

## Part 7. Molecular Statistics and the Boltzmann Distribution

**NEW TOPIC:**

**STATISTICAL THERMODYNAMICS**

PREVIOUSLY, MOSTLY "EMPIRICAL"  
THERMODYNAMICS (MEASURE  $P, T, V,$   
 $\Delta U, \Delta S, \Delta H, \Delta G, \alpha, \kappa_T, \kappa_S, c, \dots$ )

IT WOULD BE HELPFUL TO HAVE A  
MOLECULAR INTERPRETATION OF  
THERMODYNAMIC QUANTITIES, SUCH AS  
ENERGY AND ENTROPY

EXAMPLE

$$dS \equiv dq_{\text{rev}}/T$$

USED TO CALCULATE ENTROPIES FROM  
MEASURED HEAT CAPACITIES, ENTHALPY  
CHANGES FOR PHASE TRANSITIONS, ...

BUT HOW CAN THE ENTROPY BE  
EXPLAINED ON THE MOLECULAR LEVEL?

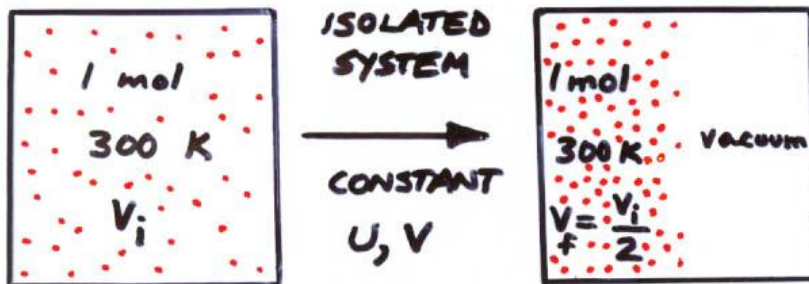
CONNECT:

**ENTROPY AND PROBABILITY**

INCREASE IN ENTROPY  $\rightarrow$  DECREASE IN  
ORDER  $\rightarrow$  INCREASE IN DISORDER  $\rightarrow$   
LOSS OF INFORMATION

1

CHANGE IN VOLUME FOR AN ISOTHERMAL IDEAL GAS



$$\Delta S_{U,V} = nR \ln\left(\frac{V_f}{V_i}\right) = (1 \text{ mol})R \ln\left(\frac{1}{2}\right) = -5.76 \frac{\text{J}}{\text{K}}$$

$\Delta S_{U,V} < 0$  IMPOSSIBLE! (BY THE 2<sup>ND</sup> LAW) BUT WHY?

MOLECULAR INTERPRETATION

THE GAS IS IDEAL, SO THERE ARE NO MOLECULAR INTERACTIONS. EACH MOLECULE CAN BE ON THE LEFT OR RIGHT SIDE OF THE CONTAINER (EQUALLY PROBABLE). FOR  $N = nL$  MOLECULES, THERE ARE

$$W = 2^N \text{ POSSIBLE CONFIGURATIONS.}$$

THE PROBABILITY OF FINDING ALL THE MOLECULES ON THE LEFT SIDE (1 CONFIGURATION) IS

$$1 \text{ IN } 2^N = \frac{1}{2^N} = \left(\frac{1}{2}\right)^{6.02 \times 10^{23}} = 10^{-1.8 \times 10^{23}} \text{ NEVER OBSERVED!}$$

## ENTROPY AND DISORDER

WHAT IS THE CONNECTION BETWEEN THE ENTROPY OF A SYSTEM (MACROSCOPIC PROPERTY  $S$ ) AND THE NUMBER OF POSSIBLE CONFIGURATIONS (MICROSCOPIC PROPERTY  $W$ )?

