

## Part 8. Statistical Thermodynamics

### MOLECULAR PARTITION FUNCTION $z$

PROBABILITY OF FINDING A MOLECULE IN ENERGY LEVEL  $i$

$$P_i = \frac{N_i}{N} = \frac{\exp(-E_i/kT)}{\sum_j \exp(-E_j/kT)}$$

MOLECULAR PARTITION FUNCTION ("SUM OVER MOLECULAR STATES", "LITTLE ZED")

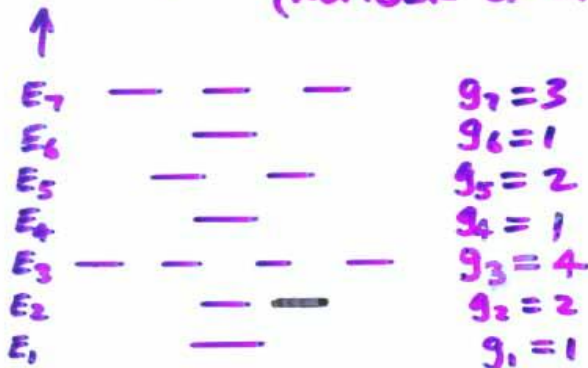
$$z \equiv \sum_j \exp(-E_j/kT)$$

IN CASES WHERE TWO OR MORE MOLECULAR STATES HAVE THE SAME ENERGY, USE

$$P_i = \frac{N_i}{N} = \frac{g_i \exp(-E_i/kT)}{\sum_j g_j \exp(-E_j/kT)}$$

$$z = \sum_j g_j \exp(-E_j/kT)$$

$g_j$  = "degeneracy" OF ENERGY LEVEL  $j$   
(NUMBER OF STATES WITH ENERGY  $E_j$ )



### SYSTEM PARTITION FUNCTION FOR N MOLECULES

THE ENERGY OF A SYSTEM OF NONINTERACTING MOLECULES (e.g., AN IDEAL GAS) A, B, C, ... IS  $E = E_A + E_B + E_C + \dots$

THE SYSTEM PARTITION FUNCTION ("BIG ZED") IS THE SUM OVER SYSTEM STATES

$$Z = \sum_i \exp\left(-\frac{E_{Ai} + E_{Bi} + E_{Ci} + \dots}{kT}\right)$$

FACTORS TO:

$$Z = \left[ \sum_i \exp\left(-\frac{E_{Ai}}{kT}\right) \right]_A \left[ \sum_i \exp\left(-\frac{E_{Bi}}{kT}\right) \right]_B \left[ \sum_i \exp\left(-\frac{E_{Ci}}{kT}\right) \right]_C \dots$$

IF THE ENERGY LEVELS FOR EACH MOLECULE ARE IDENTICAL

$$Z = \left[ \sum_i \exp\left(-\frac{E_i}{kT}\right) \right]^N \Rightarrow$$

$$Z = z^N$$

FOR N  
DISTINGUISHABLE  
MOLECULES

FOR INDISTINGUISHABLE MOLECULES, N!

INTERCHANGES OF MOLECULES CAN BE MADE WITHOUT PRODUCING A DISTINGUISHABLE STATE

$$(e.g., E = E_{A3} + E_{B7} + E_{C2} + \dots = E_{C3} + E_{B7} + E_{A2} + \dots)$$

SO THE SUM OVER STATES IS SMALLER BY A FACTOR OF  $\frac{1}{N!}$   $\Rightarrow$

$$Z = \frac{z^N}{N!}$$

**CALCULATION OF THERMODYNAMIC FUNCTIONS  
FROM PARTITION FUNCTIONS**

THE ENERGY SYSTEM ENERGY  $E = \sum_i N_i E_i$

$$E = N \sum_i \frac{N_i}{N} E_i = N \sum_i P_i E_i$$

$$P_i = \text{PROBABILITY OF STATE } i = \frac{\exp(-E_i/kT)}{z}$$

NOTICE:

$$\frac{dz}{dT} = \frac{d}{dT} \left[ \sum_i \exp\left(-\frac{E_i}{kT}\right) \right] = \frac{1}{kT^2} \sum_i E_i \exp\left(-\frac{E_i}{kT}\right)$$

MULTIPLY BY  $NkT^2/z$ :

$$\frac{NkT^2}{z} \frac{dz}{dT} = N \sum_i \frac{E_i \exp(-E_i/kT)}{z} = N \sum_i P_i E_i$$

AVERAGE ENERGY PER MOLECULE

BETTER NOTATION:

SYSTEM ENERGY  $E = NkT^2 \left( \frac{\partial \ln z}{\partial T} \right)_{N,V}$

HOLD  $N, V$   
CONSTANT TO  
FIX THE  
ENERGY LEVELS  
( $E_i$ )

USING THE SYSTEM PARTITION FUNCTION

$$Z = z^N / N! \quad \ln Z = N \ln z - \ln N!$$

$$\therefore \frac{\partial \ln Z}{\partial T} = N \frac{\partial \ln z}{\partial T}$$

(N constant)

$$E = kT^2 \left( \frac{\partial \ln Z}{\partial T} \right)_{N,V}$$

THE ENTROPYENERGY  $U = E$ 

$$d \ln z = \left( \frac{\partial \ln z}{\partial T} \right)_{N,V} dT + \left( \frac{\partial \ln z}{\partial V} \right)_{N,T} dV = \frac{U}{NkT^2} dT + \left( \frac{\partial \ln z}{\partial V} \right)_{N,T} dV$$

$$d \left( \frac{U}{T} \right) = -\frac{U}{T^2} dT + \frac{dU}{T} \Rightarrow -d \left( \frac{U}{T} \right) + \frac{dU}{T} = \frac{U}{T^2} dT$$

$$d \ln z = -\frac{1}{Nk} d \left( \frac{U}{T} \right) + \frac{dU}{NkT} + \left( \frac{\partial \ln z}{\partial V} \right)_{N,T} dV$$

REARRANGES TO:

$$dU = T \left[ d \left( \frac{U}{T} \right) + Nk d \ln z \right] - NkT \left( \frac{\partial \ln z}{\partial V} \right)_{N,T} dV$$

COMPARE WITH

$$dU = TdS - PdV$$

$$\text{FIND } dS = d \left( \frac{U}{T} \right) + Nk d \ln z$$

INTEGRATE ASSUMING

$$S(T=0) = 0$$

$$\ln(z) \text{ at } (T=0) = 0$$

$$\text{(USED } Nk d \ln z = k d \ln z^N = k d \ln Z)$$

$$S = \frac{U}{T} + Nk \ln z = \frac{U}{T} + k \ln Z$$

THE PRESSURE

NOTICE ALSO

$$P = NkT \left( \frac{\partial \ln z}{\partial V} \right)_{N,T} = kT \left( \frac{\partial \ln Z}{\partial V} \right)_{N,T}$$

HELMHOLTZ FUNCTION

$$A = U - TS = U - T\left(\frac{U}{T} + k \ln Z\right) = \boxed{-kT \ln Z}$$

ENTHALPY

$$H = U + pV = \boxed{kT^2 \left(\frac{\partial \ln Z}{\partial T}\right)_V + kTV \left(\frac{\partial \ln Z}{\partial V}\right)_T}$$

GIBBS FUNCTION

$$G = H - TS = \boxed{-kT \ln Z + kTV \left(\frac{\partial \ln Z}{\partial V}\right)_T}$$

AN INTERPRETATION OF THE ENTROPY EQUATION

PROBABILITY OF STATE  $i$       $P_i = \frac{\exp(-E_i/kT)}{Z}$       $\sum_i P_i = 1$

$$\therefore \ln P_i = -\frac{E_i}{kT} - \ln Z \Rightarrow \ln Z = -\ln P_i - \frac{E_i}{kT}$$

$$S = \frac{U}{T} + Nk \ln Z = \frac{N \sum_i P_i E_i}{T} + Nk (\sum_i P_i) \ln Z$$

$$S = \frac{N \sum_i P_i E_i}{T} - Nk \sum_i P_i \left( \ln P_i + \frac{E_i}{kT} \right)$$

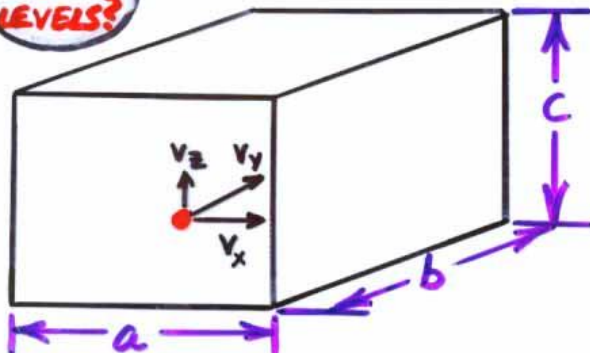
$$\boxed{S = -Nk \sum_i P_i \ln P_i}$$

(SIMILAR TO  $\Delta S_{mix}$ )

