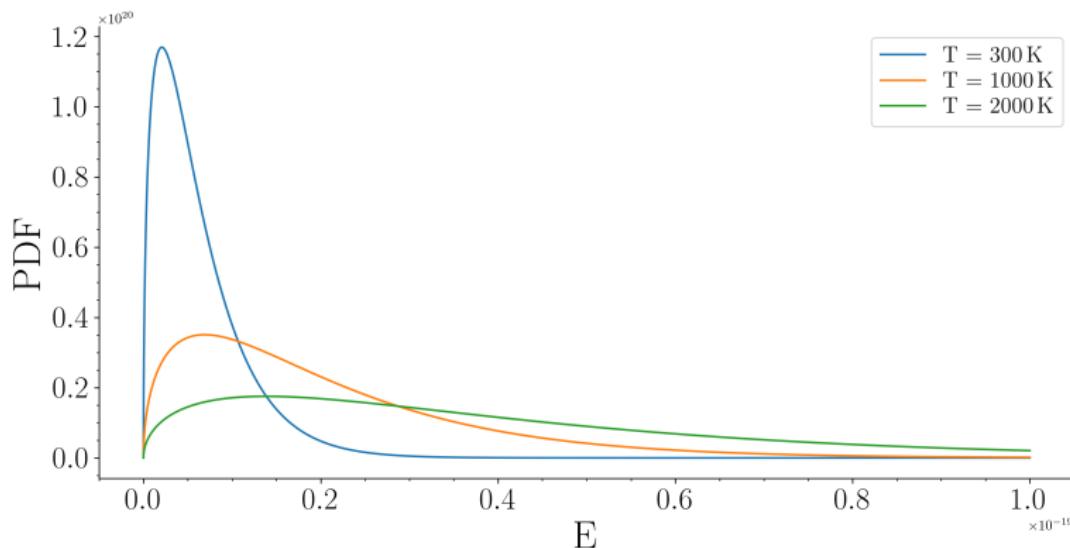


Figure: Boltzmann distribution for three different temperatures.

Partition Function

Partition Function

- ▶ Energies so far have included the zero-point. However, it can be shown that using the energy above zero point is equivalent, resulting in:

$$\frac{N_j^*}{N} = \frac{g_j e^{-\varepsilon_j/kT}}{\sum_j g_j e^{-\varepsilon_j/kT}} \quad (14)$$

- ▶ Now we define the **partition function** Q , or “state sum”:

$$Q \equiv \sum_j g_j e^{-\varepsilon_j/kT} \quad (15)$$

$$\therefore N_j^* = N \frac{g_j e^{-\varepsilon_j/kT}}{Q} \quad (16)$$

Partition Function

- The partition function Q is a very important quantity. In fact, it can be used to evaluate fundamental thermodynamic quantities (refer to Anderson [3] for derivations):

$$e = RT^2 \left(\frac{\partial \ln Q}{\partial T} \right)_v \quad (17)$$

$$h = RT + RT^2 \left(\frac{\partial \ln Q}{\partial T} \right)_v \quad (18)$$

$$S = k \ln W_{max} \quad (19)$$

$$S = Nk \left(\ln \frac{Q}{N} + 1 \right) + NkT \left(\frac{\partial \ln Q}{\partial T} \right)_v \quad (20)$$

$$p = NkT \left(\frac{\partial \ln Q}{\partial V} \right)_T \quad (21)$$

Partition Function

- ▶ Now, how do we evaluate $Q \equiv \sum_j g_j e^{-\varepsilon_j/kT}$?
- ▶ We need expressions for individual ε_j and g_j for all energy modes.
- ▶ These results come from **quantum mechanics** by solution of the time-invariant Schrödinger equation:

$$H\psi(\mathbf{r}) = E\psi(\mathbf{r}) \quad (22)$$

- ▶ Where \mathbf{r} is position, E represents energy eigenvalues of the Hamiltonian energy operator H , and ψ can be one of many eigenfunctions or wave functions which satisfy certain conditions.
- ▶ The satisfaction of these conditions results in the solution being valid for particular *quantum numbers*.
- ▶ We will not go into the fine details here, and will instead just present some results for a diatomic molecule.

