

## 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  $S_{ref} = \sum_i X_i S_{i,ref}$

1012/63

## 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:

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

- 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):

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

1014/63

## 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:

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

1015/63



AERO4470

## High Temperature Gas Dynamics Lecture 2: Equilibrium Mixtures

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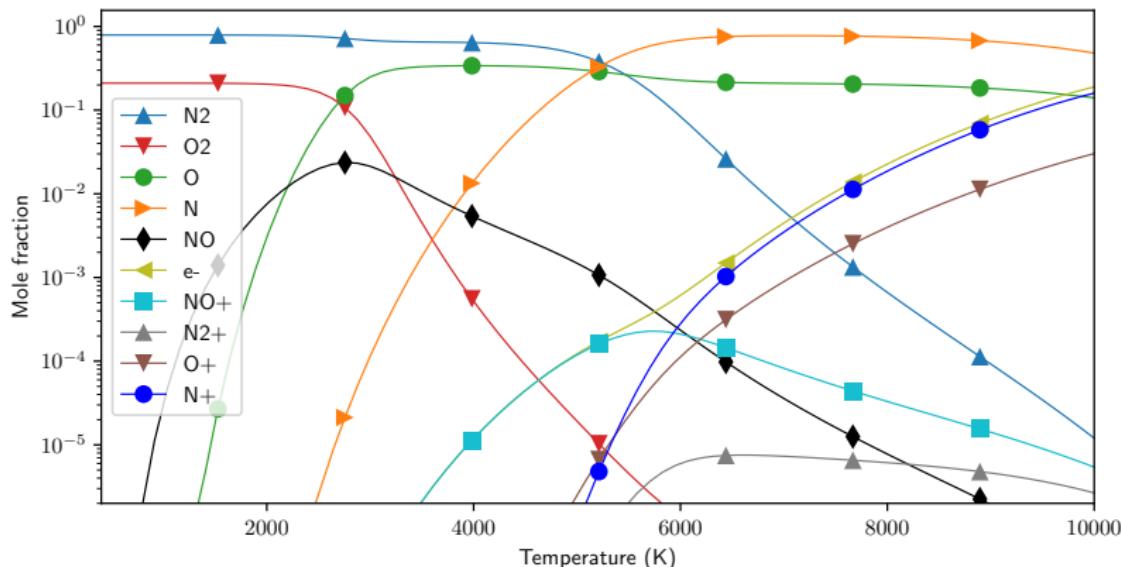


# Introduction

- ▶ 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  $dV$ ):

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

$$\delta Q = dE + pdV$$

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

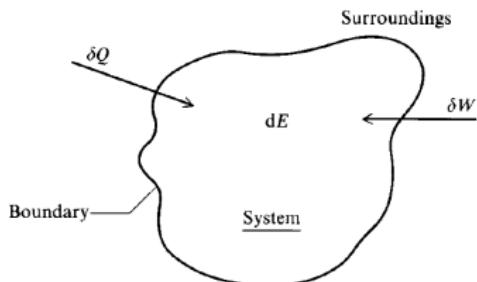


Figure: Thermodynamic system [3].

- 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:

$$e = e(T, v)$$

$$de = \left( \frac{\partial e}{\partial T} \right)_v dT + \left( \frac{\partial e}{\partial v} \right)_T dv \quad (5)$$

- ▶ 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:

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

# Perfect Gas Relationship Between $C_p$ and $C_v$

- ▶ From the definition of  $C_p$ :

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

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

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

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

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

- ▶ 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:

$R$  or  $\gamma = \frac{C_p}{C_v}$ ?

$$C_p - C_v = R$$

Gas constant

# Second Law of Thermodynamics

I<sub>sentropic</sub>

- ▶ 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:

$$ds_{irrev} > 0$$

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

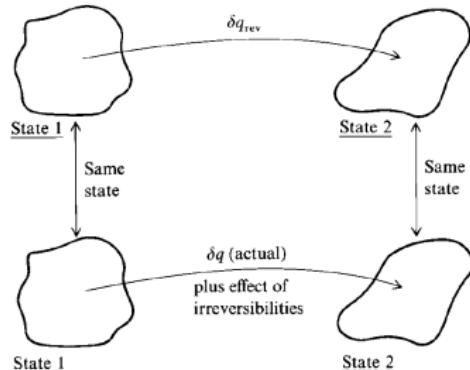


Figure: Illustration of second law [3].

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

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



## Second Law of Thermodynamics

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particles in a mole.

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

(29)

Finished lecture 2.

Start Week 3

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## The Equilibrium Constant

Hypersonics Equilibrium is the best way to analyse.

## 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:

Reactants → Products



- ▶ 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  $\frac{1}{2} H_2 \rightarrow H$ :

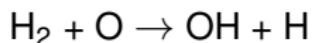
$A_1 = H_2, v_1 = -\frac{1}{2}$

$A_2 = H, v_2 = 1$

- ▶ (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  $\text{H}_2$  is a reactant)

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

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

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



$N_i$ : Δ in number of moles of species  $i$

# 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  $d\xi$ : *as far through the reaction rate / time dependent reactions.*

$$\frac{d\mathcal{N}_1}{v_1} = \frac{d\mathcal{N}_2}{v_2} = \frac{d\mathcal{N}_j}{v_j} = d\xi \text{ or: } \begin{matrix} \text{as far through the reaction} \\ \text{rate / time dependent} \\ \text{reactions.} \end{matrix} \quad (33)$$

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

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

⋮

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

# Equilibrium Constant Derivation

- The quantity  $\xi$  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  $\mathcal{N}_i = \mathcal{N}_{i,\text{ref}}$ :

*ref, room temp?*

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

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

- 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)

*Summation of Gibbs free energy from all species = 0.*

# 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:

'atmospheres'  
 reference pressure to  
 1 atm

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

# 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):

$p = p$  partial pressure

$v$  = stoichiometric mole

#

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

equilibrium  
constant. (41)

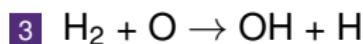
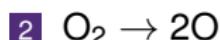
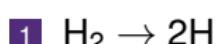
- Note that  $K_p(T)$  is a function of  $T$  only. This can either be obtained from experiment, data tables, or calculated from first principles by statistical mechanics.
- Various data tables exist. I find McBride [4] et al.'s the easiest to use:  
<https://ntrs.nasa.gov/archive/nasa/casi.ntrs.nasa.gov/19630013835.pdf>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



Remember these bad boys

4 species

# Equilibrium Composition Example

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

partial pressure  
of hydrogen etc.

$$K_{p1}(T) = \prod_i p_i^{v_i} = p_H^2 \cdot p_{\text{H}_2}^{-1} = \frac{p_H^2}{p_{\text{H}_2}} = e^{-\Delta G^{p=1}/R_u T} \quad (1)$$

- ▶ A quick note, if we used our equivalent  $\frac{1}{2} \text{H}_2 \rightarrow \text{H}$ :
  - ▶  $K_{p1} = \frac{p_H}{\sqrt{p_{\text{H}_2}}} \neq \frac{p_H^2}{p_{\text{H}_2}}$  different value!
- ▶ It won't change the final answer though.

# Equilibrium Composition Example

Assignment

- ▶ For the other three reactions we have:

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

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

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

- ▶ 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.

partial pressure of each species then find composition.

# 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: 5<sup>th</sup>

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

- Our final equation is the conservation of nuclei, which will be based on our initial conditions: 6<sup>th</sup>

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

- 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:

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

*→ plasma  
charge as  
well of  
electrons.*

# 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]:

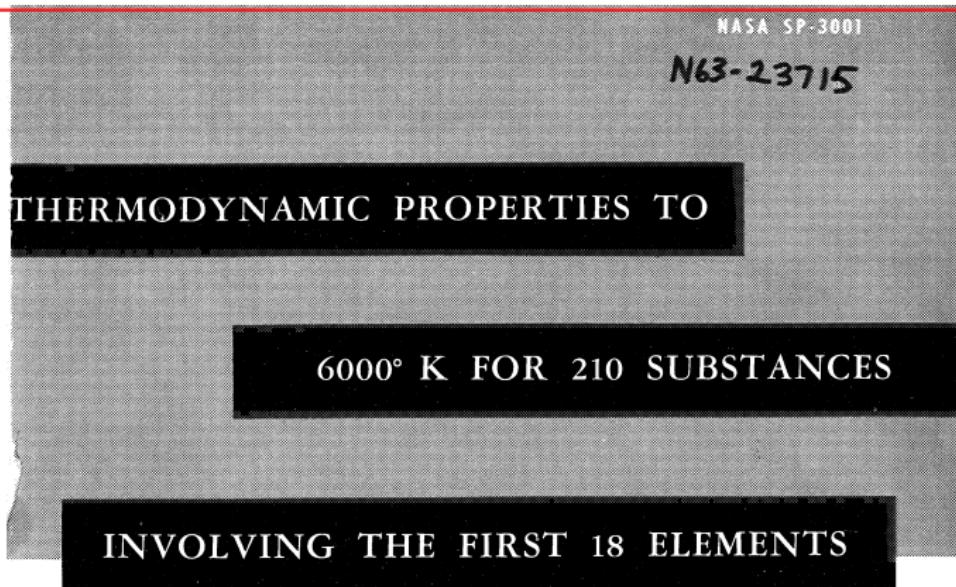


Figure: Cover of McBride et al. [4].