ENTROPY IS INCREASED BY "MIXING" A LARGE NUMBER OF POPULATED STATES

## APPLICATION TO A MONATOMIC IDEAL GAS

**E  
LEVELS?**



SOLVE THE  
SCHRÖDINGER  
EQUATION OF  
QUANTUM MECHANICS  
(**DONE ALREADY!**)  
FOR A "PARTICLE  
IN A BOX" OF  
WIDTH  $a$  LENGTH  $b$   
AND HEIGHT  $c$

THE ALLOWED KINETIC ENERGY FOR TRANSLATION  
IN 3-DIMENSIONS ARE NOT CONTINUOUS, BUT  
ARE "DISCRETE" (**ONLY CERTAIN VALUES "ALLOWED"**)

$$E(n_1, n_2, n_3) = \frac{h^2}{8m} \left( \frac{n_1^2}{a^2} + \frac{n_2^2}{b^2} + \frac{n_3^2}{c^2} \right)$$

$m$  = MOLECULAR MASS ( $m = M/L$ )

$h = 6.626 \times 10^{-34}$  J s (PLANCK'S CONSTANT)

$n_1 = 1, 2, 3, \dots$   
 $n_2 = 1, 2, 3, \dots$   
 $n_3 = 1, 2, 3, \dots$

} "QUANTUM NUMBERS"

FOR A  $100 \text{ g mol}^{-1}$  GAS IN A ONE LITER  
CONTAINER AT 300 K, TYPICAL VALUES  
OF  $n_1, n_2, n_3$  ARE  $\sim 10^{12}$ , SO THE ENERGY  
LEVELS ARE VERY CLOSELY SPACED ( $\approx$  CONTINUOUS)

$$z = \sum_{n_1} \sum_{n_2} \sum_{n_3} \exp\left[-\frac{h^2}{8mKT} \left(\frac{n_1^2}{a^2} + \frac{n_2^2}{b^2} + \frac{n_3^2}{c^2}\right)\right] \text{ MOLECULAR PARTITION FUNCTION}$$

ALMOST CONTINUOUS, SO INTEGRATE:

$$= \int_0^{\infty} \int_0^{\infty} \int_0^{\infty} \exp\left[-\frac{h^2}{8mKT} \left(\frac{n_1^2}{a^2} + \frac{n_2^2}{b^2} + \frac{n_3^2}{c^2}\right)\right] dn_1 dn_2 dn_3$$

$$\text{USE } x_1^2 = \frac{n_1^2 h^2}{8ma^2KT} \quad x_2^2 = \frac{n_2^2 h^2}{8mb^2KT} \quad x_3^2 = \frac{n_3^2 h^2}{8mc^2KT}$$

$$z = \left(\frac{a}{h} (8mKT)^{1/2} \int_0^{\infty} e^{-x_1^2} dx_1\right) \left(\frac{b}{h} (8mKT)^{1/2} \int_0^{\infty} e^{-x_2^2} dx_2\right) \left(\frac{c}{h} (8mKT)^{1/2} \int_0^{\infty} e^{-x_3^2} dx_3\right)$$

$$= \frac{(2\pi mKT)^{1/2} a}{h} \frac{(2\pi mKT)^{1/2} b}{h} \frac{(2\pi mKT)^{1/2} c}{h}$$

$$z = \frac{(2\pi mKT)^{3/2} abc}{h^3} = \boxed{\frac{(2\pi mKT)^{3/2} V}{h^3}}$$

$V = \text{VOLUME OF RECTANGULAR CONTAINER} = abc$

FOR  $N = L = \text{AVOGADRO'S NUMBER OF MOLECULES}$ ,  
THE SYSTEM PARTITION FUNCTION IS

$$\boxed{Z = \frac{z^L}{L!} = \frac{1}{L!} \left[ \frac{(2\pi mKT)^{3/2} V}{h^3} \right]^L}$$

ENERGY PER MOLE OF AN IDEAL MONATOMIC GAS  
( $N=L$ )

$$E_m = U_m = LKT^2 \left( \frac{\partial \ln z}{\partial T} \right)_{N,V} = kT^2 \left( \frac{\partial \ln Z}{\partial T} \right)_{N,V}$$

$$= kT^2 \frac{\partial (\ln T^{3L/2})}{\partial T} = \frac{3}{2} LKT^2 \frac{1}{T} = \frac{3}{2} LKT$$

$$E_m = U_m = \frac{3}{2} RT$$

OBTAINED THE SAME  
RESULT PREVIOUSLY  
USING MAXWELL'S  
KINETIC THEORY  
(CLASSICAL MECHANICS)

ENTROPY PER MOLE OF AN IDEAL MONATOMIC GAS  
( $N=L$ )

$$S_m = \frac{U_m}{T} + k \ln Z = \frac{U_m}{T} + k \ln \left[ \frac{1}{L!} \left( \frac{(2\pi mKT)^{3/2} V_m}{h^3} \right)^L \right]$$

$$= \frac{3}{2} \frac{RT}{T} - k(L \ln L - L) + Lk \ln \left[ \frac{(2\pi mKT)^{3/2} V_m}{h^3} \right]$$

$$= \frac{3}{2} R + Lk + R \ln \left[ \frac{(2\pi mKT)^{3/2} V_m}{L h^3} \right]$$

$$S_m = \frac{5}{2} R + R \ln \left[ \frac{(2\pi mKT)^{3/2} V_m}{L h^3} \right]$$

SACKUR-TETRODE  
EQUATION

**FAMOUS**



### HOW RELIABLE IS THIS RESULT?

EXAMPLE Ar(g) AT 25 °C (298.15 K), 1 bar

$$V_m = \frac{RT}{P} = \frac{(8.3145 \frac{\text{J}}{\text{K mol}}) 298.15 \text{ K}}{100,000 \text{ Pa}} = 0.024790 \frac{\text{m}^3}{\text{mol}}$$

$$m = M/L = \frac{0.039948 \text{ kg mol}^{-1}}{6.02214 \times 10^{23} \text{ mol}^{-1}} = 6.63352 \times 10^{-26} \text{ kg}$$

$$h = 6.62608 \times 10^{-34} \text{ J s}$$

$$k = 1.38066 \times 10^{-23} \text{ J K}^{-1}$$

$$S_m = \frac{5}{2} R + R \ln \left[ \frac{(2\pi m k T)^{3/2} V_m}{L h^3} \right]$$

$$S_m = 20.79 + 134.06 = 154.85 \frac{\text{J}}{\text{K mol}}$$

EXPERIMENTAL RESULT... (CLASSICAL)

MEASURE  $C_{p,m}(s)$ ;  $C_{p,m}(l)$ ;  $C_{p,m}(g)$ ;  $\Delta H_{\text{vap},m}$ ;  
 $\Delta H_{\text{fus},m}$ ;  $T_{\text{vap}}$ ,  $T_{\text{fus}}$  at (1 bar)

$$S_m(298.15 \text{ K}) = S_m(0 \text{ K}) + \int_0^{T_{\text{fus}}} \frac{C_{p,m}(s)}{T} dT + \frac{\Delta H_{\text{fus},m}}{T_{\text{fus}}}$$

$$+ \int_{T_{\text{fus}}}^{T_{\text{vap}}} \frac{C_{p,m}(l)}{T} dT + \frac{\Delta H_{\text{vap},m}}{T_{\text{vap}}} + \int_{T_{\text{vap}}}^{298.15} \frac{C_{p,m}(g)}{T} dT = 154.7 \pm 0.2 \frac{\text{J}}{\text{K mol}}$$

**!WOW!**

QUANTIZATION OF THE TRANSLATIONAL ENERGY OF A GAS IS NOT OBSERVABLE

KINETIC ENERGY IN THE X-DIRECTION

$$E_x \approx \frac{1}{2} kT \approx \frac{h^2}{8m} \frac{n_x^2}{a^2} \quad (\text{EQUIPARTITION})$$

$$\therefore n_x \approx \frac{2a}{h} \sqrt{m kT} = \frac{2a}{h} \sqrt{MRT}$$

EXAMPLE Argon(g) IN A  $1 \text{ dm}^3$  CONTAINER  
( $0.1 \text{ m}$  by  $0.1 \text{ m}$  by  $0.1 \text{ m}$ ) AT  $300 \text{ K}$ .

$$a = 0.1 \text{ m} \quad M = 0.03995 \text{ kg mol}^{-1}$$

$$n_x \approx 5 \times 10^9 \quad (\text{ENERGY LEVELS CLOSELY SPACED})$$

(NOT OBSERVABLE)

EACH ARGON ATOM HAS ACCESS TO

QUANTUM NUMBERS

$$1 \lesssim n_x \lesssim 10^{10}$$

$$1 \lesssim n_y \lesssim 10^{10}$$

$$1 \lesssim n_z \lesssim 10^{10}$$

FOR A TOTAL OF  $\approx 10^{30}$  COMBINATIONS

FOR A MOLE OF ARGON IN A 1 LITER VOLUME,  
THE NUMBER OF AVAILABLE STATES PER ATOM  
IS  $\approx 10^{30} / 6 \times 10^{23} \approx 10^6$

$$\frac{h^2}{8ma^2} \approx 8.27 \times 10^{-41} \text{ J}$$

≈ ENERGY SPACING  
( $4.98 \times 10^{-17} \frac{\text{J}}{\text{mol}}$ )

## VISUAL ILLUSTRATION OF QUANTIZATION

NOTICE THAT THE ENERGY-LEVEL SPACING IS PROPORTIONAL TO  $1/(ma^2)$ . THE DIFFERENCE IN ENERGY LEVELS WILL BE LARGE (AND OBSERVABLE) FOR LIGHT PARTICLES CONFINED TO SMALL VOLUMES.