Partition Function

- ▶ For **translational energy**, we have:

$$\varepsilon'_{trans} = \frac{h^2}{8m} \left(\frac{n_1^2}{a_1^2} + \frac{n_2^2}{a_2^2} + \frac{n_3^2}{a_3^2} \right) \quad (23)$$

- ▶ Where h is the Planck constant, m is total mass, n_1 to n_3 are quantum numbers (1, 2, 3, etc. but NOT 0), a_1 to a_3 are linear dimensions describing the extent of the system.
- ▶ For **rotational energy** we use the “rigid rotor model”:

$$\varepsilon'_{rot} = \frac{h^2}{8\pi^2 I} J(J+1) \quad (24)$$

- ▶ Where $J = 0, 1, 2, 3, \dots$ is the rotational quantum number, I is moment of inertia.

Partition Function

- ▶ For **vibrational energy** we use the “dumbbell model”:

$$\varepsilon'_{vib} = h\nu\left(n + \frac{1}{2}\right) \quad (25)$$

- ▶ Where ν is the fundamental vibrational frequency, and $n = 0, 1, 2, 3, \dots$ is the vibrational quantum number.
- ▶ **Electronic energy** has no simple expression.

Partition Function

- If we evaluate with the lowest allowable quantum numbers, we obtain the zero-point energies of each mode:

$$\varepsilon'_{0,trans} = \frac{h^2}{m} \left(\frac{1}{a_1^2} + \frac{1}{a_2^2} + \frac{1}{a_3^2} \right) \approx 0 \quad (26)$$

$$\varepsilon'_{0,rot} = 0 \quad (27)$$

$$\varepsilon'_{0,vib} = \frac{1}{2} h\nu \quad (28)$$

- Therefore, the sensible energies are:

$$\varepsilon_{trans} = \varepsilon'_{trans} - \varepsilon'_{0,trans} = \frac{h^2}{8m} \left(\frac{n_1^2}{a_1^2} + \frac{n_2^2}{a_2^2} + \frac{n_3^2}{a_3^2} \right) \quad (29)$$

$$\varepsilon_{rot} = \varepsilon'_{rot} - \varepsilon'_{0,rot} = \frac{h^2}{8\pi^2 I} J(J+1) \quad (30)$$

$$\varepsilon_{vib} = \varepsilon'_{vib} - \varepsilon'_{0,vib} = nh\nu \quad (31)$$

$$\varepsilon_{el} = \varepsilon'_{el} - \varepsilon'_{0,el} \quad (32)$$

Partition Function

- Now we can break the partition function into components:

$$Q = \sum_j g_j e^{-\varepsilon_j/kT}$$

$$Q = \sum_i \sum_j \sum_n \sum_l g_i g_j g_n g_l \exp \left[\frac{-1}{kT} (\varepsilon_{i,trans} + \varepsilon_{j,rot} + \varepsilon_{n,vib} + \varepsilon_{l,el}) \right] \quad (33)$$

$$\begin{aligned} Q &= \left(\sum_i g_i e^{-\varepsilon_{i,trans}/kT} \right) \left(\sum_j g_j e^{-\varepsilon_{j,rot}/kT} \right) \\ &\quad \times \left(\sum_n g_n e^{-\varepsilon_{n,vib}/kT} \right) \left(\sum_l g_l e^{-\varepsilon_{l,el}/kT} \right) \end{aligned} \quad (34)$$

$$Q = Q_{trans} Q_{rot} Q_{vib} Q_{el}$$

(35)

Partition Function

- Solutions of the summations provides:

$$Q_{trans} = \left(\frac{2\pi mkT}{h^2} \right)^{3/2} V \quad (36)$$

$$Q_{rot} = \frac{8\pi^2 I k T}{h^2} \quad (37)$$

$$Q_{vib} = \frac{1}{1 - e^{-hv/kT}} \quad (38)$$

$$Q_{el} = \sum_{l=0}^{\infty} g_l e^{-\varepsilon_l/kT} = g_0 + g_1 e^{-\varepsilon_1/kT} + g_2 e^{-\varepsilon_2/kT} + \dots \quad (39)$$