# Equilibrium Composition Example

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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:

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TABLE III. - Continued. THERMODYNAMIC PROPERTIES  
(94) N (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 $^{\circ}\text{K}$	$-fT^2 - H_f^0,$ cal/mole	$H_f^0,$ cal/mole	Formation from reference elements (ΔH_f^0)_r, cal/mole	Formation from gaseous atoms $\log_{10} K_f$
0		0	0	0	0	0	0
100	4.9501	4.9501	21.9630	1494.7	10041.5	21478.4	0
200	9.9001	9.9001	25.0487	4098.1	11210.1	31941.2	-11.9396
300	14.8501	14.8501	27.4231	6496.4	13210.9	52100.8	-8.5782
400	19.8001	19.8001	29.0223	8756.9	15210.9	73100.8	-6.1717
500	24.7501	24.7501	29.7923	10912.4	17210.9	94100.8	-4.0137
600	29.7001	29.7001	30.6627	12969.4	19210.9	115100.8	0
700	34.6501	34.6501	31.6226	14845.2	21010.9	136100.8	-1.9482
800	39.6001	39.6001	32.6726	16621.0	22810.9	157100.8	-0.9336
900	44.5501	44.5501	33.7123	18397.7	24610.9	178100.8	-0.0000
1000	49.5001	49.5001	34.7523	20174.4	26410.9	199100.8	0
1100	54.4501	54.4501	35.7824	21851.0	28210.9	220100.8	-7.5089
1200	59.4001	59.4001	36.8124	23527.6	30010.9	241100.8	-0.7053
1300	64.3501	64.3501	37.8424	25194.1	31810.9	262100.8	-0.3117
1400	69.3001	69.3001	38.8724	26861.7	33610.9	283100.8	-0.7981
1500	74.2501	74.2501	39.9024	28529.3	35410.9	304100.8	0
1600	79.2001	79.2001	40.9324	30196.9	37210.9	325100.8	-0.2643
1700	84.1501	84.1501	41.9624	31864.5	39010.9	346100.8	-0.5323
1800	89.1001	89.1001	42.9924	33532.1	40810.9	367100.8	-0.8077
1900	94.0501	94.0501	43.0224	35199.7	42610.9	388100.8	-0.2702
2000	99.0001	99.0001	43.0524	36867.3	44410.9	409100.8	-0.7952
2100	103.9501	103.9501	37.0907	48534.9	56010.9	520100.8	0
2200	108.9001	108.9001	37.1218	51178.6	57810.9	54100.8	-0.2915
2300	113.8501	113.8501	37.1528	53842.3	59610.9	56200.8	-0.5828
2400	118.8001	118.8001	37.1838	56506.0	61410.9	58300.8	-0.8741
2500	123.7501	123.7501	37.2148	59169.7	63210.9	60400.8	-0.2654
2600	128.7001	128.7001	38.1117	66777.4	63161.7	66510.8	-0.1617
2700	133.6501	133.6501	38.3392	80101.9	64031.5	68420.8	-0.4673
2800	138.6001	138.6001	38.5598	93426.5	64901.3	70320.8	-0.8079
2900	143.5501	143.5501	38.7793	106751.1	65771.1	72220.8	-0.2115
3000	148.5001	148.5001	39.9827	121083.3	65620.9	74120.8	-0.8039
3100	153.4501	153.4501	39.5264	105257.0	66217.8	76020.8	-0.4766
3200	158.4001	158.4001	39.6564	121933.6	67014.6	77920.8	-0.2523
3300	163.3501	163.3501	39.7864	138619.2	67811.4	79820.8	-0.6399
3400	168.3001	168.3001	39.9164	155294.8	68608.2	81720.8	-0.0211
3500	173.2501	173.2501	39.9464	171980.5	69395.0	83620.8	-0.2209
3600	178.2001	178.2001	39.9764	188666.1	70181.8	85520.8	-0.1351
3700	183.1501	183.1501	40.0064	205351.7	69878.6	87420.8	-0.5965
3800	188.1001	188.1001	40.0364	222037.3	70675.4	89320.8	-0.8878
3900	193.0501	193.0501	40.0664	238723.9	69972.1	91220.8	-0.2427
4000	198.0001	198.0001	40.0964	255409.5	70768.9	93120.8	-0.8390
4100	202.9501	202.9501	40.1264	272095.1	70465.6	95020.8	-0.2379
4200	207.9001	207.9001	40.1564	288780.7	71262.3	96920.8	-0.5450
4300	212.8501	212.8501	40.1864	305466.3	72059.0	98820.8	-0.8378
4400	217.8001	217.8001	40.2164	322151.9	72855.8	100720.8	-0.2309
4500	222.7501	222.7501	40.2464	338837.5	73652.5	102620.8	-0.8366
4600	227.7001	227.7001	40.2764	355523.1	74449.2	104520.8	-0.2291
4700	232.6501	232.6501	40.3064	372208.7	75246.9	106420.8	-0.8329
4800	237.6001	237.6001	40.3364	388894.3	76043.6	108320.8	-0.2276
4900	242.5501	242.5501	40.3664	405579.9	76840.3	110220.8	-0.8268
5000	247.5001	247.5001	40.3964	422265.5	77637.0	112120.8	-0.2264
5100	252.4501	252.4501	40.4264	438951.1	78433.7	114020.8	-0.8251
5200	257.4001	257.4001	40.4564	455636.7	79230.4	115920.8	-0.2258
5300	262.3501	262.3501	40.4864	472322.3	79927.1	117820.8	-0.8245
5400	267.3001	267.3001	40.5164	488997.9	79723.8	119720.8	-0.2255
5500	272.2501	272.2501	40.5464	505683.5	79520.5	121620.8	-0.8232
5600	277.2001	277.2001	40.5764	522369.1	79317.2	123520.8	-0.2240
5700	282.1501	282.1501	40.6064	539054.7	79113.9	125420.8	-0.8219
5800	287.1001	287.1001	40.6364	555740.3	78910.6	127320.8	-0.2248
5900	292.0501	292.0501	40.6664	572425.9	78707.3	129220.8	-0.8207
6000	297.0001	297.0001	40.6964	589111.5	78504.0	131120.8	-0.2237
6100	301.9501	301.9501	40.7264	605797.1	78299.7	133020.8	-0.8196
6200	306.9001	306.9001	40.7564	622482.7	78096.4	134920.8	-0.2226
6300	311.8501	311.8501	40.7864	639168.3	77893.1	136820.8	-0.8184
6400	316.8001	316.8001	40.8164	655853.9	77689.8	138720.8	-0.2215
6500	321.7501	321.7501	40.8464	672539.5	77486.5	140620.8	-0.8153
6600	326.7001	326.7001	40.8764	689225.1	77283.2	142520.8	-0.2184
6700	331.6501	331.6501	40.9064	705910.7	77079.9	144420.8	-0.8113
6800	336.6001	336.6001	40.9364	722596.3	76876.6	146320.8	-0.2112
6900	341.5501	341.5501	40.9664	739281.9	76673.3	148220.8	-0.8071
7000	346.5001	346.5001	40.9964	755967.5	76469.9	150120.8	-0.2078
7100	351.4501	351.4501	41.0264	772653.1	76266.6	152020.8	-0.8037
7200	356.4001	356.4001	41.0564	789338.7	76063.3	153920.8	-0.2045
7300	361.3501	361.3501	41.0864	805924.3	75860.0	155820.8	-0.8004
7400	366.3001	366.3001	41.1164	822609.9	75656.7	157720.8	-0.2053
7500	371.2501	371.2501	41.1464	839295.5	75453.4	159620.8	-0.8022
7600	376.2001	376.2001	41.1764	855981.1	75250.1	161520.8	-0.2062
7700	381.1501	381.1501	41.2064	872666.7	75046.8	163420.8	-0.8001
7800	386.1001	386.1001	41.2364	889352.3	74843.5	165320.8	-0.2071
7900	391.0501	391.0501	41.2664	905937.9	74639.9	167220.8	-0.8030
8000	395.9501	395.9501	41.2964	922623.5	74436.6	169120.8	-0.2039
8100	400.9001	400.9001	41.3264	939309.1	74233.3	171020.8	-0.8009
8200	405.8501	405.8501	41.3564	955994.7	74030.0	172920.8	-0.2048
8300	410.8001	410.8001	41.3864	972680.3	73826.7	174820.8	-0.8008
8400	415.7501	415.7501	41.4164	989365.9	73623.4	176720.8	-0.2057
8500	420.7001	420.7001	41.4464	100604.5	73420.1	178620.8	-0.8017
8600	425.6501	425.6501	41.4764	102272.1	73216.8	180520.8	-0.2066
8700	430.6001	430.6001	41.5064	103940.7	73013.5	182420.8	-0.8026
8800	435.5501	435.5501	41.5364	105608.3	72809.9	184320.8	-0.2075
8900	440.5001	440.5001	41.5664	107276.9	72606.6	186220.8	-0.8035
9000	445.4501	445.4501	41.5964	108945.5	72403.3	188120.8	-0.2084
9100	450.4001	450.4001	41.6264	110614.1	72199.9	190020.8	-0.8044
9200	455.3501	455.3501	41.6564	112282.7	71996.6	191920.8	-0.2093
9300	460.3001	460.3001	41.6864	113951.3	71793.3	193820.8	-0.8053
9400	465.2501	465.2501	41.7164	115619.9	71589.9	195720.8	-0.2062
9500	470.2001	470.2001	41.7464	117288.5	71386.6	197620.8	-0.8062
9600	475.1501	475.1501	41.7764	118957.1	71183.3	199520.8	-0.2071
9700	480.1001	480.1001	41.8064	120625.7	70979.9	201420.8	-0.8071
9800	485.0501	485.0501	41.8364	122294.3	70776.6	203320.8	-0.2080