FOR DELOCALIZED ELECTRONS (VERY LIGHT,  $m_e = 9.11 \times 10^{-31}$  kg) IN CONJUGATED DOUBLE BONDS (VERY SMALL), THE ENERGY SPACING IS

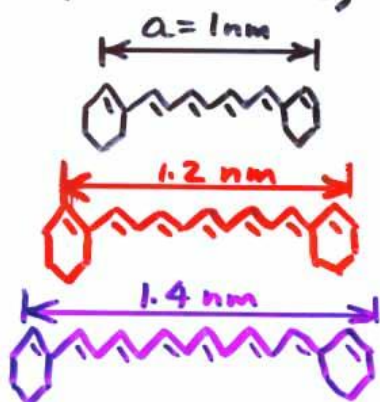
$$\frac{h^2}{8m_e a^2} = \text{ENERGY OF ABSORBED LIGHT} = h\nu = h \frac{c}{\lambda}$$

$$\text{FIND } \lambda = \frac{8m_e a^2 c}{h}$$

$$c = \text{SPEED OF LIGHT} \\ = 3.00 \times 10^8 \frac{\text{m}}{\text{s}}$$

$\lambda$  = WAVELENGTH OF ABSORBED LIGHT  
 $\nu$  = FREQUENCY OF ABSORBED LIGHT

FOR DYE MOLECULES, FIND:



$\lambda = 330 \text{ nm}$  (ULTRAVIOLET)  
COLORLESS

$\lambda = 475 \text{ nm}$  (IN THE BLUE)  
 ABSORBS BLUE LIGHT,  
 LOOKS RED

$\lambda = 650 \text{ nm}$  (IN THE RED)  
 ABSORBS RED LIGHT,  
 LOOKS BLUE

## APPLICATION: DIATOMIC MOLECULES

HAVE ROTATIONAL AND VIBRATIONAL ENERGIES IN ADDITION TO TRANSLATIONAL ENERGY

MOLECULAR  
PARTITION  
FUNCTION

$$z = \sum_i e^{-E_i/kT}$$

(SUM OVER ALL ENERGIES: TRANSLATION, ROTATION, VIBRATION.)

$$z = \sum_l \sum_j \sum_v e^{-[E_{l(tr)} + E_j(rot) + E_v(vib)]/kT}$$

IN MOST CASES THE DIFFERENT ENERGIES CAN BE SEPARATED (TO A GOOD APPROXIMATION)

$$z = \left( \sum_l e^{-E_{l(tr)}/kT} \right) \left( \sum_j e^{-E_j(rot)/kT} \right) \left( \sum_v e^{-E_v(vib)/kT} \right)$$

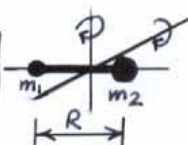
$$z = z_{tr} z_{rot} z_{vib}$$

$$E = NkT^2 \left( \frac{\partial \ln z}{\partial T} \right)_{N,V} = NkT^2 \left[ \frac{\partial \ln z_{tr}}{\partial T} + \frac{\partial \ln z_{rot}}{\partial T} + \frac{\partial \ln z_{vib}}{\partial T} \right]_{N,V}$$

$$\begin{aligned} E &= E_{tr} + E_{rot} + E_{vib} \\ C_v &= C_{vtr} + C_{vrot} + C_{vvib} \\ S &= S_{tr} + S_{rot} + S_{vib} \\ &\text{etc.} \end{aligned}$$

PROVIDES DEEPER INSIGHT BY SEPARATING THERMODYNAMIC FUNCTIONS INTO CONTRIBUTIONS FROM TRANSLATION, ROTATION AND VIBRATION

## ROTATION OF DIATOMIC MOLECULES



SOLVE SCHRÖDINGER'S EQUATION FOR A **RIGID ROTATOR** (BOND DOES NOT STRETCH) (AS ROTATION INCREASES)

FIND THAT ONLY CERTAIN ROTATIONAL ENERGIES ARE ALLOWED:

$$E_{J(\text{rot})} = J(J+1) \frac{h^2}{8\pi^2 I}$$

QUANTUM NUMBERS:  
( $J=0, 1, 2, 3, \dots$ )

$$g_J = 2J+1$$

DEGENERACY OF LEVEL  $J$

CONVENIENT TO DEFINE THE ROTATIONAL CONSTANT

$$\theta_{\text{rot}} = \frac{h^2}{8\pi^2 I k}$$

$$\left( \text{MOMENT OF INERTIA} \right. \\ \left. I = \frac{m_1 m_2}{m_1 + m_2} R^2 \right)$$

FOR UNSYMMETRIC MOLECULES (e.g. CO):

$$z_{\text{rot}} = \sum_{\text{ALL } J} g_J e^{-E_{J(\text{rot})}/kT} = \sum_{J=0}^{\infty} (2J+1) e^{-J(J+1)\theta_{\text{rot}}/T}$$

$$z_{\text{rot}} \approx \int_0^{\infty} (2J+1) e^{-J(J+1)\theta_{\text{rot}}/T} dJ$$

FOR CLOSELY SPACED ENERGY LEVELS

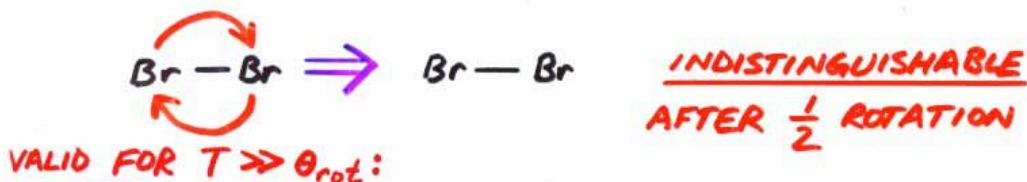
$$T \gg \theta_{\text{rot}}$$

$$z_{\text{rot}} = \frac{T}{\theta_{\text{rot}}}$$

GAS	$\theta_{\text{rot}}/K$
CO	2.78
HF	30.13
HCl	15.24
HI	9.43

FROM SPECTRA

FOR SYMMETRIC MOLECULES (e.g.  $\text{Br}_2$ ):



VALID FOR  $T \gg \theta_{\text{rot}}$ :

$$z_{\text{rot}} = \frac{T}{2\theta_{\text{rot}}}$$

GAS	$\theta_{\text{rot}} / \text{K}$
$\text{N}_2$	2.89
$\text{O}_2$	2.08
$\text{Cl}_2$	0.351
$\text{Br}_2$	0.116

2 = "SYMMETRY NUMBER"

FOR  $N$  ROTATING DIATOMIC MOLECULES:

$$\begin{aligned}
 U_{\text{rot}} &= NKT^2 \left( \frac{\partial \ln z_{\text{rot}}}{\partial T} \right)_{N,V} = NKT^2 \frac{d(\ln T + \text{CONSTANT})}{dT} \\
 &= NKT^2 \left( \frac{1}{T} \right) = NKT
 \end{aligned}$$

$$* U_{\text{rot},m} = LkT = RT$$

SAME AS LAST  
TERM'S CLASSICAL  
RESULT FOR 2  
AXES OF  
ROTATION

$$* C_{v,m,\text{rot}} = \left( \frac{\partial U_{\text{rot},m}}{\partial T} \right)_{N,V} = R$$

( $\approx$  CONTINUOUS ENERGY  
 $T \gg \theta_{\text{rot}}$ )

\* WARNING: THESE EQUATIONS ARE NOT ACCURATE AT VERY LOW TEMPERATURES OR FOR COOL  $\text{H}_2$  (ENERGY-LEVEL SPACING, NOT NEGLIGIBLE)

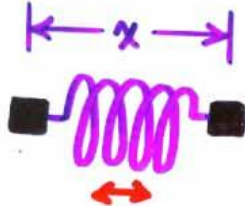
## VIBRATION OF DIATOMIC MOLECULES

HIGHER ENERGY

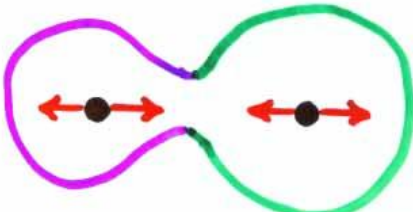
TRANSLATION AND ROTATION (EXCEPT AT VERY LOW TEMPERATURES) CAN BE TREATED USING CLASSICAL (NEWTON'S) MECHANICS BECAUSE THE SPACING OF THE ENERGY LEVELS IS  $\lll$  THE THERMAL ENERGIES OF THE MOLECULES ( $\approx kT$ ).