$S_1$	$S_2$
$W_1$	$W_2$

DIVIDE A SYSTEM INTO 2 PARTS

THE ENTROPY OF A SYSTEM IS AN EXTENSIVE (ADDITIVE) PROPERTY, SO  $S = S_1 + S_2$ . FOR EVERY CONFIGURATION OF SUBSYSTEM 1, THERE ARE  $W_2$  POSSIBLE CONFIGURATIONS OF SUBSYSTEM 2, SO THE TOTAL SYSTEM HAS  $W = W_1 W_2$  CONFIGURATIONS.

$$S = S_1 + S_2$$

$$W = W_1 W_2$$

IMPORTANT CONCLUSION:

THE RELATION BETWEEN  $S$  AND  $W$  MUST BE LOGARITHMIC:  $S = a \ln W + b$   
 ( $a, b$  CONSTANTS TO BE DETERMINED)  
 EXPECT  $b = 0$  SINCE  $S = 0$  FOR A PERFECT CRYSTAL AT 0 K ( $W = 1$ ,  $\ln 1 = 0$ )

### NUMBER OF CONFIGURATIONS

NUMBER OF DIFFERENT WAYS OF  
PLACING  $N$  INDISTINGUISHABLE MOLECULES  
ON  $Z$  SITES

$$W = \frac{Z!}{N! (Z-N)!}$$

EXAMPLE 2 INDISTINGUISHABLE  
MOLECULES ON 5 SITES:

$$W = \frac{5!}{2! (5-2)!} = \frac{(5)(4)(3)(2)(1)}{[(2)(1)][(3)(2)(1)]} = \frac{20}{2} = 10$$

CHECK:

10 CONFIG.

	5 SITES				
1.	•	•	—	—	—
2.	•	—	•	—	—
3.	•	—	—	•	—
4.	•	—	—	—	•
5.	—	•	•	—	—
6.	—	•	—	•	—
7.	—	•	—	—	•
8.	—	—	•	•	—
9.	—	—	•	—	•
10.	—	—	—	•	•

$$\ln W = \ln \left( \frac{5!}{2! 3!} \right) = \ln 10 = 2.302$$

## STIRLING'S APPROXIMATION



$\ln W$  AND  $\ln \frac{z!}{N!(z-N)!}$  CAN'T BE EVALUATED DIRECTLY FOR LARGE NUMBERS ( $\sim 10^{23}$ ). INSTEAD, USE:

$$\ln N! = \ln N + \ln(N-1) + \ln(N-2) + \dots + \ln(1)$$

$$\approx \int_1^N \ln x \, dx = [x \ln x - x] \Big|_1^N$$

$$\approx N \ln N - N - \cancel{\ln(1)} + 1$$

NEGLIGIBLE

(FOR LARGE N VALUES)

$$\ln N! \approx N \ln N - N$$

FOR LARGE VALUES OF N

ERROR COMPLETELY NEGLIGIBLE  
FOR  $N \gtrsim 10^{10}$

$$\left( \begin{array}{l} \text{ERROR IN } \ln N! \approx N \ln N - N \\ \text{IS } \approx \frac{1}{2} \ln N \end{array} \right)$$

## ENTROPY CHANGE FOR GAS EXPANSION

ISOTHERMAL EXPANSION OF  $n$  MOLES OF AN IDEAL GAS FROM  $V_i$  TO  $V_f$

$$\Delta S = nR \ln\left(\frac{V_f}{V_i}\right) = (nL) \frac{R}{L} \ln\left(\frac{V_f}{V_i}\right)$$

$$\Delta S = N k_B \ln\left(\frac{V_f}{V_i}\right)$$

(MACROSCOPIC)

$L = \text{Avogadro's number}$   
 $= 6.022 \times 10^{23} \text{ mol}^{-1}$

$k = \frac{R}{L} = \text{BOLTZMANN'S CONSTANT}$

$$= 1.381 \times 10^{-23} \frac{\text{J}}{\text{K}}$$

MOLECULAR INTERPRETATION (NEW!)

$$\Delta S = S_f - S_i = (a \ln W_f - a \ln W_i)$$

$W_f = \text{NUMBER OF FINAL CONFIGURATIONS}$

$W_i = \text{NUMBER OF INITIAL CONFIGURATIONS}$

$$\Delta S = a \ln\left(\frac{W_f}{W_i}\right)$$

(MICROSCOPIC)

NEW!