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:

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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	$\log_{10} K_f$	$\Delta H_f^o$ , cal/mole	$\log_{10} K$
0	-----	0	-----	0	50616.5	51628.4	-----	0	-----
100	4.9681	496.8	21.9650	1699.7	51113.5	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:

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$T_c$ °R	$\frac{P_c}{R}$ psi/mole °R	$M_p - M_{IO}$ cal/mole	$S_p^o$ cal/mole °K	$-(F_p^o - M_{IO}^o)$ cal/mole °K	$H_p^o$ cal/mole	Formation from assigned reference elements		Formation from gasless atoms	
						$\Delta H_{p,IO}^o$ cal/mole	$\log_{10} K_p$	$\Delta H_{f,IO}^o$ cal/mole	$\log_{10} K'$
100	0	0	0	0	0	0	0	0	0
200	0.5102	1.1204	20.347	-107.87	21.761	-107.87	0	-107.87	0
208.15	0.4914	2.0216	21.207	-209.0	21.207	-209.0	0	-209.0	0
300	0.4405	2.5137	23.204	-251.7	23.204	-251.7	0	-251.7	0
400	0.4752	2.7141	23.426	-308.4	23.426	-308.4	0	-308.4	0
500	0.4927	2.8472	23.574	-350.0	23.574	-350.0	0	-350.0	0
600	0.5000	2.9473	23.652	-386.7	23.652	-386.7	0	-386.7	0
700	0.5072	3.0213	23.756	-419.2	23.756	-419.2	0	-419.2	0
800	0.5136	3.0813	23.834	-447.9	23.834	-447.9	0	-447.9	0
900	0.5190	3.1303	23.892	-472.7	23.892	-472.7	0	-472.7	0
1000	0.5234	3.1703	23.939	-494.9	23.939	-494.9	0	-494.9	0
1100	0.5267	3.2013	23.976	-515.9	23.976	-515.9	0	-515.9	0
1200	0.5290	3.2242	24.003	-535.7	24.003	-535.7	0	-535.7	0
1300	0.5309	3.2382	24.021	-553.8	24.021	-553.8	0	-553.8	0
1400	0.5326	3.2482	24.039	-570.8	24.039	-570.8	0	-570.8	0
1500	0.5339	3.2559	24.051	-586.3	24.051	-586.3	0	-586.3	0
1600	0.5350	3.2629	24.062	-599.8	24.062	-599.8	0	-599.8	0
1700	0.5359	3.2692	24.071	-612.3	24.071	-612.3	0	-612.3	0
1800	0.5366	3.2752	24.078	-623.8	24.078	-623.8	0	-623.8	0
1900	0.5372	3.2809	24.084	-634.3	24.084	-634.3	0	-634.3	0
2000	0.5377	3.2856	24.089	-644.7	24.089	-644.7	0	-644.7	0
2100	0.5380	3.2899	24.093	-654.2	24.093	-654.2	0	-654.2	0
2200	0.5382	3.2934	24.096	-663.6	24.096	-663.6	0	-663.6	0
2300	0.5384	3.2964	24.098	-672.9	24.098	-672.9	0	-672.9	0
2400	0.5385	3.2989	24.100	-681.2	24.100	-681.2	0	-681.2	0
2500	0.5385	3.3009	24.101	-689.5	24.101	-689.5	0	-689.5	0
2600	0.5385	3.3029	24.102	-697.7	24.102	-697.7	0	-697.7	0
2700	0.5385	3.3049	24.103	-705.9	24.103	-705.9	0	-705.9	0
2800	0.5385	3.3069	24.104	-713.9	24.104	-713.9	0	-713.9	0
2900	0.5385	3.3088	24.105	-721.8	24.105	-721.8	0	-721.8	0
3000	0.5385	3.3108	24.106	-729.7	24.106	-729.7	0	-729.7	0
3100	0.5385	3.3127	24.107	-737.5	24.107	-737.5	0	-737.5	0
3200	0.5385	3.3147	24.108	-745.3	24.108	-745.3	0	-745.3	0
3300	0.5385	3.3166	24.109	-752.9	24.109	-752.9	0	-752.9	0
3400	0.5385	3.3186	24.110	-760.5	24.110	-760.5	0	-760.5	0
3500	0.5385	3.3205	24.111	-768.1	24.111	-768.1	0	-768.1	0
3600	0.5385	3.3224	24.112	-775.6	24.112	-775.6	0	-775.6	0
3700	0.5385	3.3243	24.113	-783.1	24.113	-783.1	0	-783.1	0
3800	0.5385	3.3262	24.114	-789.6	24.114	-789.6	0	-789.6	0
3900	0.5385	3.3281	24.115	-796.0	24.115	-796.0	0	-796.0	0
4000	0.5385	3.3299	24.116	-802.3	24.116	-802.3	0	-802.3	0
4100	0.5385	3.3318	24.117	-808.6	24.117	-808.6	0	-808.6	0
4200	0.5385	3.3337	24.118	-814.9	24.118	-814.9	0	-814.9	0
4300	0.5385	3.3356	24.119	-821.1	24.119	-821.1	0	-821.1	0
4400	0.5385	3.3375	24.120	-827.3	24.120	-827.3	0	-827.3	0
4500	0.5385	3.3394	24.121	-833.5	24.121	-833.5	0	-833.5	0
4600	0.5385	3.3413	24.122	-839.7	24.122	-839.7	0	-839.7	0
4700	0.5385	3.3432	24.123	-845.9	24.123	-845.9	0	-845.9	0
4800	0.5385	3.3451	24.124	-852.1	24.124	-852.1	0	-852.1	0
4900	0.5385	3.3470	24.125	-858.3	24.125	-858.3	0	-858.3	0
5000	0.5385	3.3489	24.126	-864.5	24.126	-864.5	0	-864.5	0
5100	0.5385	3.3508	24.127	-870.7	24.127	-870.7	0	-870.7	0
5200	0.5385	3.3527	24.128	-876.9	24.128	-876.9	0	-876.9	0
5300	0.5385	3.3546	24.129	-883.1	24.129	-883.1	0	-883.1	0
5400	0.5385	3.3565	24.130	-889.3	24.130	-889.3	0	-889.3	0
5500	0.5385	3.3584	24.131	-895.5	24.131	-895.5	0	-895.5	0
5600	0.5385	3.3603	24.132	-901.7	24.132	-901.7	0	-901.7	0
5700	0.5385	3.3622	24.133	-907.9	24.133	-907.9	0	-907.9	0
5800	0.5385	3.3641	24.134	-914.1	24.134	-914.1	0	-914.1	0
5900	0.5385	3.3660	24.135	-919.3	24.135	-919.3	0	-919.3	0
6000	0.5385	3.3679	24.136	-925.5	24.136	-925.5	0	-925.5	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:

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TABLE III. - Continued. THERMODYNAMIC PROPERTIES

 (95) H<sub>2</sub> (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	$\log_{10} K_f$	$\Delta H_f^o$ , 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  $H$ :

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

*Enthalpy at 0 Kelvin.*

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

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

$$F_T^0 = G_H^{p=1} = [-45,676.3 + 50,616.5] \frac{\text{cal}}{\text{mol}} \quad \left| \begin{array}{l} 4.18 \frac{\text{J}}{\text{cal}} \\ \text{Calories to Joules} \end{array} \right.$$

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

*Gibbs free energy?*

# Equilibrium Composition Example

- For  $H_2$ :

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

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

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

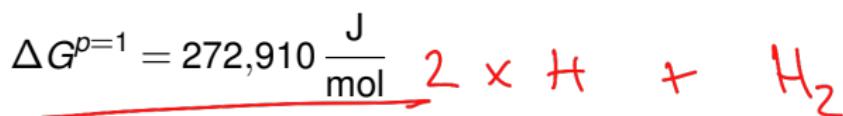
$$F_T^0 = G_H^{p=1} = [-53,385.4 + -2,023.8] \frac{\text{cal}}{\text{mol}} \cdot 4.18 \frac{\text{J}}{\text{cal}}$$

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

# Equilibrium Composition Example

- Now:

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



- From here:

+                    -

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

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

pressure squared = atm.  
pressure

- (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 [N<sub>2</sub>/O<sub>2</sub>] in the assignment.)



# Equilibrium Composition Example

Assignment.



- ▶ 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:
- free stream*  
*u = velocity*

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

*pressure + dynamic pressure*

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

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

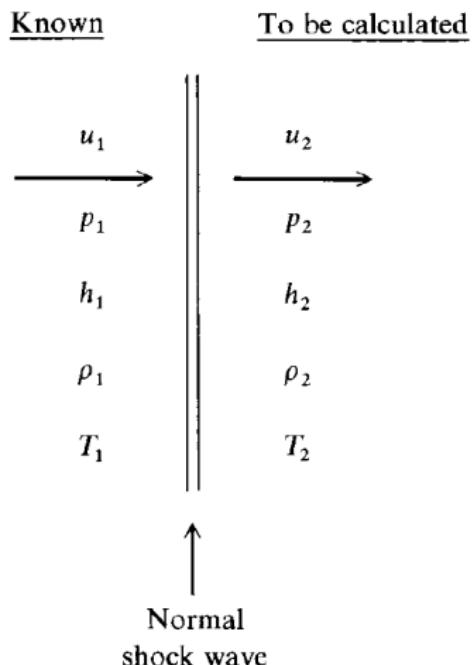


Figure: EQ normal shock [3].

# 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  $\rho_1/\rho_2$  (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  $\rho_2$
  - 4 Iterate until converged (typically in 5 or so steps)
- ▶ This sounds easy, BUT in practice  $\rho_2$  is calculated from  $p$ ,  $T$  rather than  $p$ ,  $h$ , and there is no straightforward way of getting  $T$  from  $h$ .

ideal gas guess of Temp behind shock then reiterate.

# 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  $\rho_1/\rho_2$  (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  $\rho_2$
  - 3 Iterate until converged (typically in 5 or so steps)

*that's what he's saying after iteration it's pretty close.*
- 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. *Need composition to get enthalpy then Temperature*

## Post shock conditions - no analytical way.

- ▶ 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  $\rho_2$ :

*R for room temp.*

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

- ▶  $\rho_2$  can then be used to find a new  $u_2$  value:

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

- ▶  $u_2$  and  $\rho_2$  can then be fed into the next iteration until  $\rho_2$  stops changing between iterations. *mainly want T over composition.*

# Equilibrium Normal Shock

EXAM

- ▶ 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:

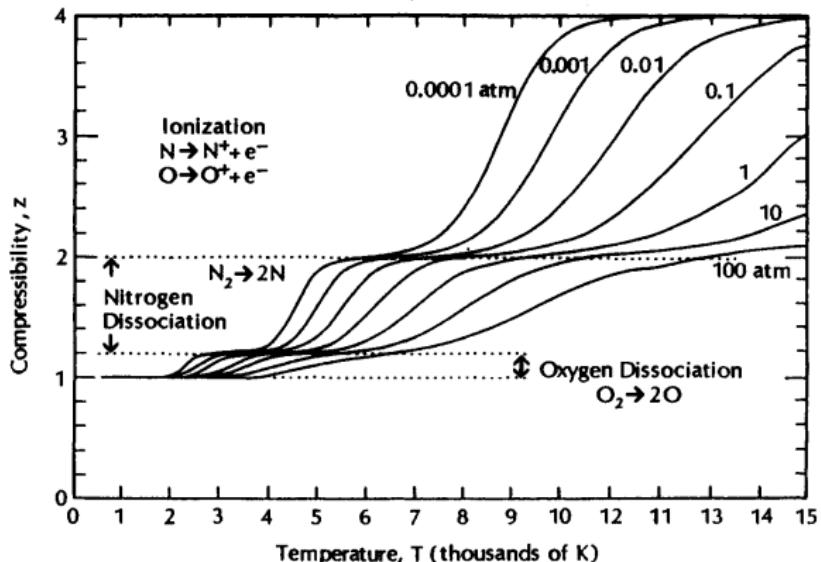


Figure: How the compressibility factor changes from Bertin [2].

# 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). *Assume  $u_2 = 0 \text{ m/s}$*
- ▶ 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

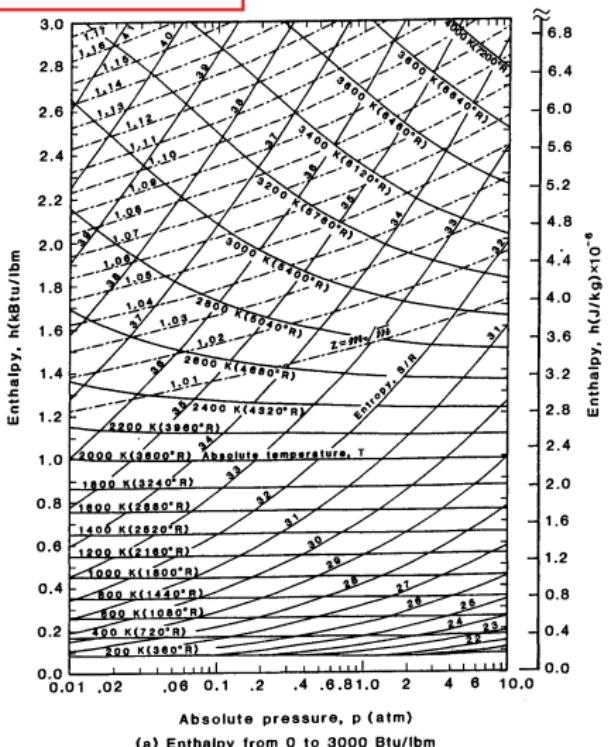


Fig. 1.17 Detailed charts for thermodynamic properties of air in chemical equilibrium, as taken from Ref. 18.

Figure: Fig 1.17a from Bertin [2].

# Equilibrium Normal Shock

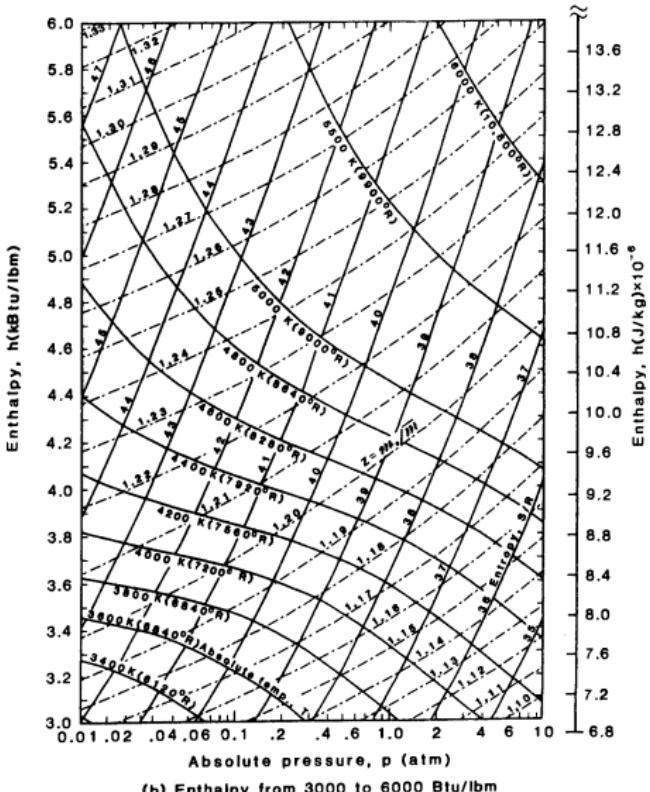


Fig. 1.17 Continued.