BUT MOLECULAR VIBRATION IS NOT CLASSICAL, EVEN AT HIGH TEMPERATURES

SOLVING THE QUANTUM MECHANICAL EQUATIONS FOR THE HARMONIC OSCILLATION OF A DIATOMIC



Force =  $-k_{\text{spring}}(x - x_0)$



FUNDAMENTAL FREQUENCY  $\nu = \frac{1}{2\pi} \sqrt{\frac{(m_1 + m_2) k_{\text{spring}}}{m_1 m_2}}$

GIVES THE EVENLY-SPACED ENERGY LEVELS

$$E_{\text{vib}} = (n_v + \frac{1}{2}) h \nu$$

VIBRATION QUANTUM NUMBERS

$$n_v = 0, 1, 2, 3, \dots$$

QUANTUM MECHANICAL SURPRISE! A HARMONIC OSCILLATOR CAN'T HAVE ZERO ENERGY. THE LOWEST ALLOWED ENERGY (ZERO-POINT ENERGY) IS  $h\nu/2$ . AN OSCILLATOR WITH ZERO ENERGY WOULD BE LOCATED AT THE MINIMUM IN THE POTENTIAL ENERGY, WHICH WOULD VIOLATE THE "UNCERTAINTY PRINCIPLE"

DIATOMIC	FREQUENCY $\nu / \text{s}^{-1}$	VIBRATIONAL TEMP. $\theta_v / \text{K}$
H <sub>2</sub>	$131.8 \times 10^{12}$	6323.8
HI	$69.24 \times 10^{12}$	3323
N <sub>2</sub>	$70.74 \times 10^{12}$	3395
O <sub>2</sub>	$47.38 \times 10^{12}$	2274
Br <sub>2</sub>	$9.793 \times 10^{12}$	470

FROM SPECTRA

(H<sub>2</sub> BOND  $\Rightarrow$  STRONG AND STIFF, HIGH FREQUENCY  $\nu$  AND LARGE SPACING OF VIBRATIONAL ENERGY LEVELS ( $\Delta E = h\nu$ )).

CONVENIENT TO DEFINE THE "VIBRATION TEMPERATURE" AS A MEASURE OF THE SPACING OF THE VIBRATIONAL ENERGY LEVELS:

$$\theta_v = \frac{h\nu}{k_B} \sim \frac{\text{J}}{\text{J K}^{-1}} \sim \text{K}$$

\* BECAUSE OF THE STIFFNESS OF CHEMICAL BONDS, VIBRATIONAL ENERGY SPACINGS ( $h\nu$ ) ARE USUALLY GREATER THAN THE THERMAL ENERGIES OF ROOM-TEMPERATURE MOLECULES ( $\approx kT$ ).

$$\theta_v > 300 \text{ K} \quad (\text{USUALLY})$$

\* MOLECULAR VIBRATIONS ARE NOT CLASSICAL



MOLECULAR VIBRATIONAL PARTITION FUNCTION

$$z_{\text{vib}} = \sum_{n_v=0}^{\infty} \exp(-E_v/kT) = \sum_{n_v=0}^{\infty} \exp[-(n_v + \frac{1}{2})\theta_v/T]$$

$$z_{\text{vib}} = \exp(-\theta_v/2T) \sum_{n_v=0}^{\infty} \exp[-n_v \theta_v/T]$$

DEFINE  $x = \exp(-\theta_v/T)$

$$z_{\text{vib}} = x^{1/2} (1 + x + x^2 + x^3 + \dots) = \frac{x^{1/2}}{1-x}$$

$$z_{\text{vib}} = \frac{\exp(-\theta_v/2T)}{1 - \exp(-\theta_v/T)}$$

DERIVE THE EXPRESSIONS:

$$E_{\text{vib}} = NkT^2 \left( \frac{\partial \ln z_{\text{vib}}}{\partial T} \right)_{N,V} = \frac{Nk\theta_v}{2} \frac{1 + \exp(-\theta_v/T)}{1 - \exp(-\theta_v/T)}$$

$$C_{v(\text{vib})} = \left( \frac{\partial E_{\text{vib}}}{\partial T} \right)_{N,V} = Nk \left( \frac{\theta_v}{T} \right)^2 \frac{\exp(-\theta_v/T)}{[1 - \exp(-\theta_v/T)]^2}$$

$T \rightarrow 0$

TRICKY!

$T \rightarrow \infty$

$C_{v(\text{vib})} \rightarrow 0$

$E_v \rightarrow \frac{Nk\theta_v}{2}$

(ZERO-POINT ENERGY)

$C_{v(\text{vib})} \rightarrow Nk$  (R per mole)

$E_v \rightarrow NkT$  (RT per mole)

CONVENIENT TO REWRITE EQUATIONS AS

$$E_{\text{vib}} = Nk \left( \frac{\theta_v}{2} + \frac{\theta_v}{e^{\theta_v/T} - 1} \right)$$

$$C_{v(\text{vib})} = Nk \left( \frac{\theta_v}{T} \right)^2 \frac{e^{\theta_v/T}}{(e^{\theta_v/T} - 1)^2}$$

\*WARNING\* IN SOME TEXTBOOKS (ABOUT ONE HALF) VIBRATIONAL ENERGIES ARE EXPRESSED RELATIVE TO  $h\nu/2$  (THE ZERO-POINT ENERGY IS IGNORED) WHICH GIVES

**X**  $E_{\text{vib}} = Nk\theta_v / (e^{\theta_v/T} - 1)$  (NOT RECOMMENDED)

EXAMPLE CO(g) AT 25 °C N=L

LOOK UP  $\theta_v = 3122 \text{ K}$

FROM SPECTRA

$$E_{\text{vib}(m)} = R \left( \frac{\theta_v}{2} + \frac{\theta_v}{e^{\theta_v/T} - 1} \right) = 12,979 \text{ J mol}^{-1}$$

$$C_{v(\text{vib})m} = R \left( \frac{\theta_v}{T} \right)^2 \frac{e^{\theta_v/T}}{(e^{\theta_v/T} - 1)^2} = 0.00311 R$$

$$\frac{N(v=1)}{N(v=0)} = \frac{e^{-E_1/KT}}{e^{-E_0/KT}} = e^{-(E_1-E_0)/KT} = e^{-h\nu/KT} = e^{-\theta_v/T}$$

$$= e^{-10.47} = 0.000028 \quad (\text{VIBRATION NOT SIGNIFICANT})$$

## THERMODYNAMIC CALCULATIONS

(STATISTICAL NOT CLASSICAL)

EXAMPLE CALCULATE THE MOLAR ENERGY, ENTROPY AND HEAT CAPACITY (AT CONSTANT PRESSURE) FOR CO(g).