Macroscopic Properties

Specific Heat

- If we substitute our expressions for Q into (17) ($e = RT^2 \left(\frac{\partial \ln Q}{\partial T} \right)_V$), we obtain:

$$e_{trans} = \frac{3}{2}RT \quad (40)$$

$$e_{rot} = RT \quad (41)$$

$$e_{vib} = \left(\frac{h\nu/kT}{e^{h\nu/kT} - 1} \right) RT \quad (42)$$

- Leading to:

$$e_{atom} = \frac{3}{2}RT + e_{el} \quad (43)$$

$$e_{diatomic} = \frac{3}{2}RT + RT + \left(\frac{h\nu/kT}{e^{h\nu/kT} - 1} \right) RT + e_{el} \quad (44)$$

- Note that these are above the zero-point, i.e. *sensible energy*.

Specific Heat

- ▶ Now, from the definition $C_v \equiv \left(\frac{\partial e}{\partial T} \right)_v$ we obtain:

$$C_{v,atom} = \frac{3}{2}R + \frac{\partial e_{el}}{\partial T} \quad (45)$$

$$C_{v,diatomic} = \frac{3}{2}R + R + \left(\frac{(hv/kT)^2 e^{hv/kT}}{(e^{hv/kT} - 1)^2} \right) R + \frac{\partial e_{el}}{\partial T} \quad (46)$$

- ▶ Typically $\frac{\partial e_{el}}{\partial T}$ small except at very high temperatures.
- ▶ How does this compare to kinetic theory, where $C_v = \#DOF \times R/2$?

Specific Heat

- Now, from the definition $C_v \equiv \left(\frac{\partial e}{\partial T} \right)_v$, we obtain:

$$C_{v,atom} = \frac{3}{2}R + \frac{\partial e_{el}}{\partial T} \quad (45)$$

$$C_{v,diatomic} = \frac{3}{2}R + R + \left(\frac{(hv/kT)^2 e^{hv/kT}}{(e^{hv/kT} - 1)^2} \right) R + \frac{\partial e_{el}}{\partial T} \quad (46)$$

- Typically $\frac{\partial e_{el}}{\partial T}$ small except at very high temperatures.
- How does this compare to kinetic theory, where $C_v = \#DOF \times R/2$?*
- This can predict the whole transition from no vibrational excitation to full vibrational excitation. Kinetic theory cannot do this.