VALUES OF

$a?$

$W_i?$

$W_f?$

## EXPAND $N$ GAS MOLECULES FROM VOLUME $V_i$ TO $V_f$

DIVIDE THE INITIAL VOLUME INTO A HUGE NUMBER ( $Z_i \gg N$ ) OF MICROSCOPIC CELLS

THE NUMBER OF WAYS  $N$  MOLECULES CAN BE DISTRIBUTED OVER  $Z_i$  SITES:

$$W_i = \frac{Z_i!}{N! (Z_i - N)!}$$

USE STIRLING'S APPROXIMATION FOR

THE LOGARITHM OF THE NUMBER OF INITIAL CONFIGURATIONS

$$\ln W_i = \ln(Z_i!) - \ln(N!) - \ln(Z_i - N)!$$

$$= Z_i \ln Z_i - Z_i - N \ln N + N$$

$$- (Z_i - N) \ln(Z_i - N) + Z_i - N$$

$$= Z_i \ln Z_i - N \ln N - (Z_i - N) \ln \left[ Z_i \left( 1 - \frac{N}{Z_i} \right) \right]$$

$$= Z_i \ln Z_i - N \ln N - (Z_i - N) \ln Z_i - (Z_i - N) \ln \left( 1 - \frac{N}{Z_i} \right)$$

$$= -N \ln N + N \ln Z_i - (Z_i - N) \left( \frac{-N}{Z_i} \right)$$

NEGLECTIBLE COMPARED TO  $Z_i$

$$\ln W_i = N \ln \left( \frac{Z_i}{N} \right) + N$$

$$\begin{aligned} \therefore \ln \left( 1 - \frac{N}{Z_i} \right) \\ = - \frac{N}{Z_i} \end{aligned}$$

NUMBER OF  
FINAL CONFIGURATIONS

$W_f$

EXPAND THE GAS FROM VOLUME  $V_i$  TO  $V_f$

NUMBER OF MICROSCOPIC CELLS INCREASES  
FROM  $Z_i$  TO  $\frac{V_f}{V_i} Z_i = Z_f$  (PROPORTIONAL TO  
THE VOLUME)

$$\ln W_f = N \ln \left( \frac{Z_f}{N} \right) + N = N \ln \left( \frac{\frac{V_f}{V_i} Z_i}{N} \right) + N$$

FOR THE EXPANSION OF A GAS FROM  $V_i$  TO  $V_f$ :

$$\begin{aligned} \ln \left( \frac{W_f}{W_i} \right) &= \ln W_f - \ln W_i = N \ln \left( \frac{Z_f}{N} \right) + N - [N \ln \left( \frac{Z_i}{N} \right) + N] \\ &= N \left[ \ln \left( \frac{Z_f}{N} \right) - \ln \left( \frac{Z_i}{N} \right) \right] = N \ln \left( \frac{Z_f}{Z_i} \right) \end{aligned}$$

$$\ln \left( \frac{W_f}{W_i} \right) = N \ln \left( \frac{V_f}{V_i} \right) = \frac{\Delta S}{k}$$

MICROSCOPIC  
COMPARE

MACROSCOPIC

$$\begin{aligned} \Delta S &= S_f - S_i = a \ln W_f - a \ln W_i \\ &= a \ln \left( \frac{W_f}{W_i} \right) \end{aligned} \quad \boxed{a=k}$$

$$\frac{Z_f}{Z_i} = \frac{V_f}{V_i}$$

$$\boxed{a=k}$$

$$\boxed{S = k \ln W}$$

BOLTZMANN'S  
EQUATION



EXAMPLE

EXPAND 1 mol OF IDEAL GAS  
FROM 1 dm<sup>3</sup> to 2 dm<sup>3</sup>

$$\begin{aligned}\Delta S &= nR \ln\left(\frac{V_f}{V_i}\right) = nR \ln 2 \\ &= Nk \ln 2 = (1)(8.314) \ln 2 \\ &= 5.76 \frac{\text{J}}{\text{K}} \quad \text{(OLD)}\end{aligned}$$

$$\Delta S = k \ln\left(\frac{W_f}{W_i}\right)$$

$$\frac{W_f}{W_i} = \exp\left(\frac{\Delta S}{k}\right) = \exp(4.18 \times 10^{23})$$