Figure: Fig 1.17b from Bertin [2].

# Equilibrium Normal Shock

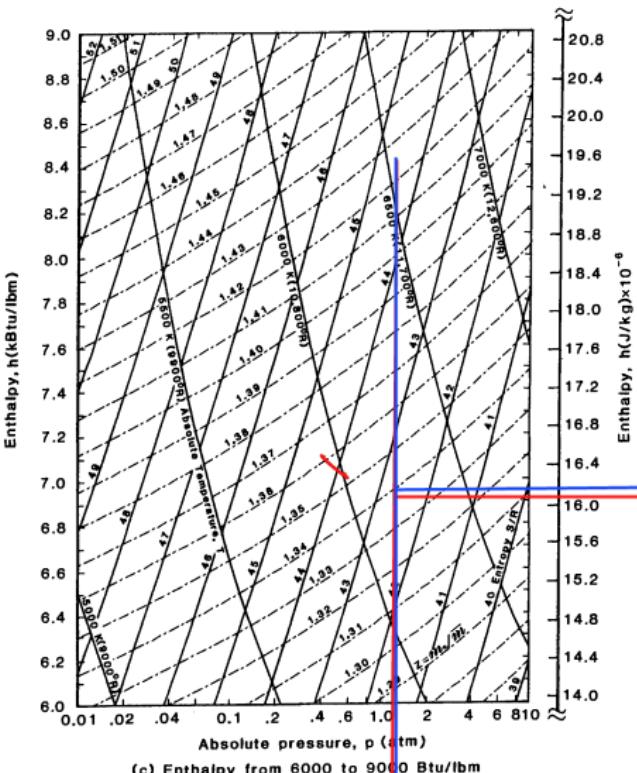


Fig. 1.17 Continued.

Figure: Fig 1.17c from Bertin [2].

Iteration 1:

$$T_2 \approx 5000\text{ K}$$

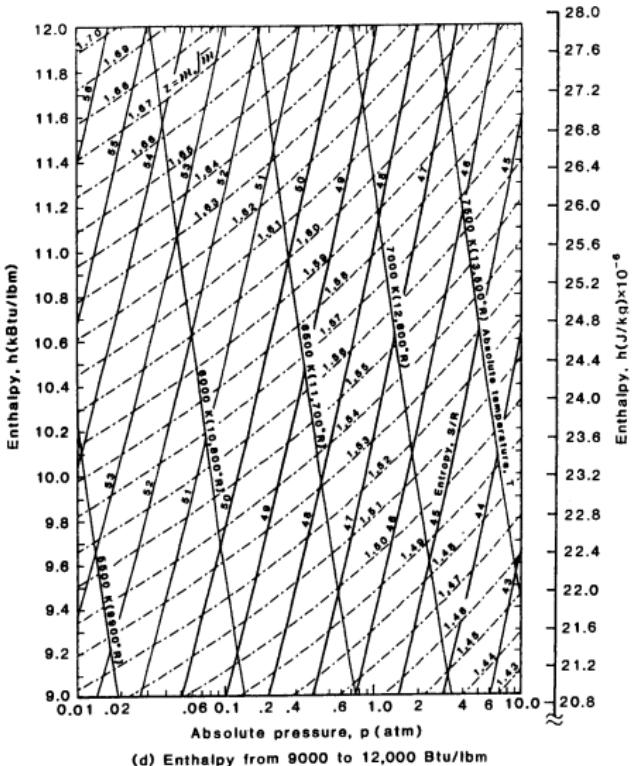
$$\Sigma = 1.235$$

Iteration 2:

$$T_2 \approx 4950\text{ K}$$

$$\Sigma_2 = 1.23$$

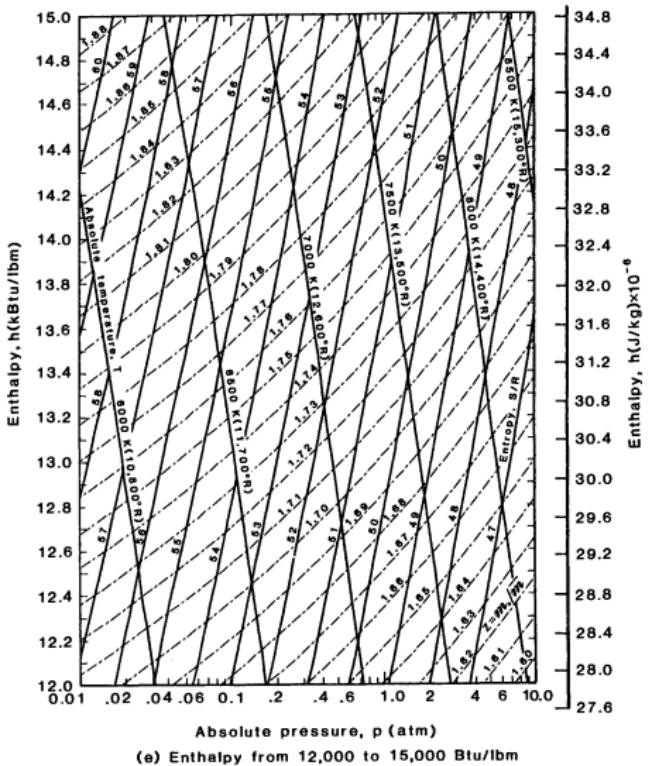
# Equilibrium Normal Shock



**Fig. 1.17 Continued.**

Figure: Fig 1.17d from Bertin [2]

# 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.)

Okay, let us start by setting up the problem:

$$U_1 = 15,000 \text{ ft/s} = 4572 \text{ m/s} \approx 4600 \text{ m/s}$$

$$\text{altitude} = 150,000 \text{ ft} = 45.72 \text{ km} \approx 46 \text{ km}$$

$$p_1 = 126 \text{ Pa}, T_1 = 268 \text{ K}, \rho_1 = 0.00164 \text{ kg/m}^3$$

$$R = 287 \text{ J/kg.K}, C_p = 1.003 \text{ kJ/kg.K}$$

@ 250K

FROM  
US Standard  
Atmosphere table

$$a_1 = 328 \text{ m/s}$$

$$M_1 = \frac{U_1}{a_1}$$

$$M_1 = \frac{4600}{328} \approx 14,$$

## Equilibrium Normal Shock Example

Now we start by getting Bertin's Equation 1-10 and 1.11 [our equations 8 and 9] conservation of momentum and energy, in terms of post shock pressure "p" and enthalpy "h".

$$\rho_{MOM} = \rho_1 + \rho_1 \cdot U_1^2 = \rho_2 + \rho_2 \cdot U_2^2$$

$$H_{TOT} = h_1 + 0.5 \cdot U_1^2 = h_2 + 0.5 \cdot U_2^2 = H_t$$

$$\Rightarrow \rho_2 = \rho_1 + \rho_1 \cdot U_1^2 - \rho_2 \cdot U_2^2 = \rho_{MOM} - \rho_2 \cdot U_2^2$$

$$\Rightarrow h_2 = h_1 + 0.5 \cdot U_1^2 - 0.5 \cdot U_2^2 = H_{TOT} - 0.5 \cdot U_2^2$$

Once we find  $\rho_2$  and  $h_2$  we can use Fig 1.17b to find  $T_2$  and  $Z_2$ . Then we can use equation 1.20 [our equation 13] to calculate  $\rho_2$

$$\rho_2 = \frac{\rho_2}{Z_2 \cdot R \cdot T_2}$$

## Equilibrium Normal Shock Example

Then we can re-arrange equation 1.9 [our equation 7]  
 Conservation of mass to get  $U_2$ :  $U_2 = \frac{P_1 \cdot U_1}{P_2}$

Then we compare values of  $P_2$  calculated in successive iterations until the desired accuracy is obtained.