MOLECULAR PARTITION FUNCTION:

$$Z = z_{tr} z_{rot} z_{vib}$$

$$z_{tr} = \frac{(2\pi m k T)^{3/2} V}{h^3}$$

$$z_{rot} = \frac{T}{\sigma \theta_{rot}} \quad \left( \begin{array}{l} \text{ASSUME} \\ T \gg \theta_{rot} \end{array} \right)$$

$$z_{vib} = \frac{\exp(-\theta_v/2T)}{1 - \exp(-\theta_v/T)}$$

$$\left( \begin{array}{l} \text{unsymmetric} \\ \sigma = 1 \end{array} \right)$$

### MOLAR ENERGY OF A DIATOMIC GAS

$$\begin{aligned} E_m &= L k T^2 \left( \frac{\partial \ln z}{\partial T} \right)_{N,V} = R T^2 \left[ \frac{\partial \ln (z_{tr} z_{rot} z_{vib})}{\partial T} \right]_{N,V} \\ &= R T^2 \left[ \frac{\partial \ln z_{tr}}{\partial T} + \frac{\partial \ln z_{rot}}{\partial T} + \frac{\partial \ln z_{vib}}{\partial T} \right]_{N,V} \\ &= R T^2 \left[ \frac{\partial \ln T^{3/2}}{\partial T} + \frac{\partial \ln T}{\partial T} + \frac{\partial}{\partial T} \left( \frac{e^{-\theta_v/2T}}{1 - e^{-\theta_v/T}} \right) \right]_{N,V} \end{aligned}$$

$$E_m = \underbrace{\frac{3}{2} RT}_{\text{TRANS.}} + \underbrace{RT}_{\text{ROT.}} + \underbrace{\frac{R\theta_v}{2} + \frac{R\theta_v}{e^{\theta_v/T} - 1}}_{\text{VIBRATION}}$$

### MOLAR HEAT CAPACITY OF A DIATOMIC GAS

$$C_{pm} = R + C_{vm} = R + \left( \frac{\partial E_m}{\partial T} \right)_{N,V}$$

$$C_{pm} = R + \left( \frac{\partial E_{m, tr}}{\partial T} + \frac{\partial E_{m, rot}}{\partial T} + \frac{\partial E_{m, vib}}{\partial T} \right)_{N,V}$$

$$C_{pm} = R + \underbrace{\frac{3}{2}R}_{\text{TRANS.}} + \underbrace{R}_{\text{ROT.}} + \underbrace{R \left( \frac{\theta_v}{T} \right)^2 \frac{e^{\theta_v/T}}{(e^{\theta_v/T} - 1)^2}}_{\text{VIBRATION}}$$

$$(T \gg \theta_r)$$

### MOLAR ENTROPY OF A DIATOMIC GAS

$$S_m = \frac{E_m}{T} + R \ln z$$

$$= \frac{E_{tr,m} + E_{rot,m} + E_{vib,m}}{T} + R (\ln z_{tr} + \ln z_{rot} + \ln z_{vib})$$

$$S_m = S_{tr,m} + S_{rot,m} + S_{vib,m}$$

$$S_{tr,m} = \frac{3}{2}R + R \ln \left[ \frac{(2\pi m k T)^{3/2} V}{L h^3} \right] \quad (\text{SACKUR-TETRODE EQ.})$$

$$S_{rot,m} = R + R \ln(T/\sigma R)$$

$$S_{vib,m} = \frac{R}{T} \left( \frac{\theta_v}{2} + \frac{\theta_v}{e^{\theta_v/T} - 1} \right) + R \ln \left( \frac{e^{-\theta_v/2T}}{1 - e^{-\theta_v/T}} \right)$$

## PRESSURE OF THE GAS

HAVE DERIVED  $p = NKT \left( \frac{\partial \ln z}{\partial V} \right)_{N,T}$

INTERNAL

$$z = z_{tr} z_{rot} z_{vib}$$

ONLY  $z_{tr}$  DEPENDS ON  $V$

$$p = NKT \left( \frac{\partial \ln z_{tr}}{\partial V} \right)_{N,T} = NKT \left[ \frac{\partial}{\partial V} \ln \left( \frac{(2\pi mKT)^{3/2} V}{h^3} \right) \right]_{N,T}$$

$$p = NKT \left( \frac{\partial \ln V}{\partial V} \right)_{N,T} = \frac{NKT}{V}$$

$$p = \frac{NKT}{V} = \frac{LKT}{V_m} = \frac{RT}{V_m}$$

(IDEAL GAS LAW)

FROM THE TRANSLATION OF THE GAS

\* (NO CONTRIBUTION TO  $p$  FROM  $z_{rot}$  OR  $z_{vib}$ ) \*

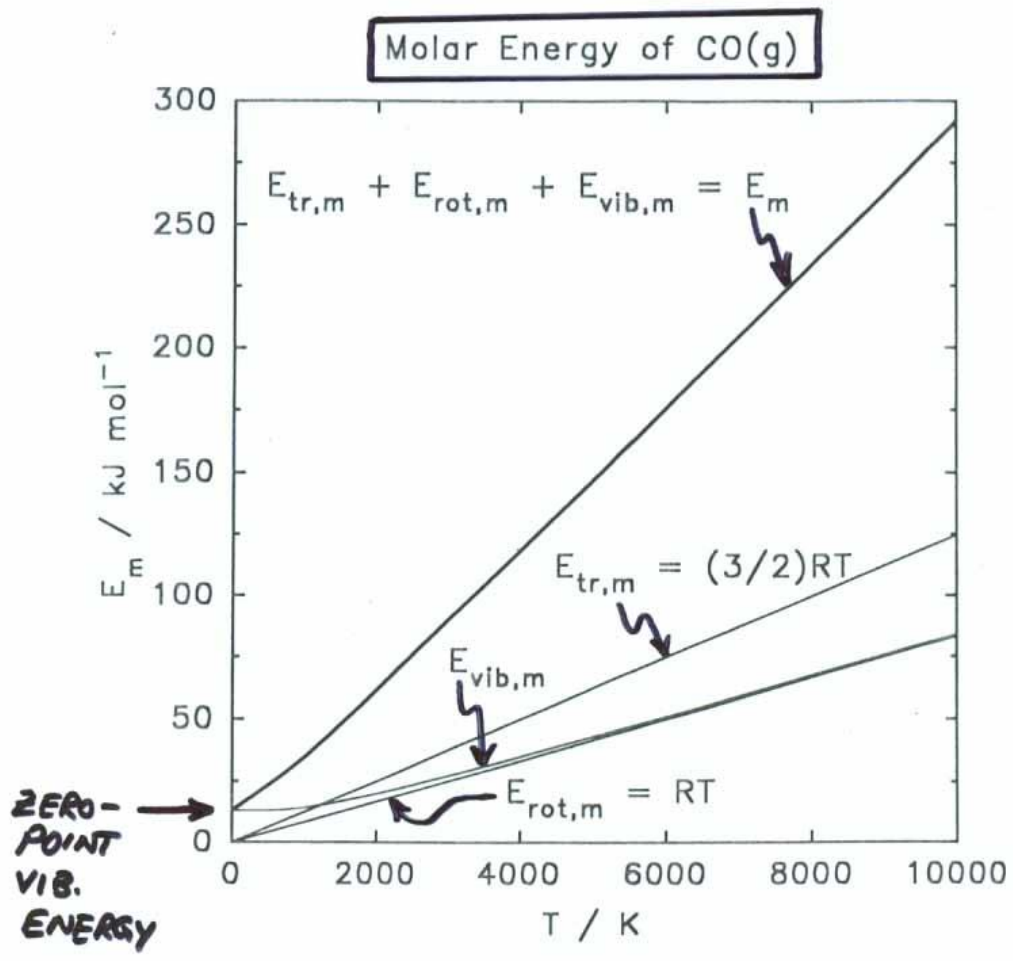
"INTERNAL" →

FROM CALCULATED VALUES OF  $E_m, S_m, p, \dots$

$$H_m = E_m + pV = E_m + RT \quad (\text{ENTHALPY})$$

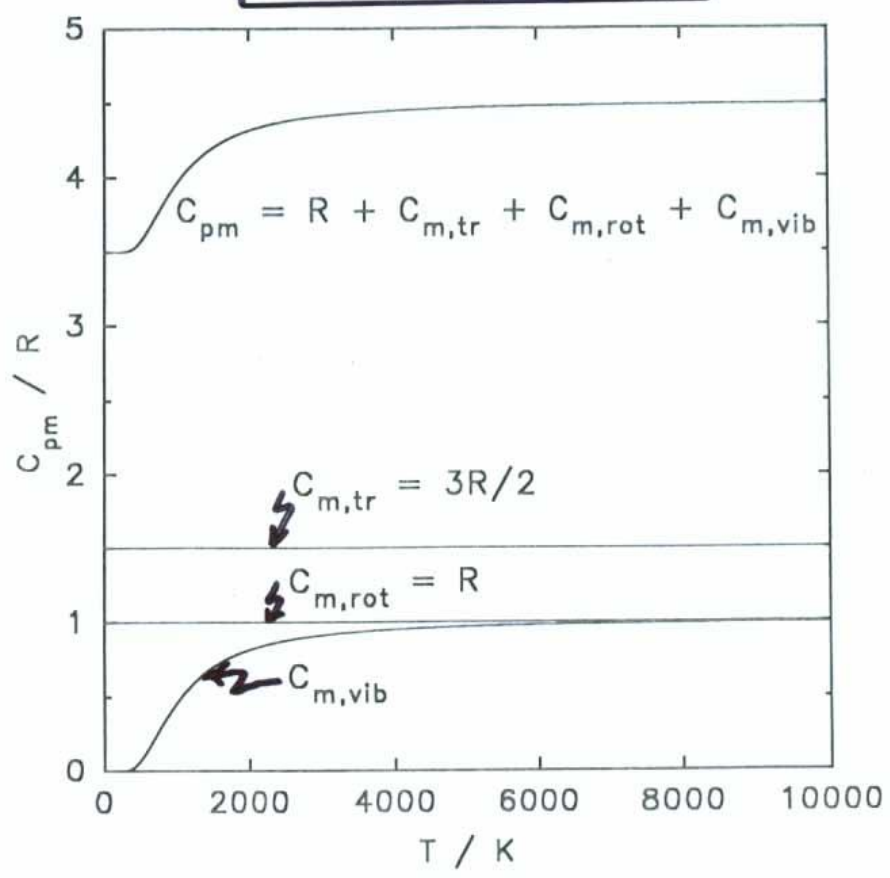
$$G_m = H_m - TS_m = E_m + RT - TS_m \quad (\text{GIBBS FUNCTION})$$