**NEW!**

## ENTROPY OF MIXING

### THERMODYNAMIC EQUATIONS (MACROSCOPIC)

MIX  $n_A$  moles OF PURE GAS A WITH  
 $n_B$  moles OF PURE GAS B AT  
 CONSTANT  $T, P, V$ . FOR IDEAL

$$\Delta S_{\text{MIX}} = -R \left[ n_A \ln \left( \frac{n_A}{n_A + n_B} \right) + n_B \ln \left( \frac{n_B}{n_A + n_B} \right) \right] \quad (\text{OK, BUT WHY?})$$

$$\Delta S_{\text{MIX}} = -k \left[ N_A \ln \left( \frac{N_A}{N_A + N_B} \right) + N_B \ln \left( \frac{N_B}{N_A + N_B} \right) \right]$$

$$k = \frac{R}{L}$$

NUMBER OF MOLECULES  $N_A = L n_A$   
 $N_B = L n_B$

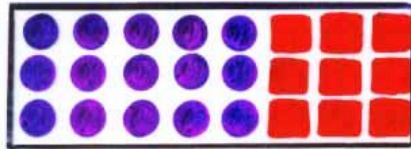
$L = \text{Avogadro's Constant} = 6.022 \times 10^{23} \text{ mol}^{-1}$

\* COMPARE THE THERMODYNAMIC EXPRESSION

FOR  $\Delta S_{\text{MIX}}$  WITH THE EXPRESSION

FROM BOLTZMANN'S EQUATION  $S = k \ln W$

MIX  $N_A$  MOLECULES OF PURE LIQUID CRYSTAL A  
WITH  $N_B$  MOLECULES OF PURE LIQUID CRYSTAL B



INITIAL UNMIXED STATE

NUMBER OF  
INITIAL  
CONFIGURATIONS

$$W_i = 1$$

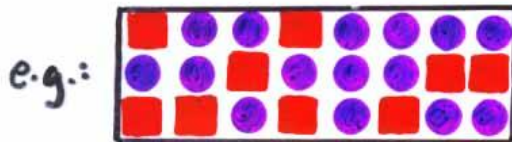
$N_A$  MOLECULES ON  $N_A$  SITES:

$$\frac{N_A!}{N_A! (N_A - N_A)!} = \frac{1}{0!} = 1 \text{ CONFIGURATION}$$

$N_B$  MOLECULES ON  $N_B$  SITES:

$$\frac{N_B!}{N_B! (N_B - N_B)!} = \frac{1}{0!} = 1 \text{ CONFIGURATION}$$

ALLOW RANDOM MIXING...



$N_A$  MOLECULES  
+  
 $N_B$  MOLECULES

ON  
 $N_A + N_B$   
SITES

NUMBER OF  
FINAL  
CONFIGURATIONS

$$W_f = \frac{(N_A + N_B)!}{N_A! N_B!} = \frac{24!}{15! 9!}$$

(number of sites =  $N_A + N_B$ )

= 1,307,504  
(HUGE)

MICROSCOPIC  
INTERPRETATION

$$\Delta S_{\text{MIX}} = k \ln W_f - k \ln W_i$$

$$\Delta S_{\text{MIX}} = k \ln \left( \frac{(N_A + N_B)!}{N_A! N_B!} \right) - k \ln(1)$$

$$= k [\ln(N_A + N_B)! - \ln N_A! - \ln N_B!]$$

$$= k \left[ (N_A + N_B) \ln(N_A + N_B) - \cancel{(N_A + N_B)} - N_A \ln N_A + \cancel{N_A} - N_B \ln N_B + \cancel{N_B} \right]$$