Since freestream air can be modelled using perfect gas relations:

$$h_1 = C_p \cdot T_1 = 1.003 \text{ kJ/kg} \cdot K \cdot 268 K = 269 \text{ kJ/kg} = 269e^3 \text{ J/kg}$$

$$\rho_{MOM} = \rho_1 + \rho_1 \cdot U_1^2 = 126 \text{ Pa} + 0.0014 \text{ kg/m}^3 \cdot (4600 \text{ m/s})^2 = 34.8 \text{ kPa}$$

$\rho_{MOM} \approx 0.35 \text{ atm}$

$$H_{TOT} = h_1 + 0.5 \cdot U_1^2 = 269e^3 \text{ J/kg} + 0.5(4600 \text{ m/s})^2 = 10.85 \text{ MJ/kg}$$

$H_{TOT} = 10.85e^6 \text{ J/kg}$

## Equilibrium Normal Shock Example

For Iteration 1, to make it easy [and because  $U_2$  is always close to 0 anyway] we start by assuming  $U_2 = 0 \text{ m/s}$

~~$$P_2 = P_{MOM} - \rho_2 U_2^2$$~~

when  $P_{MOM} \approx 0.35 \text{ atm}$

~~$$\text{as } U_2 \approx 0 \text{ m/s} \quad : \quad P_2 = P_{MOM.} = 0.35 \text{ atm}$$~~

~~$$h_2 = H_{TOT} - 0.5 U_2^2$$~~

as  $U_2 \approx 0 \text{ m/s}$       :       $h_2 = H_{TOT} = 10.9 \times 10^6 \text{ J/kg}$

Using Fig 1.17b :  $T_2 \approx 5000 \text{ K}$ ,  $\gamma_1 \approx 1.235$

$$\rho_2 = \frac{34.8 \times 10^3 \text{ Pa}}{1.235 \cdot 2875 \text{ J/kg.K} \cdot 5000 \text{ K}} = 0.02 \text{ kg/m}^3$$

$$U_2 = \frac{\rho_1 \cdot U_1}{\rho_2} = \frac{0.0016 \text{ kg/m}^3 \cdot 4600 \text{ m/s}}{0.02 \text{ kg/m}^3} \therefore U_2 = 377 \text{ m/s}$$

## Equilibrium Normal Shock Example

For Iteration 2:  $U_2 = 377 \text{ m/s}$  instead of  $0 \text{ m/s}$ .  $\rho_2 = 0.02 \text{ kg/m}^3$

$$\rho_2 = \rho_{\text{MOM}} - \rho_2 U_2^2$$

$$\Rightarrow 34.8 e^3 \text{ Pa} - 0.02 \text{ kg/m}^3 (377 \text{ m/s})^2$$

$$\underline{\rho_2 = 32 \text{ kPa} \approx 0.32 \text{ atm}}$$

$$h_2 = H_{\text{TOT}} - 0.5 U_2^2$$

$$\Rightarrow 10.85 e^6 \text{ J/kg} \cdot 0.5 (377 \text{ m/s})^2$$

$$h_2 = 10.8 e^6 \text{ J/kg}$$

Using Fig 1.17b again:  $T_2 \approx 4950 \text{ K}$ ,  $\gamma_2 = 1.23$

$$\text{Now } \underline{\rho_2 = \frac{32 e^3 \text{ Pa}}{1.23 \cdot 287 \text{ J/kg} \cdot \text{K} \cdot 4950 \text{ K}}} \therefore \underline{\rho_2 = 0.018 \text{ kg/m}^3}$$

$$\underline{U_2 = \frac{\rho_1 \cdot U_1}{\rho_2} = \frac{0.00164 \cancel{\text{kg/m}^3} \cdot 4600 \text{ m/s}}{0.018 \cancel{\text{kg/m}^3}}} \therefore \underline{U_2 = 419 \text{ m/s}}$$

## Equilibrium Normal Shock Example

Iteration 3;  $U_2 \text{ Now} = 419 \text{ m/s}$        $\rho_2 = 0.018 \text{ kg/m}^3$

$$p_2 = \rho M \infty - \rho_2 U_2^2$$

$$\Rightarrow 34.8 e^3 \text{ Pa} - 0.18 \text{ kg/m}^3 (419 \text{ m/s})^2$$

$$\underline{p_2 = 31.6 \text{ kPa}}$$

$$h_2 = H_{TOT} - 0.5 U_2^2$$

$$\Rightarrow 10.85 e^6 \text{ J/kg} \cdot 0.5 (419 \text{ m/s})^2$$

$$\underline{h_2 = 10.75 e^6 \text{ J/kg}}$$

This is to the full accuracy of Fig 1.17b.

Our Results:  $U_2 = 419 \text{ m/s}$

$$\rho_2 = 32 \text{ kPa}$$

$$T_2 = 4950 \text{ K}$$

$$\rho_2 = 0.018 \text{ kg/m}^3$$

CEA Results:  $U_2 = 421 \text{ m/s}$

$$\rho_2 = 0.316 \text{ bar} = 31.6 \text{ kPa}$$

$$T_2 = 4999 \text{ K}$$

$$\rho_2 = 0.0179 \text{ kg/m}^3$$

# 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.

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## High Temperature Gas Dynamics Lecture 3: Statistical Thermodynamics

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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

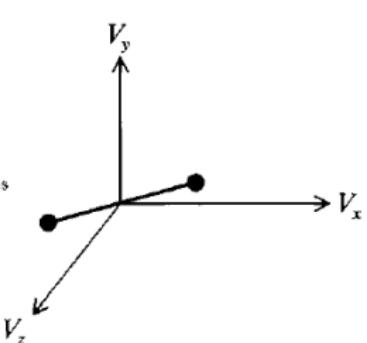
a) Diatomic molecule



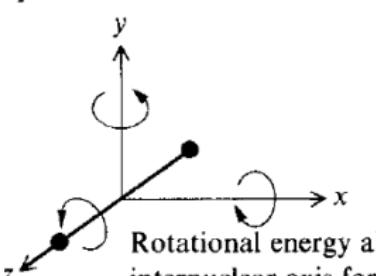
Source

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

b) Translational energy  $\epsilon'_{\text{trans}}$



c) Rotational energy  $\epsilon'_{\text{rot}}$



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

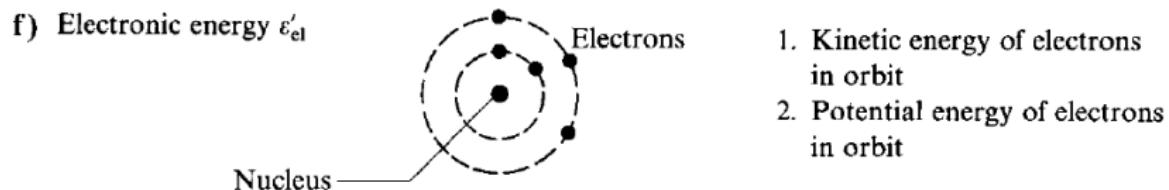
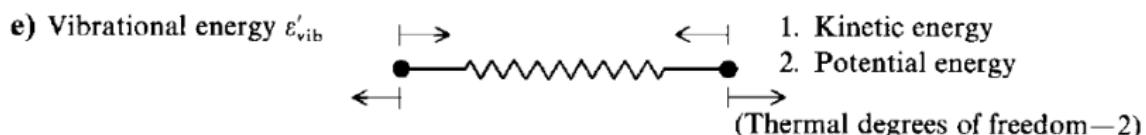
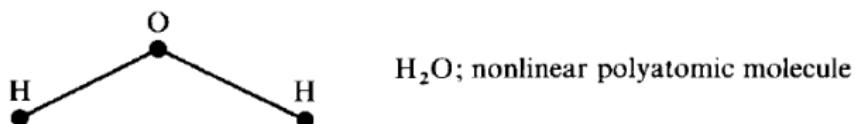


Figure: Modes of molecular energy [3].