$$A_m = E_m - TS_m = -RT \ln z \quad (\text{HELMHOLTZ FUNCTION})$$

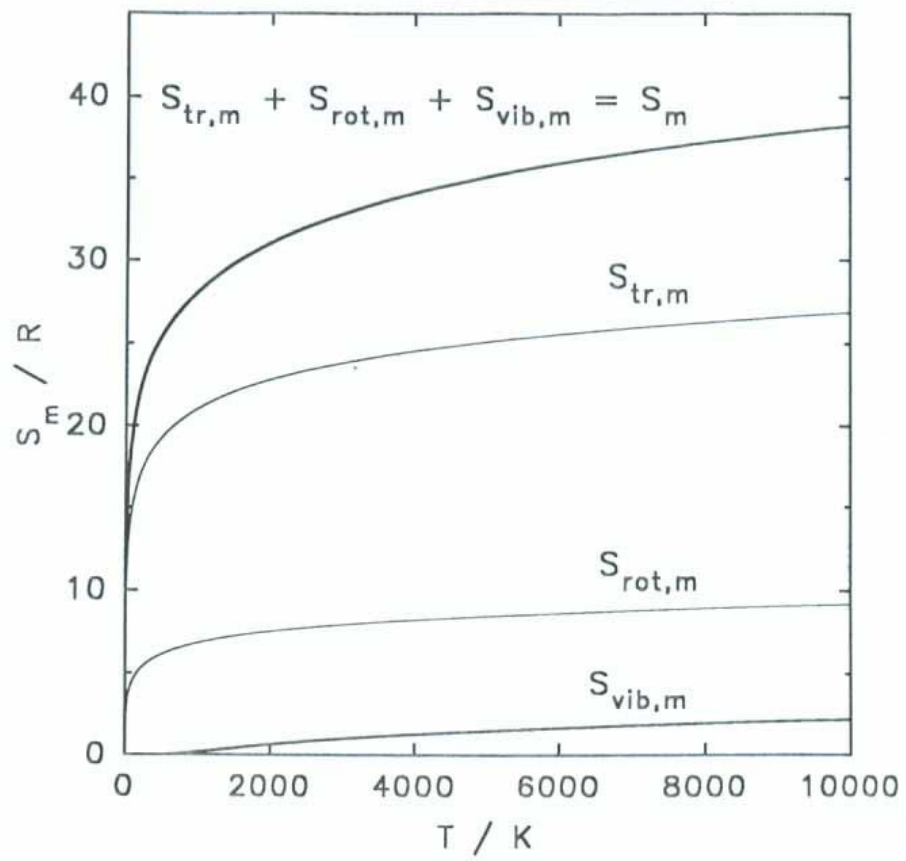


assuming: \*no dissociation\*

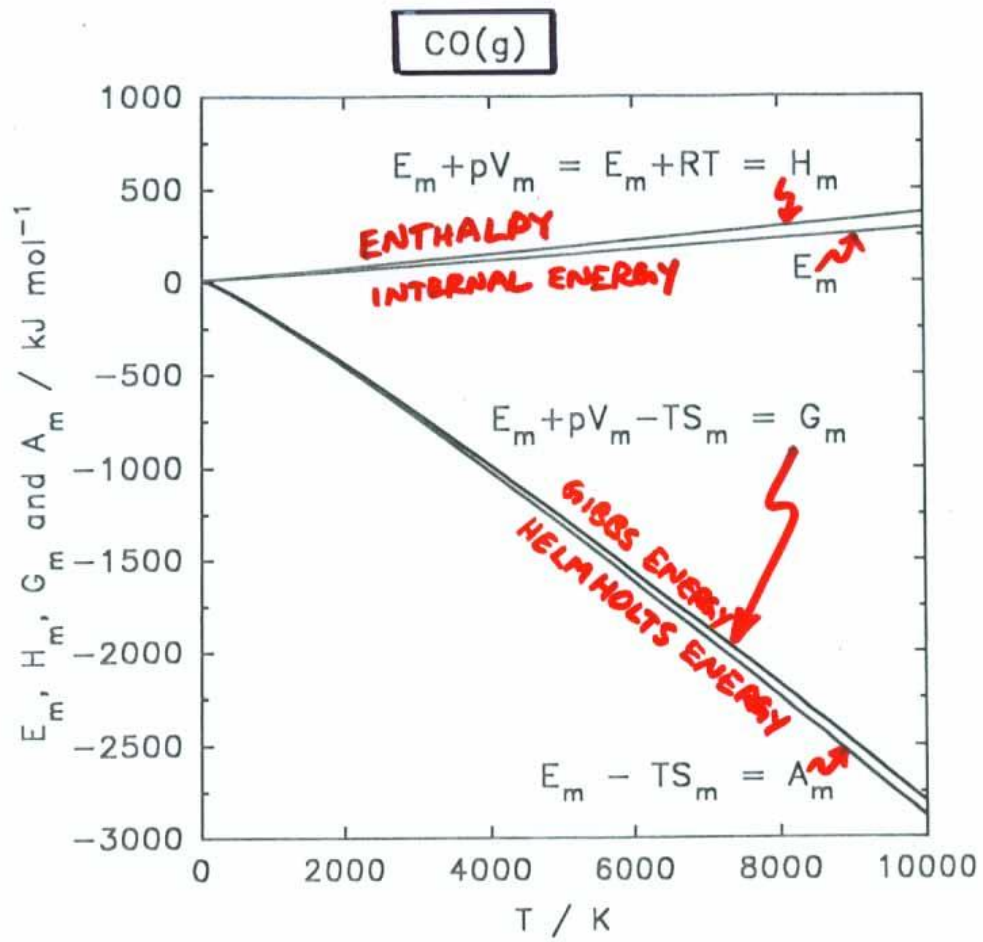
Heat Capacity of CO(g)



### Molar Entropy of CO(g)







## WHERE'S THE ~~BEEF~~ CHEMISTRY?

ONE OF THE MOST IMPORTANT APPLICATIONS OF STATISTICAL THERMODYNAMICS IS THE ACCURATE CALCULATION OF THE PROPERTIES AND EQUILIBRIUM CONSTANTS FOR THE FORMATION OF REACTIVE INTERMEDIATES.

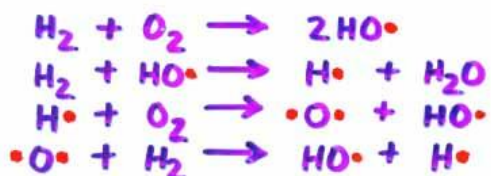
THIS INFORMATION IS ESSENTIAL FOR UNDERSTANDING:

- COMBUSTION PROCESSES
- PHOTOCHEMISTRY
- ATMOSPHERIC CHEMISTRY (SUCH AS SMOG FORMATION, OZONE DEPLETION)
- FREE RADICALS (e.g.  $\text{Br}\cdot$ )
- CHEMICAL REACTION MECHANISMS
- CHEMICAL BONDING
- MATTER UNDER EXTREME CONDITIONS

EXAMPLE EVERYONE KNOWS THAT HYDROGEN AND OXYGEN REACT (SOMETIMES **EXPLOSIVELY!**).

THE OVERALL REACTION IS:  $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{g})$

BUT THE ACTUAL MECHANISM IS MORE INTERESTING:



THE LIFETIMES OF THE REACTIVE  $\text{HO}\cdot$ ,  $\text{H}\cdot$ ,  $\cdot\text{O}\cdot$  SPECIES ARE TOO SHORT FOR DIRECT THERMODYNAMIC MEASUREMENTS.