(sterling's approximation - three times)

$$= k \left[ N_A [\ln(N_A + N_B) - \ln N_A] + N_B [\ln(N_A + N_B) - \ln N_B] \right]$$

$$\Delta S_{\text{MIX}} = -k \left[ N_A \ln \left( \frac{N_A}{N_A + N_B} \right) + N_B \ln \left( \frac{N_B}{N_A + N_B} \right) \right]$$

$$= +k \ln \left( \frac{W_{\text{MIXED}}}{W_{\text{UNMIXED}}} \right) \quad \text{(SAME AS MACROSCOPIC RESULT)}$$

EXAMPLE MIX  $\frac{1}{2}$  MOLE A AND  $\frac{1}{2}$  MOLE B.

$$\Delta S_{\text{MIX}} = -1.381 \times 10^{-23} \frac{\text{J}}{\text{K}} \left[ \frac{(6.022 \times 10^{23})}{2} \ln \frac{1}{2} + \frac{(6.022 \times 10^{23})}{2} \ln \frac{1}{2} \right]$$

$$\Delta S_{\text{MIX}} = 5.76 \text{ J K}^{-1}$$

HUGE NUMBER!

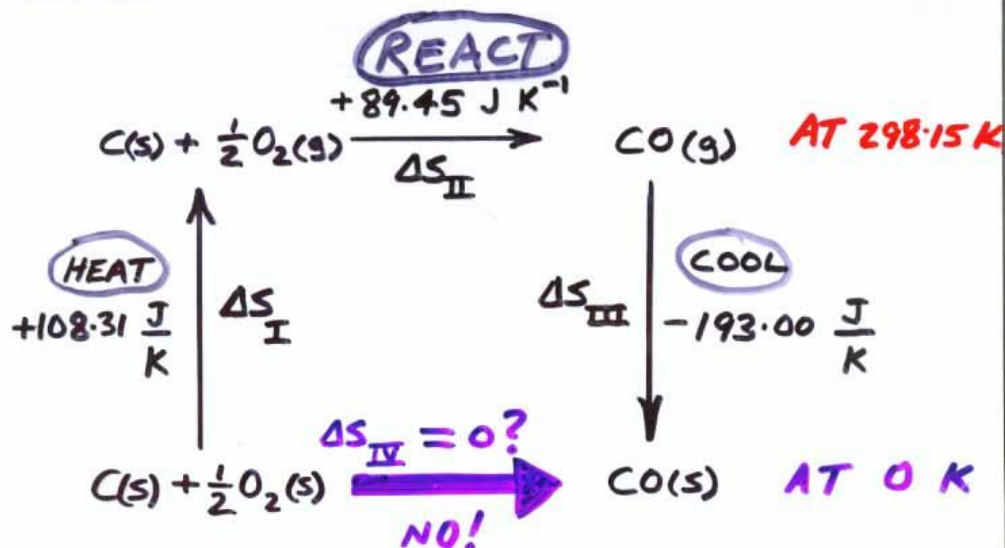
$$\frac{W_{\text{MIXED}}}{W_{\text{UNMIXED}}} = \exp \left( \frac{\Delta S_{\text{MIX}}}{k} \right) = \exp(4.17 \times 10^{23})$$

### THIRD LAW ANOMALIES

EXPLAINED!

THE ENTROPIES OF PERFECT CRYSTALS AT 0 K ARE ASSIGNED THE VALUE ZERO ( $W=1$ )

BUT....



MEASURE  $\Delta S_{\text{IV}} = 108.31 + 89.45 - 193.00 = +4.76 \frac{\text{J}}{\text{K}} ?$   
 BUT  $\Delta S_{\text{IV}}$  FOR THE CONVERSION OF C(S) AND O<sub>2</sub>(S) PERFECT CRYSTALS TO CO(S) PERFECT CRYSTALS SHOULD BE ZERO.