Specific Heat

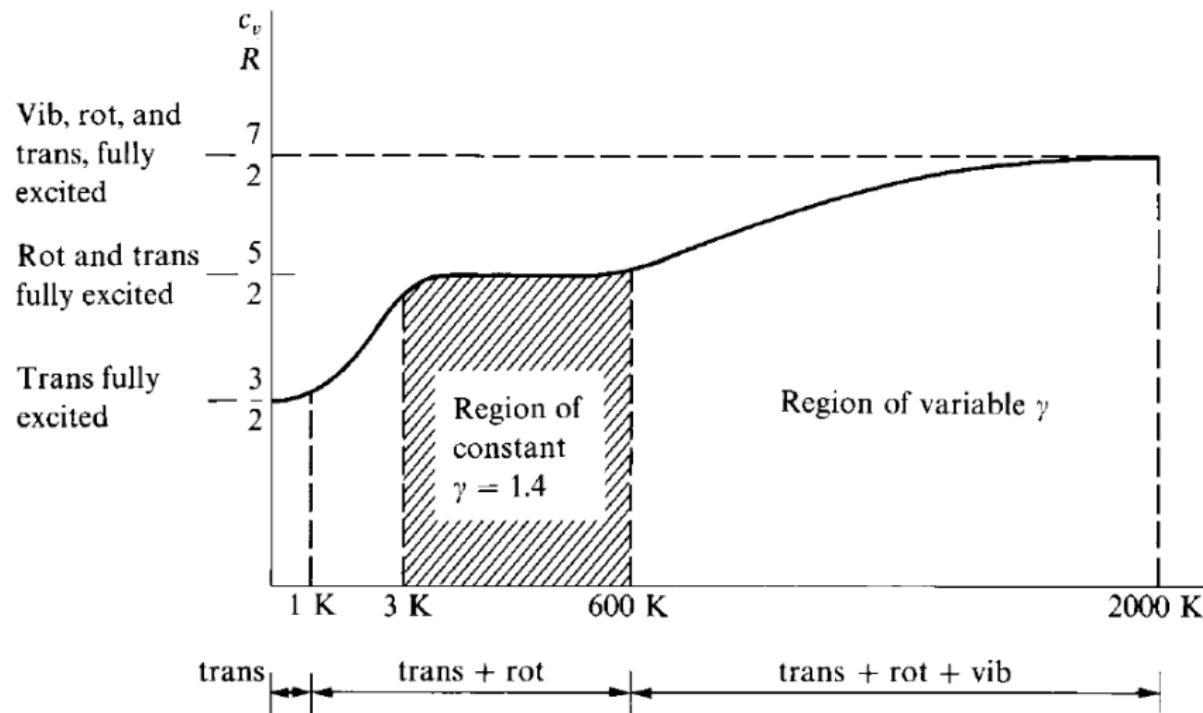


Figure: Variation of specific heat with temperature for a diatomic gas from Anderson [3].

Characteristic Temperature Version

- ▶ I always found the results presented in Anderson [3] hard to use due to a lack of physical data which I could find to use with them.
- ▶ I did some checking in Chapter 4 of Vincenti and Kruger [2] and found a slightly better way to introduce things.
- ▶ Vincenti and Kruger reduced the above equations to versions making use of 'characteristic temperatures' which are tabulated in the back of the book for air.
- ▶ The characteristic temperature for rotation, Θ_r , is defined as $\frac{h^2}{8\pi^2Ik}$
This reduces the rotational partition function to:

$$Q_{rot} = \frac{8\pi^2IkT}{h^2} = \frac{T}{\Theta_r}$$

Characteristic Temperature Version

- ▶ Similarly, they define the characteristic temperature for vibration, Θ_v , as $\frac{hv}{k}$ which reduces the vibrational partition function to:

$$Q_{vib} = \frac{1}{1 - e^{-hv/kT}} = \frac{1}{1 - e^{-\Theta_v/T}}$$

- ▶ The related internal energy and C_v terms are:

$$e_{vib} = \frac{R\Theta_v}{e^{\Theta_v/T} - 1} \quad (47)$$

$$C_{v,vib} = \left(\frac{(\Theta_v/T)^2 e^{\Theta_v/T}}{(e^{\Theta_v/T} - 1)^2} \right) R = \left[\frac{\Theta_v/2T}{\sinh(\Theta_v/2T)} \right]^2 R \quad (48)$$

Characteristic Temperature Version

- ▶ The characteristic temperatures can be found in Appendix 3 of Vincenti and Kruger [2]:

3 PHYSICAL CONSTANTS FOR CONSTITUENTS OF AIR

Values of the physical constants for certain of the important constituents of high-temperature air, some of which are given in various places in the text, are summarized in the following table:

	O ₂	N ₂	NO	O	N
Molecular weight, \hat{M} , gm mole ⁻¹	32.0	28.0	30.0	16.0	14.0
Characteristic temperature for rotation, Θ_r , °K	2.1	2.9	2.5	—	—
Characteristic temperature for vibration, Θ_v , °K	2,270	3,390	2,740	—	—
Characteristic temperature for dissociation, Θ_d , °K	59,500	113,000	75,500	—	—
Characteristic temperature for single ionization, Θ_i , °K	142,000	181,000	108,000	158,000	169,000

Figure: Physical constant of constituents of air from Vincenti and Kruger [2].