$\Rightarrow$  USE STATISTICAL THERMODYNAMICS

**\* WARNING \***

MANY REACTIVE INTERMEDIATES (e.g.  $H\cdot$  AND  $HO\cdot$ )  
AND A FEW IMPORTANT STABLE MOLECULES  
[e.g.  $NO$  (ODD NUMBER OF ELECTRONS (15))]  
HAVE

- UNPAIRED ELECTRONS
- DEGENERATE ENERGY LEVELS ( $g_i > 1$ )  
(electron spin  $\uparrow$  or  $\downarrow$ )
- LOW-LYING ELECTRONIC ENERGY LEVELS  
(accessible at room temperature)

NO PROBLEM, JUST INCLUDE THE ELECTRONIC  
PARTITION FUNCTION ( $z_{elec}$ ) TOGETHER  
WITH THE TRANSLATIONAL, ROTATIONAL,  
AND VIBRATIONAL PARTITION FUNCTIONS.

FOR ELECTRONIC ENERGY LEVELS ( $E_i$ ) AND  
DEGENERACIES ( $g_i$ ):  $(\theta_{i(e)} = E_{i(e)}/k)$

$$\begin{aligned} z_{elec} &= \sum_{i=0}^{\infty} g_{i(e)} \exp[-E_{i(e)}/kT] \\ &= g_0 + g_1 e^{-E_{1(e)}/kT} + g_2 e^{-E_{2(e)}/kT} + \dots \\ &= g_0 + g_1 e^{-\theta_{1e}/T} + g_2 e^{-\theta_{2e}/T} + \dots \end{aligned}$$

**EXAMPLE**NITRIC OXIDE (NO)

LOWEST ELECTRONIC ENERGY LEVEL ( $E_{0(e)} = 0$ )

HAS DEGENERACY  $g_0 = 2$  ( $\uparrow$  OR  $\downarrow$ ).

FIRST EXCITED ELECTRONIC STATE HAS

$\theta_{1(e)} = 174.2$  K AND DEGENERACY  $g_1 = 2$ .

$$z_{elec} = g_0 + g_1 e^{-\theta_{1(e)}/T}$$

$$z_{elec} = 2 + 2e^{-174.2/T}$$

1 UNPAIRED  
ELECTRON  
 $S = 1/2$   
 $2S+1 = 2$

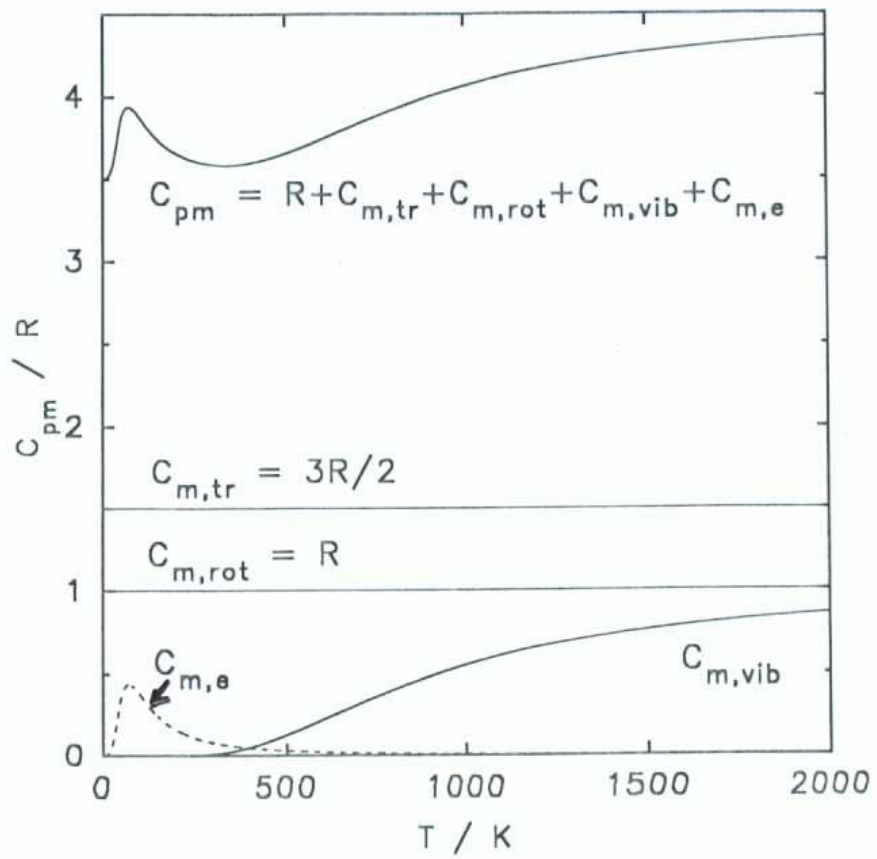
EASY TO CALCULATE:

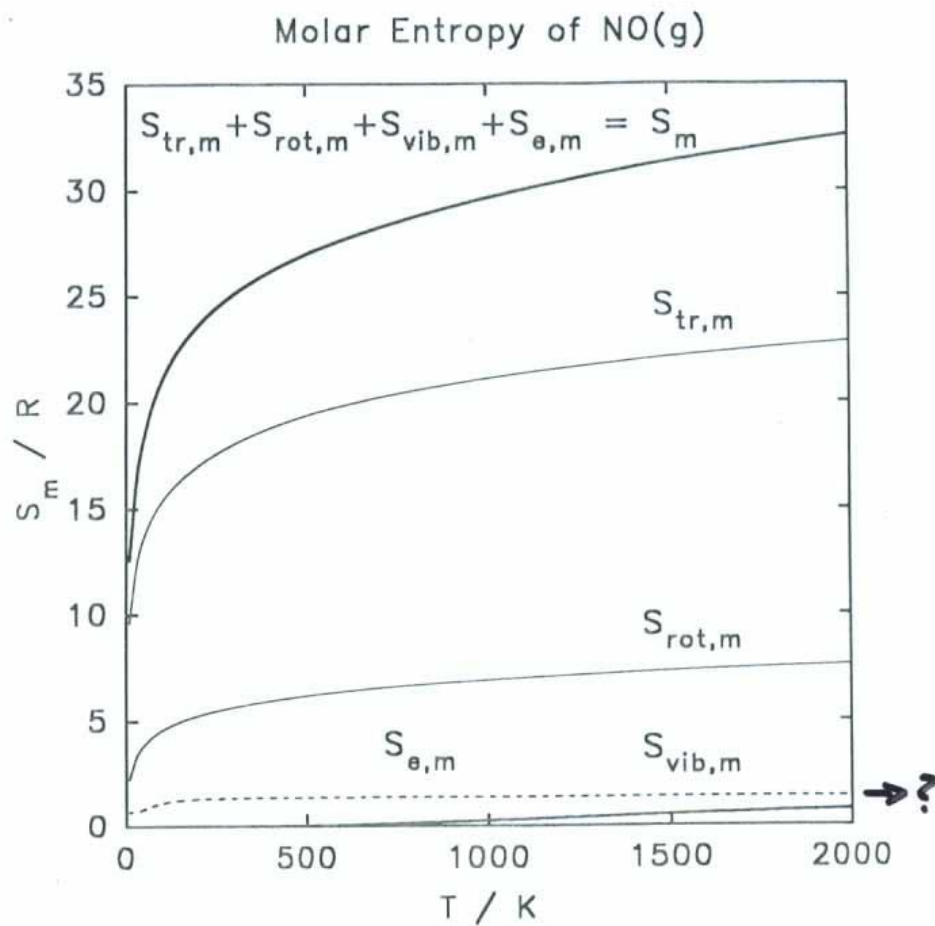
ELECTRONIC ENERGY  $E_e = NKT^2 \left( \frac{\partial \ln z_{elec}}{\partial T} \right)_{N,V}$

$$E_{e,m} = R\theta_{1(e)} \left( \frac{1}{e^{\theta_{1(e)}/T} + 1} \right) \begin{matrix} \rightarrow \frac{R\theta_{1(e)}}{2} \text{ as } T \rightarrow \infty \\ \rightarrow 0 \text{ as } T \rightarrow 0 \end{matrix}$$

$$C_{ve,m} = R \left( \frac{\theta_{1(e)}}{T} \right)^2 \frac{e^{\theta_{1(e)}/T}}{(e^{\theta_{1(e)}/T} + 1)^2} \begin{matrix} \rightarrow 0 \text{ as } T \rightarrow \infty \\ \rightarrow 0 \text{ as } T \rightarrow 0 \end{matrix}$$

### Heat Capacity of NO(g)





AS  $T \rightarrow \infty$ ,  $S_{e,m} \rightarrow R \ln 4 = k_B \ln 4^L$

ONE ELECTRON DISTRIBUTED OVER 4 LEVELS  
(EQUIVALENT AS  $T \rightarrow \infty$ )  $W = \frac{4!}{1! 3!} = 4$

THIS IS A CHEMISTRY COURSE, SO ...

WHERE'S THE CHEMISTRY ???