EXPLANATION CO, IF FROZEN TOO QUICKLY, HAS FROZEN-IN DISORDER: TWO POSSIBLE CONFIGURATIONS PER MOLECULE. (CO OR OC)



$$\begin{aligned}
 S_m(0\text{K}) &= k \ln W = k \ln 2^L \\
 &= Lk \ln 2 = R \ln 2 = \underline{5.76 \frac{\text{J}}{\text{K}}}
 \end{aligned}$$

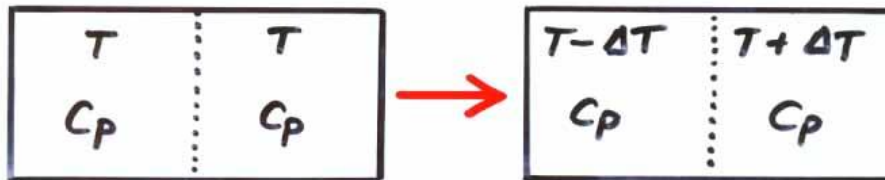
## FLUCTUATIONS FROM EQUILIBRIUM

THE EQUILIBRIUM STATE OF A SYSTEM IS THE MOST PROBABLE STATE. BUT, FOLLOWING THE LAWS OF PROBABILITY, SMALL DEVIATIONS IN THE TEMPERATURE, DENSITY, PRESSURE, ENTROPY, ... FROM THEIR EQUILIBRIUM VALUES CAN HAPPEN.

\* IMPORTANT FOR NUCLEATION, LIGHT SCATTERING (WHY THE SKY IS BLUE!), VERY SMALL SYSTEMS

EXAMPLE TWO SYSTEMS OF IDENTICAL HEAT CAPACITY ARE IN THERMAL CONTACT AT EQUILIBRIUM TEMPERATURE  $T$ .

WHAT IS THE PROBABILITY OF THE FLUCTUATION:



(RECALL,  
HEATING A SYSTEM FROM  $T_1$  TO  $T_2$  CAUSES  
ITS ENTROPY TO CHANGE BY  $\int_{T_1}^{T_2} \frac{C_p dT}{T}$ )

THE TEMPERATURE FLUCTUATION PRODUCES  
THE ENTROPY CHANGE

$$\begin{aligned}\Delta S &= \int_T^{T-\Delta T} \frac{C_p dT}{T} + \int_T^{T+\Delta T} \frac{C_p dT}{T} \\ &= C_p \ln\left(\frac{T-\Delta T}{T}\right) + C_p \ln\left(\frac{T+\Delta T}{T}\right) \\ &= C_p \ln\left[\frac{(T-\Delta T)(T+\Delta T)}{T^2}\right] \\ &= C_p \ln\left[\frac{T^2 - (\Delta T)^2}{T^2}\right] \\ &= C_p \ln\left[1 - \left(\frac{\Delta T}{T}\right)^2\right]\end{aligned}$$

SMALL  
FLUCTUATIONS:  
 $\frac{\Delta T}{T} \ll 1$

$$\Delta S \approx -C_p \left(\frac{\Delta T}{T}\right)^2$$

(FOR  $x \ll 1$ )  
 $\ln(1-x) \approx -x$

THE FLUCTUATION IN TEMPERATURE FROM THE  
EQUILIBRIUM VALUE REDUCES THE NUMBER  
OF CONFIGURATIONS FROM  $w_{eq}$  TO  $w$

$$\text{PROBABILITY} = \frac{w}{w_{eq}} = \exp\left(\frac{\Delta S}{k}\right)$$

WHAT IS THE PROBABILITY OF THE FLUCTUATION  
 $\Delta T = 10^{-6} \text{ K} = 1 \mu\text{K}$  FOR 2 mol  $\text{H}_2\text{O}(\text{l})$   
 AT 300 K?