Characteristic Temperature Version

- ▶ A nice thing in Vincenti and Kruger [2] is that it gives us a form which lets us calculate the contribution of electronic excitation.
- ▶ The terms of the form ε/k in the electronic partition function are used to define characteristic *temperatures* for electronic excitation, denoted by $\Theta_1, \Theta_2, \dots$, this gives us:

$$Q_{el} = g_0 + g_1 e^{-\Theta_1/T} + g_2 e^{-\Theta_2/T} + \dots \quad (49)$$

- ▶ Ignoring all but the first two terms, we are left with:

$$Q_{el} = g_0 + g_1 e^{-\Theta_1/T} \quad (50)$$

- ▶ The related internal energy and C_v terms are:

$$e_{el} = R\Theta_1 \frac{(g_1/g_0) e^{-\Theta_1/T}}{1 + (g_1/g_0) e^{-\Theta_1/T}} \quad (51)$$

$$C_{v,el} = R \left(\frac{\Theta_1}{T} \right)^2 \frac{(g_1/g_0) e^{-\Theta_1/T}}{\left[1 + (g_1/g_0) e^{-\Theta_1/T} \right]^2} \quad (52)$$

Characteristic Temperature Version

- ▶ The following data from Vincenti and Kruger [2] can be plugged into the equations on the previous slide to get some results.
- ▶ (While everything is presented in the form of partition functions, the constants g_0 , g_1 , Θ_1 can be pulled out of these equations):

$$Q_{el}^O = 5 + 3e^{-288/T} + e^{-326/T} \quad (53)$$

- ▶ where terms of the order of $e^{-23,000/T}$ have been neglected. (Page 132 says that the second and third terms are sufficiently close that $C_{v,el}^O$ will behave very similarly with $\Theta_1 = 270$, $g_1 = 3 + 1 = 4$.)

$$Q_{el}^N = 4 \quad (54)$$

- ▶ where terms of the order of $e^{-28,000/T}$ have been neglected.

$$Q_{el}^{O_2} = 3 + 2e^{-11,390/T} \quad (55)$$

$$Q_{el}^{N_2} = 1 \quad (56)$$

$$Q_{el}^{NO} = 2 + 2e^{-174/T} \quad (57)$$

Characteristic Temperature Version

- Now just to summarise, here are our new versions of C_v for atoms and molecules, assuming that the gas is rotationally excited (as most gases above a Kelvin will be)

$$C_{v,atom} = \frac{3}{2}R + R\left(\frac{\Theta_1}{T}\right)^2 \frac{(g_1/g_0)e^{-\Theta_1/T}}{\left[1 + (g_1/g_0)e^{-\Theta_1/T}\right]^2} \quad (58)$$

$$C_{v,diatomic} = \frac{3}{2}R + R + \left(\frac{(\Theta_v/T)^2 e^{\Theta_v/T}}{(e^{\Theta_v/T} - 1)^2} \right) R + R\left(\frac{\Theta_1}{T}\right)^2 \frac{(g_1/g_0)e^{-\Theta_1/T}}{\left[1 + (g_1/g_0)e^{-\Theta_1/T}\right]^2} \quad (59)$$

- (It is also worth noting that one can still assume no electronic excitation for most practical cases which removes the last term for both equations.)

Equation of State

- ▶ Recall (21):

$$p = NkT \left(\frac{\partial \ln Q}{\partial V} \right)_T$$

- ▶ From our Q component expressions, only Q_{trans} depended on V , leading to:

$$p = NkT \left(\frac{1}{V} \right) \tag{60}$$

$$pV = NkT \tag{61}$$

- ▶ So we see that the perfect gas equation is derived from first principles!

Equilibrium Constant

- ▶ From Lecture 2 we introduced the equilibrium constant:

$$\prod_i p_i^{v_i} = e^{\Delta G^{p=1}/R_u T} \equiv K_p(T)$$

- ▶ This was based on classical thermodynamics where $\Delta G^{p=1}$ is considered a measured quantity. An equivalent expression based on statistical thermodynamics (see Anderson [3] 11.11 for details):

$$K_p(T) = \left(\frac{kT}{V}\right)^{\sum v_i} e^{-\Delta \varepsilon_0/kT} \prod_i Q_i^{v_i} \quad (62)$$

- ▶ This provides a means to *calculate* the equilibrium constant. This is not a simple exercise, but it becomes increasingly necessary at high temperatures due to the difficulty and uncertainty of taking measurements.