# Energy States

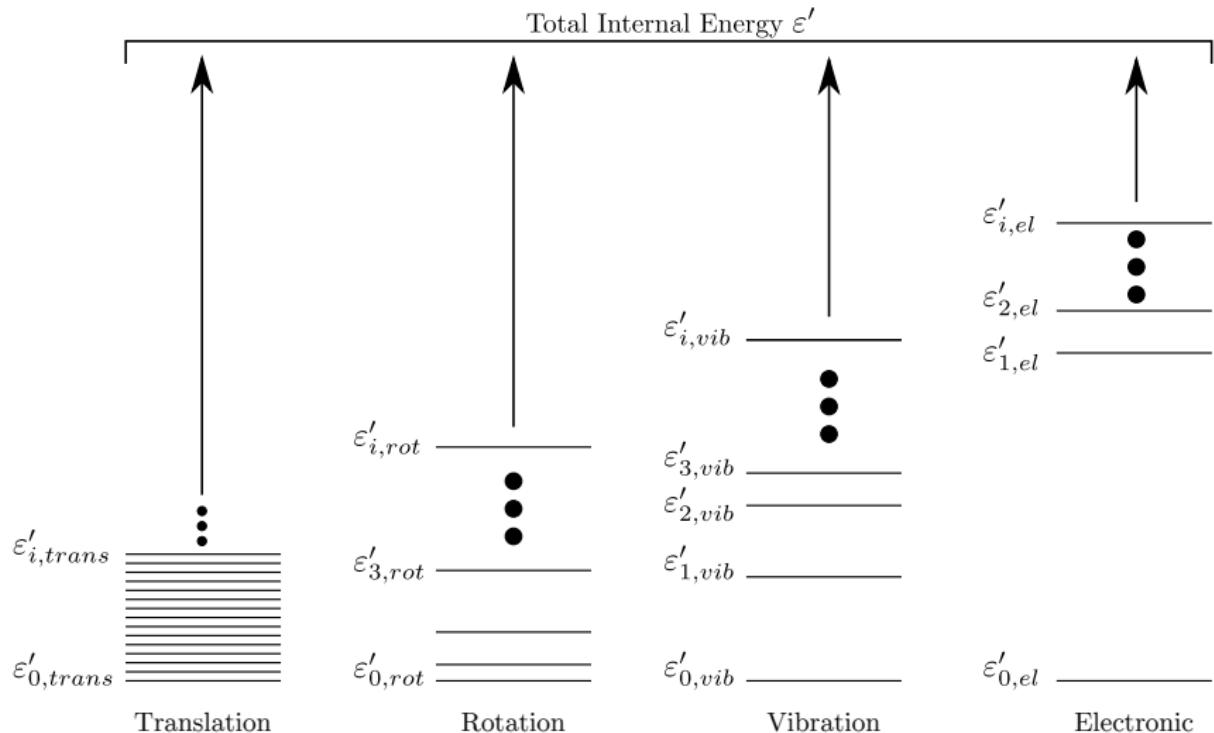


Figure: Molecular energy modes and discretisation (adapted from Anderson [3]).

# Energy States

*O rotational @ zero kelvin.*

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

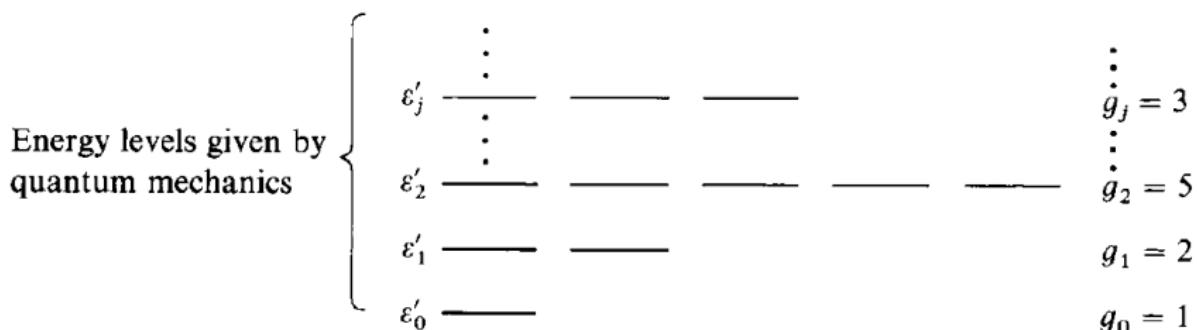


Figure: Illustration of degeneracy [3].

# Energy States

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

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

- ▶ 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:	$\varepsilon'_0$	$\varepsilon'_1$	$\varepsilon'_2$	...	$\varepsilon'_j$	...
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.

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

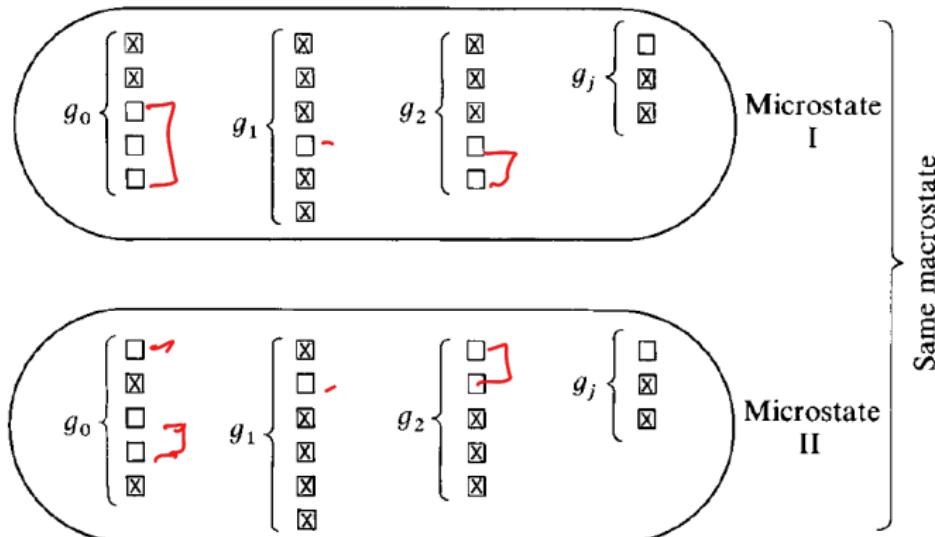


Figure: Illustration of microstates [3].

## 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.

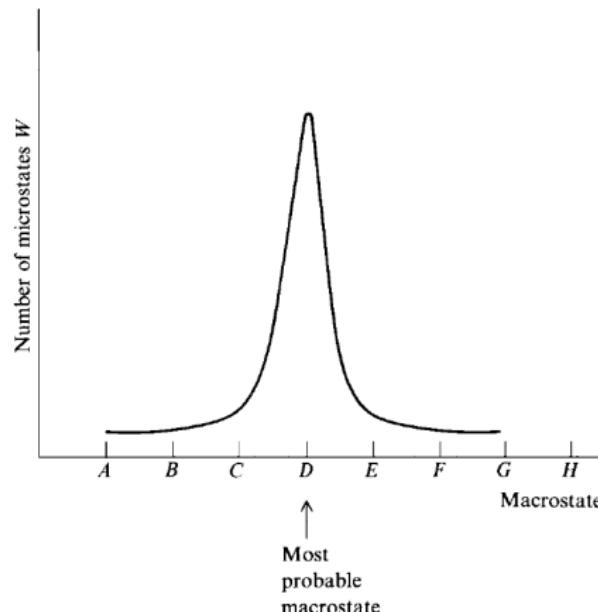


Figure: Most probable macrostate [3].

# 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  $N_j$ :

$g = \text{macrostate}$

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

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

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

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

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

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

*degeneracy*

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

# Thermodynamic Equilibrium

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

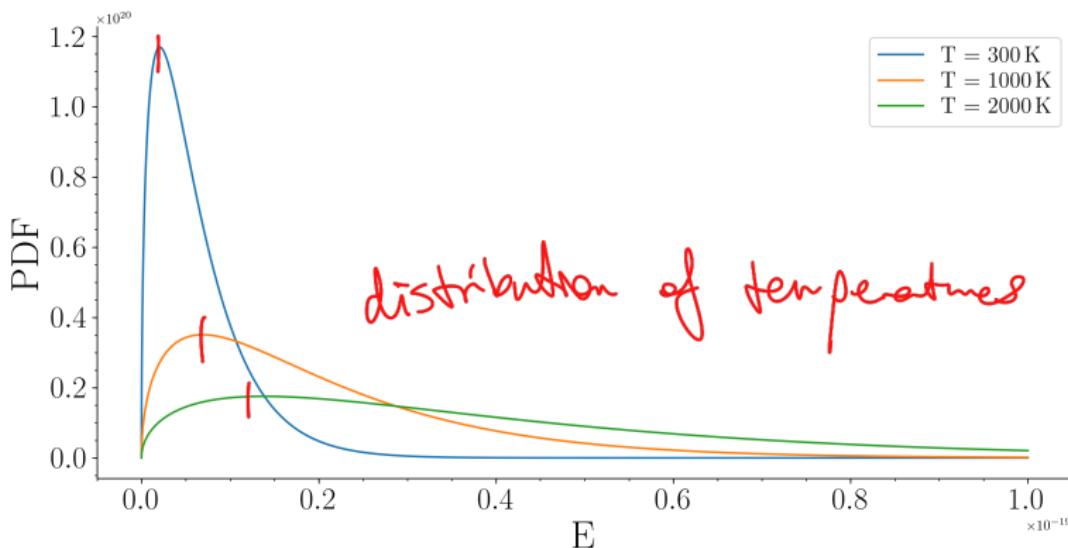


Figure: Boltzmann distribution for three different temperatures.

# Partition Function

rip.