$T - 1 \mu\text{K}$	$T + 1 \mu\text{K}$
$C_p = 75 \frac{\text{J}}{\text{K}}$ 1 mol $\text{H}_2\text{O}$	$C_p = 75 \frac{\text{J}}{\text{K}}$ 1 mol $\text{H}_2\text{O}$

$C_p$ :  
 PROPORTIONAL  
 TO THE SIZE  
 OF THE  
 SYSTEM

$$\text{PROBABILITY} = \exp\left(\frac{\Delta S}{k_B}\right) = \exp\left[-\frac{C_p}{k_B} \left(\frac{\Delta T}{T}\right)^2\right]$$

$$\frac{W_f}{W_{eq}} = \exp\left[-\frac{75 \text{ J K}^{-1}}{1.381 \times 10^{-23} \text{ J K}^{-1}} \left(\frac{1 \times 10^{-6} \text{ K}}{300 \text{ K}}\right)^2\right]$$

$$= \exp(-6.034 \times 10^7) = 10^{-26,200,000}$$

! "NEVER" OBSERVED!

REPEAT THIS CALCULATION FOR A VERY  
SMALL SYSTEM:  $2 \times 10^{-7}$  mol  $\text{H}_2\text{O}(\text{l})$  AT 300 K.

(NOW  $C_p$  IS ONLY  $75 \times 10^{-7} \text{ J K}^{-1}$ )

$$\text{PROBABILITY} = \exp(-6.034) = 0.0024$$

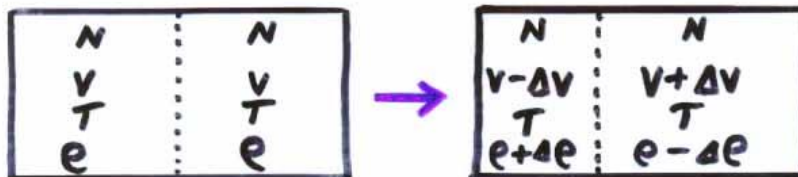
OR 0.24% (NOT NEGLIGIBLE)

CONCLUSION  $\rightarrow$  FLUCTUATIONS FROM  
 EQUILIBRIUM ARE SIGNIFICANT  
 ONLY FOR VERY SMALL SYSTEMS



## WHY IS THE DAYTIME SKY BLUE?

**FIRST:** A) CALCULATE THE ENTROPY CHANGE  
THE FLUCTUATION



IN THE DENSITY ( $\rho$ ) OF AN ISOTHERMAL IDEAL GAS.

$$\Delta S = \Delta S(\text{LEFT VOLUME}) + \Delta S(\text{RIGHT VOLUME})$$

$$= nR \int_{V}^{V-\Delta V} \frac{dV}{V} + nR \int_{V}^{V+\Delta V} \frac{dV}{V}$$

$$= Nk \int_{V}^{V-\Delta V} \frac{dV}{V} + Nk \int_{V}^{V+\Delta V} \frac{dV}{V}$$

$$= Nk \ln\left(\frac{V-\Delta V}{V}\right) + Nk \ln\left(\frac{V+\Delta V}{V}\right)$$

$$= Nk \ln\left[\frac{(V-\Delta V)(V+\Delta V)}{V^2}\right] = Nk \ln\left[\frac{V^2 - (\Delta V)^2}{V^2}\right]$$

$$\Delta S = Nk \ln\left[1 - \left(\frac{\Delta V}{V}\right)^2\right] \approx -Nk \left(\frac{\Delta V}{V}\right)^2 \quad \left(\text{FOR SMALL FLUCTUATIONS}\right)$$

$\Delta V \ll V$

$$\text{DENSITY} = \frac{\text{MASS}}{\text{VOLUME}} = m \frac{N}{V} = \rho$$

( $m$  = mass of 1 molecule)

FOR A FIXED MASS OF GAS ( $N$  CONSTANT)

$$d\rho = mN d\left(\frac{1}{V}\right) = mN \left(-\frac{1}{V^2}\right) dV = -\frac{mN}{V} \frac{dV}{V}$$

$$d\rho = -\rho \frac{dV}{V} \quad \therefore \quad \frac{d\rho}{\rho} = -\frac{dV}{V}$$

$$\text{AND } \left(\frac{\Delta\rho}{\rho}\right)^2 = \left(\frac{\Delta V}{V}\right)^2 \quad \text{FOR SMALL FLUCTUATIONS}$$

$$\therefore \boxed{\Delta S = -Nk \left(\frac{\Delta V}{V}\right)^2 = -Nk \left(\frac{\Delta\rho}{\rho}\right)^2}$$