Vibrational Energy Example

- ▶ What is the C_v and γ of molecular oxygen at 1,000 K?
- ▶ $R_{univ} = 8,314 \text{ J/kmol/K}$, $\mathcal{M}_{O_2} = 32 \text{ kg/kmol}$.
- ▶ From Vincenti and Kruger [2], the characteristic temperature for vibration of O_2 (Θ_{v,O_2}) is 2,270 K.
- ▶ We also know from Vincenti and Kruger [2] that $Q_{el}^{O_2} = 3 + 2e^{-11,390/T}$, so $\Theta_{1,O_2} = 11,390 \text{ K}$, $g_0 = 3$ and $g_1 = 2$.

- ▶ What is the C_v and γ of molecular oxygen at 1,000 K?
- ▶ $R_{univ} = 8,314 \text{ J/kmol/K}$, $\mathcal{M}_{O_2} = 32 \text{ kg/kmol}$.
- ▶ From Vincenti and Kruger [2], the characteristic temperature for vibration of O_2 (Θ_{v,O_2}) is 2,270 K.
- ▶ We also know from Vincenti and Kruger [2] that $Q_{el}^{O_2} = 3 + 2e^{-11,390/T}$, so $\Theta_{1,O_2} = 11,390 \text{ K}$, $g_0 = 3$ and $g_1 = 2$.
- ▶ This is quite simple. We just need Equation 59 to get C_v and then we can get γ from $\gamma = \frac{C_p}{C_v} = \frac{C_v + R}{C_v}$:

$$C_{v,diatomic} = \frac{3}{2}R + R + \left(\frac{(\Theta_v/T)^2 e^{\Theta_v/T}}{(e^{\Theta_v/T} - 1)^2} \right) R + R \left(\frac{\Theta_1}{T} \right)^2 \frac{(g_1/g_0) e^{-\Theta_1/T}}{[1 + (g_1/g_0) e^{-\Theta_1/T}]}$$

- ▶ If we ignore electronic excitation, it is fairly simple solution too:

$$C_{v,diatomic} = \frac{3}{2}R + R + \left(\frac{(\Theta_v/T)^2 e^{\Theta_v/T}}{(e^{\Theta_v/T} - 1)^2} \right) R$$

- ▶ The numerical result is $C_v = 821.81 \text{ J/kg K}$ and $\gamma = 1.316$.
- ▶ If we ignore electronic excitation: $C_v = 821.55 \text{ J/kg K}$ and $\gamma = 1.316$

- ▶ What is the C_v and γ of molecular oxygen at 1,000 K?
- ▶ Now that we have a solution, it is interesting to consider how our result compares to CEA and kinetic theory:

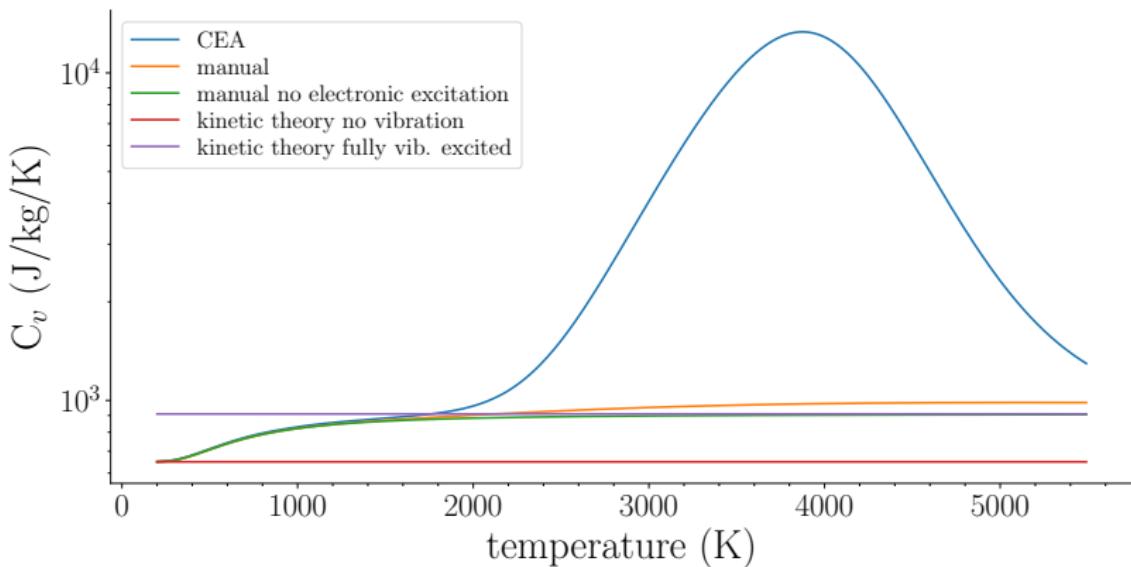


Figure: C_v for O_2 with changing temperature.

- ▶ What is the C_v and γ of molecular oxygen at 1,000 K?
- ▶ Now that we have a solution, it is interesting to consider how our result compares to CEA and kinetic theory:

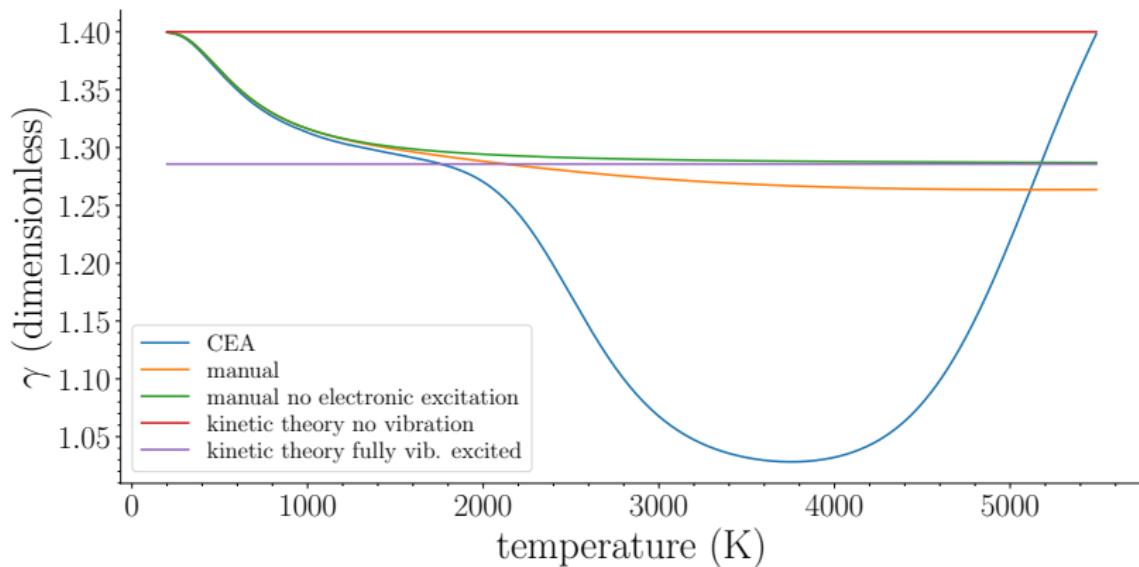


Figure: γ for O_2 with changing temperature.

Summary

- ▶ We have seen that statistical thermodynamics is a powerful tool that can be used to explain some of the odd behaviour observed in high temperature gas dynamics. Using quantum mechanics we can derive the macroscopic properties of a gas from first principles
- ▶ The concepts of discretised energy modes will be important when we discuss thermal nonequilibrium.

References |

- [1] Anderson, J. D., *Hypersonic and High-Temperature Gas Dynamics*, American Institute of Aeronautics and Astronautics, Inc., Reston, Virginia, USA, 3rd ed., 2019.
- [2] Vincenti, W. G. and Kruger, C. H., *Introduction to Physical Gas Dynamics*, Robert E. Krieger Publishing Co., Inc., Huntington, N.Y., U.S.A., 1977.
- [3] Anderson, J. D., *Hypersonic and High-Temperature Gas Dynamics*, American Institute of Aeronautics and Astronautics, Inc., 1801 Alexander Bell Drive, Reston, Virginia 20191-4344, 2nd ed., 2006.