# 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):

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

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

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

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

*ideal gas law of quantum state,*

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

# Partition Function

- ▶ Now, how do we evaluate  $Q \equiv \sum_j g_j e^{-\varepsilon_j/kT}$ ?
- ▶ We need expressions for individual  $\varepsilon_j$  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  $\psi$  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”:

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

- ▶ Where  $\nu$  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: *energy above 0 point.*

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

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

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

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

# 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:

*Exam*

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

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

- 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

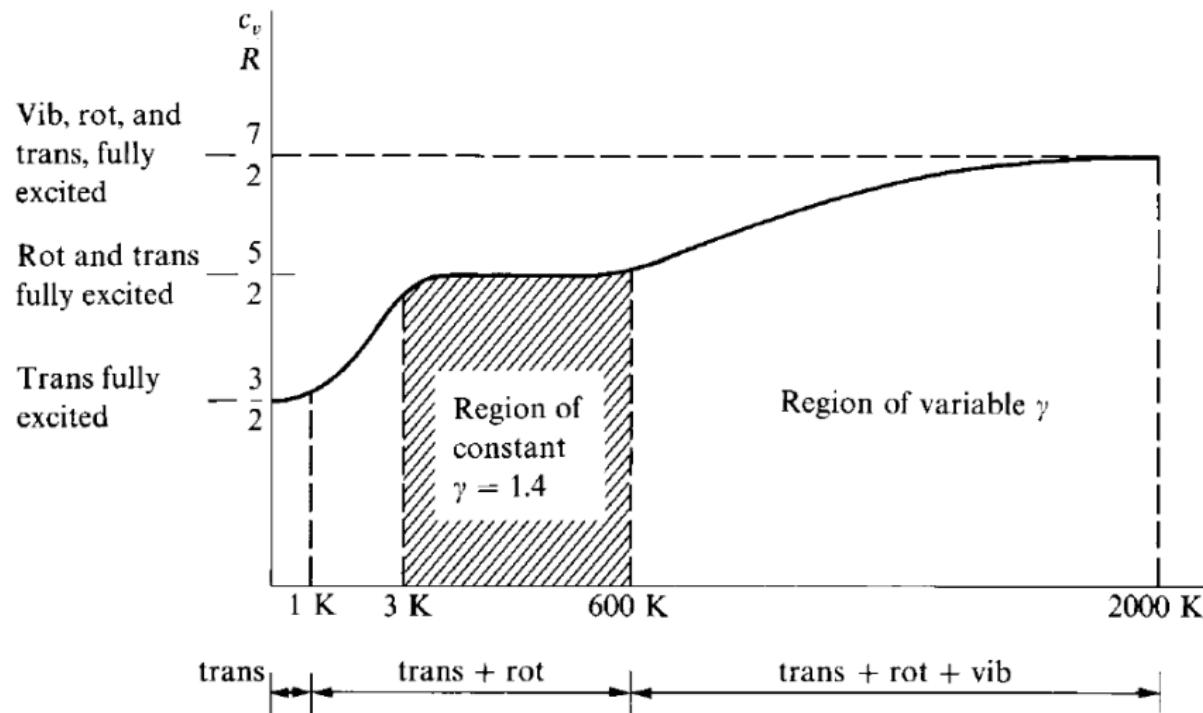
- Now, from the definition  $C_v \equiv \left( \frac{\partial e}{\partial T} \right)_v$ , we obtain:

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

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

- 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,  $\Theta_r$ , 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,  $\Theta_v$ , 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 <sub>2</sub>	N <sub>2</sub>	NO	O	N
Molecular weight, $\hat{M}$ , gm mole <sup>-1</sup>	32.0	28.0	30.0	16.0	14.0
Characteristic temperature for rotation, $\Theta_r$ , °K	2.1	2.9	2.5	—	—
Characteristic temperature for vibration, $\Theta_v$ , °K	2,270	3,390	2,740	—	—
Characteristic temperature for dissociation, $\Theta_d$ , °K	59,500	113,000	75,500	—	—
Characteristic temperature for single ionization, $\Theta_i$ , °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  $\varepsilon/k$  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  $g_0$ ,  $g_1$ ,  $\Theta_1$  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.)

*no electrons on exam.*

# 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  $\gamma$  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  $O_2$  ( $\Theta_{v,O_2}$ ) 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  $\gamma$  of molecular oxygen at 1,000 K?
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- ▶ This is quite simple. We just need Equation 59 to get  $C_v$  and then we can get  $\gamma$  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  $\gamma$  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:

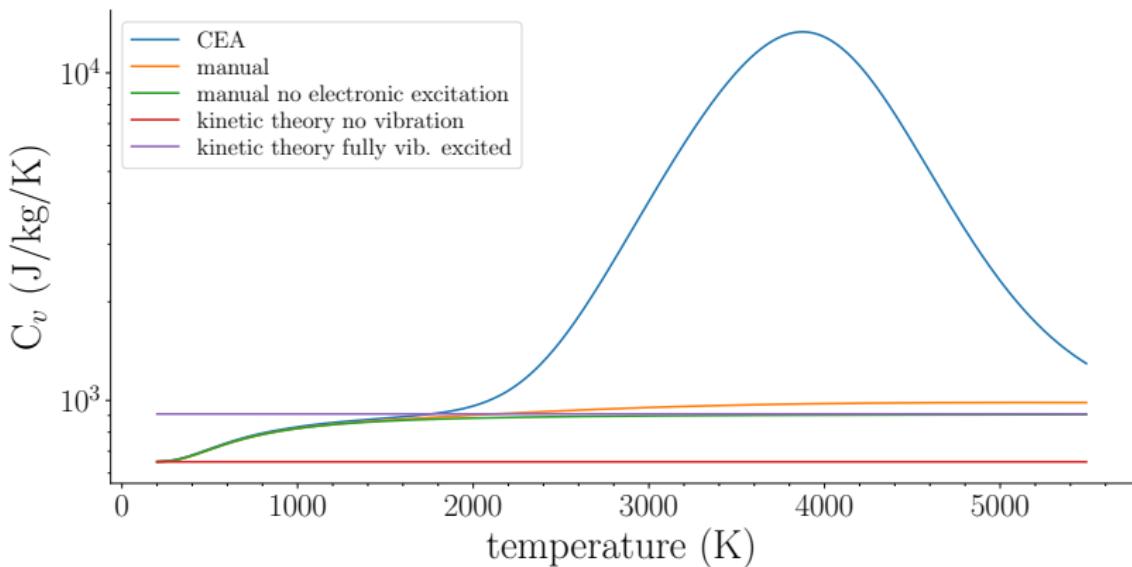


Figure:  $C_v$  for  $O_2$  with changing temperature.

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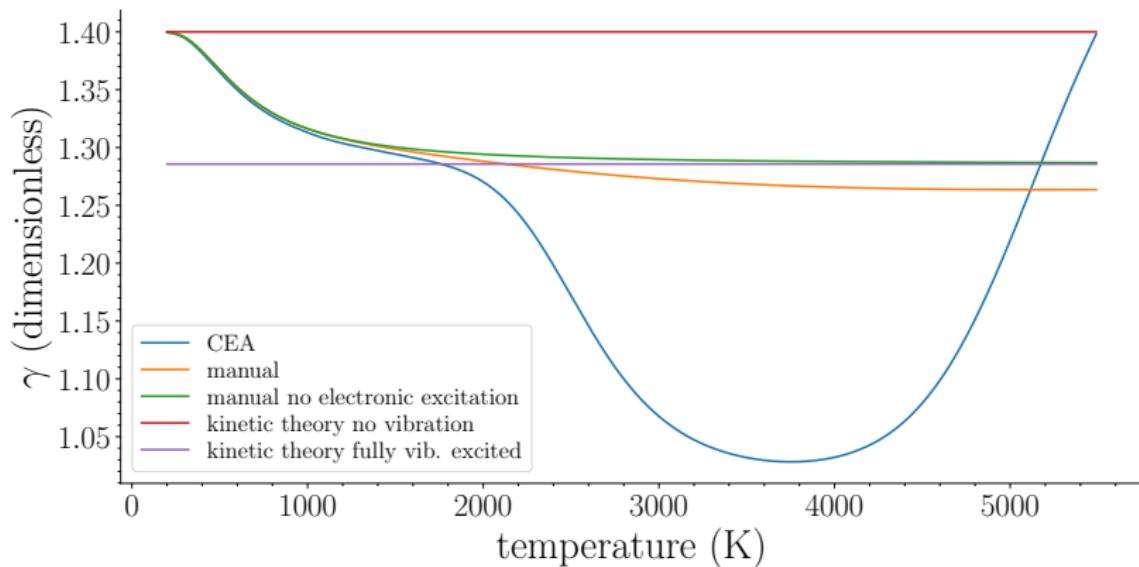


Figure:  $\gamma$  for  $O_2$  with changing temperature.

## 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.

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- [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.