SUPPOSE GASES A AND B REACT TO FORM  
PRODUCT GASES C AND D:



GOAL: PREDICT THE EQUILIBRIUM  
COMPOSITION FROM MOLECULAR  
PROPERTIES

PLACE THE REACTING GASES IN A CONTAINER  
OF VOLUME  $V$  AT TEMPERATURE  $T$ .

$$\text{AT EQUILIBRIUM: } dA_{T,V} = 0$$

( $A = E - TS \equiv$  HELMHOLTZ FUNCTION)

$A$  IS A FUNCTION OF  $T, V$  (LAST TERM—  
FOR PURE SUBSTANCES) AND NOW ALSO A  
FUNCTION OF  $N_A, N_B, N_C, N_D$

$$dA = \frac{\partial A}{\partial T} dT + \frac{\partial A}{\partial V} dV + \frac{\partial A}{\partial N_A} dN_A + \frac{\partial A}{\partial N_B} dN_B + \frac{\partial A}{\partial N_C} dN_C + \frac{\partial A}{\partial N_D} dN_D$$

$A(T, V, N_A, N_B, N_C, N_D)$  LOOKS HORRIBLY COMPLICATED  
BUT ...  
6 VARIABLES ?

## REACTION EQUILIBRIUM AT CONSTANT $T, V$

$$dT = 0 \quad dV = 0 \quad dA_{T,V} = 0$$

$$\therefore \frac{\partial A}{\partial N_A} dN_A + \frac{\partial A}{\partial N_B} dN_B + \frac{\partial A}{\partial N_C} dN_C + \frac{\partial A}{\partial N_D} dN_D = 0$$

4 VARIABLES?

BUT  $dN_A, dN_B, dN_C$  AND  $dN_D$  ARE NOT  
INDEPENDENT. REACTION STOICHIOMETRY

DICTATES THAT THE CHANGE IN THE  
NUMBER OF MOLES OF A REACTANT OR  
PRODUCT IS PROPORTIONAL TO ITS  
STOICHIOMETRIC COEFFICIENT.

### EXAMPLE



(FOR EVERY MOLE  
OF REACTANT A  
CONSUMED, 4 MOLES  
OF PRODUCT C ARE  
PRODUCED)

DEFINES:

$$\nu_A = -1 \quad \nu_B = -2 \quad \nu_C = 4 \quad \nu_D = 3$$

$$\left( \frac{\nu_A}{\nu_C} = \frac{-1}{4} \right)$$

$$\frac{dN_A}{\nu_A} = \frac{dN_B}{\nu_B} = \frac{dN_C}{\nu_C} = \frac{dN_D}{\nu_D} \equiv d\xi$$

ONLY 1  
VARIABLE!

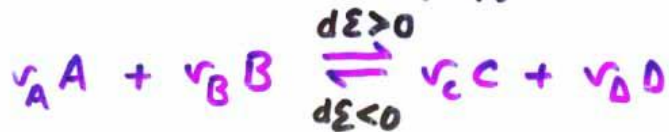


$\xi$  = EXTENT OF THE REACTION

$$dA_{T,V} = \frac{\partial A}{\partial N_A} dN_A + \frac{\partial A}{\partial N_B} dN_B + \frac{\partial A}{\partial N_C} dN_C + \frac{\partial A}{\partial N_D} dN_D$$

$$0 = \frac{\partial A}{\partial N_A} v_A d\xi + \frac{\partial A}{\partial N_B} v_B d\xi + \frac{\partial A}{\partial N_C} v_C d\xi + \frac{\partial A}{\partial N_D} v_D d\xi$$

$$0 = \sum_i v_i \left( \frac{\partial A}{\partial N_i} \right)_{T,V,N_{j \neq i}} d\xi \quad \text{AT EQUILIBRIUM}$$



$$\therefore \boxed{\sum_i v_i \left( \frac{\partial A}{\partial N_i} \right)_{T,V,N_{j \neq i}} = 0} \quad \text{AT EQUILIBRIUM}$$

HELMHOLTZ  
FUNCTION

$$A = -kT \ln Z$$

SYSTEM  
PARTITION  
FUNCTION  
(BIG ZED)

$$Z = \frac{z_A^{N_A}}{N_A!} \frac{z_B^{N_B}}{N_B!} \frac{z_C^{N_C}}{N_C!} \frac{z_D^{N_D}}{N_D!}$$

$$\left( \frac{\partial A}{\partial N_i} \right)_{T,V,N_{j \neq i}} = kT \frac{\partial \ln \left( \frac{z_i^{N_i}}{N_i!} \right)}{\partial N_i} = kT \frac{\partial}{\partial N_i} (N_i \ln z_i) - kT \frac{\partial}{\partial N_i} (\ln N_i!)$$

$$\left(\frac{\partial A}{\partial N_i}\right)_{T, V, N_{j \neq i}} = kT \left[ N_i \frac{\partial \ln z_i}{\partial N_i} + \ln z_i \frac{\partial N_i}{\partial N_i} - \frac{\partial}{\partial N_i} (N_i \ln N_i - N_i) \right]$$

(MOLECULAR PARTITION FUNCTION ( $N_i=1$ ) IS INDEPENDENT OF  $N_i$ )

$$\therefore \left(\frac{\partial A}{\partial N_i}\right)_{T, V, N_{j \neq i}} = kT \left[ \ln z_i - N_i \frac{1}{N_i} - \ln N_i \frac{\partial N_i}{\partial N_i} + \frac{\partial N_i}{\partial N_i} \right]$$

$$\boxed{\left(\frac{\partial A}{\partial N_i}\right)_{T, V, N_{j \neq i}} = kT \ln \left(\frac{z_i}{N_i}\right)}$$

AT EQUILIBRIUM:

$$0 = \sum_i v_i \left(\frac{\partial A}{\partial N_i}\right)_{T, V, N_{j \neq i}} = kT \sum_i v_i \ln \left(\frac{z_i}{N_i}\right) = kT \sum_i \ln \left(\frac{z_i}{N_i}\right)^{v_i}$$

$$\left[ z_i = z_{i, tr} z_{i, rot} z_{i, vib} z_{i, e} \right] \quad * \text{ ONLY } z_{i, tr} (\propto V) \text{ DEPENDS ON } V$$

$$0 = \sum_i \ln \left(\frac{z_i}{V} \frac{V}{N_i}\right)^{v_i} \Rightarrow \sum_i \ln \left(\frac{N_i}{V}\right)^{v_i} = \sum_i \ln \left(\frac{z_i}{V}\right)^{v_i}$$

$$c_i = \frac{N_i}{V} = \text{CONCENTRATION OF MOLECULE } i$$

FUNCTION OF T ONLY



$$c_A^{-1} c_B^{-2} c_C^4 c_D^3 = \frac{c_C^4 c_D^3}{c_A c_B^2} = \frac{(z_C/V)^4 (z_D/V)^3}{(z_A/V) (z_B/V)^2} = K(T)_{eq} \quad \text{EQUILIBRIUM CONSTANT}$$

EXAMPLE



DISSOCIATION  
EQUILIBRIUM

$$\nu_{A_2} = -1$$

$$\nu_A = +2$$

$$z_A = z_{A, \text{tr}} = \frac{(2\pi m_A kT)^{3/2} V}{h^3}$$

NOTE:  $z_A/V$   
AND  $z_{A_2}/V$   
ARE FUNCTIONS  
OF  $T$  (NOT  $V$ )

$$z_{A_2} = (z_{A_2, \text{tr}} z_{A_2, \text{rot}} z_{A_2, \text{vib}})$$

$$z_{A_2} = \left( \frac{(2\pi m_{A_2} kT)^{3/2} V}{h^3} \right) \left( \frac{T}{2\theta_r} \right) \left( \frac{e^{-\theta_v/2T}}{1 - e^{-\theta_v/T}} \right)$$

AT EQUILIBRIUM:

$$0 = \sum_i \nu_i \frac{\partial A}{\partial N_i} = kT \sum_i \nu_i \ln \left( \frac{z_i}{N_i} \right) = kT \sum_i \nu_i \ln \left( \frac{z_i}{N_i} \right)^{\nu_i}$$

$$0 = \sum_i \nu_i \ln \left( \frac{z_i}{V} \frac{V}{N_i} \right)^{\nu_i} = \ln \left( \frac{z_{A_2}}{V} \frac{V}{N_{A_2}} \right)^{-1} + \ln \left( \frac{z_A}{V} \frac{V}{N_A} \right)^2$$

$$0 = \ln \left[ \frac{(z_A/V)^2 (N_{A_2}/V)}{(z_{A_2}/V) (N_A/V)^2} \right] \Rightarrow 0 = \ln[1]$$

$$\therefore \frac{(z_A/V)^2}{(z_{A_2}/V)} = \frac{(N_A/V)^2}{(N_{A_2}/V)} = \frac{c_A^2}{c_{A_2}} = K_c(T)$$