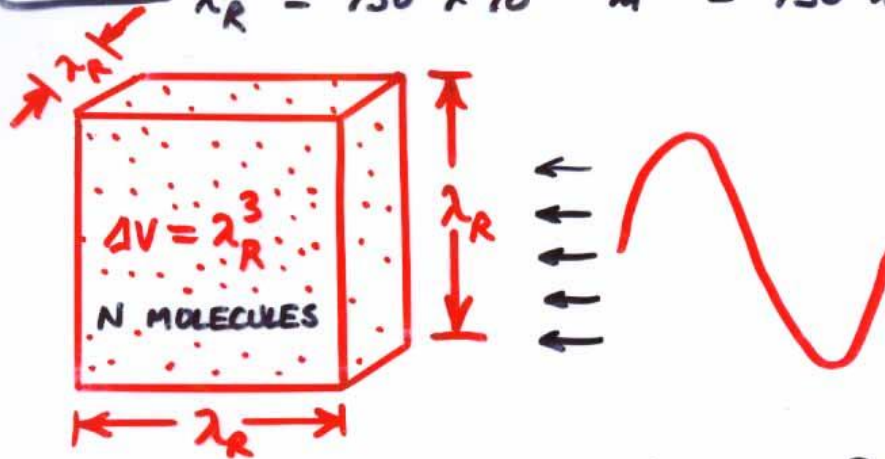
**B)** AT AN ALTITUDE OF 20 km THE MEAN TEMPERATURE AND PRESSURE OF THE ATMOSPHERE ARE 217 K AND 5470 Pa.

CALCULATE  $\Delta S$  (AND THE PROBABILITY) OF A 0.1% CHANGE IN THE DENSITY FOR

$$\Delta V = (\text{WAVELENGTH OF RED LIGHT})^3 = \lambda_R^3$$

$$\text{AND } \Delta V = (\text{WAVELENGTH OF BLUE LIGHT})^3 = \lambda_B^3$$

RED LIGHT  $\lambda_R = 750 \times 10^{-9} \text{ m} = 750 \text{ nm}$



FOR RED LIGHT  $N = \frac{p(\Delta V)}{kT} = \frac{p\lambda_R^3}{kT}$

$N = \frac{5470 \text{ Pa} (750 \times 10^{-9} \text{ m})^3}{1.38 \times 10^{-23} \text{ J K}^{-1} (217 \text{ K})} = \boxed{771,000} *$

$\Delta S = -Nk \left( \frac{\Delta p}{p} \right)^2 = -(771,000) \left( 1.38 \times 10^{-23} \frac{\text{J}}{\text{K}} \right) (0.001)^2$

$\Delta S = -1.06 \times 10^{-23} \text{ J K}^{-1}$

PROBABILITY =  $\frac{W}{W_{eq}} = \exp\left(\frac{\Delta S}{k}\right) = \exp(-0.771)$

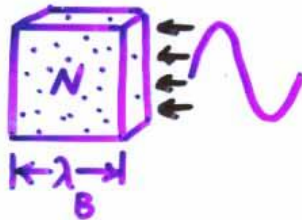
$\boxed{\text{PROBABILITY} = 0.462}$

REPEAT THIS CALCULATION FOR **BLUE LIGHT**.

(SHORTER) WAVELENGTH  $\lambda_B = 400 \times 10^{-9} \text{ m}$

$$\Delta V = \lambda_B^3$$

$\therefore$  SMALLER VOLUME



$$N = \frac{p(\Delta V)}{kT} = \frac{p \lambda_B^3}{kT}$$

$$N = 117,000 \quad *$$

$$\Delta S = -Nk \left( \frac{\Delta p}{p} \right)^2 = -117,000 (1.38 \times 10^{-23}) (0.001)^2$$

$$\Delta S = -0.161 \times 10^{-23} \text{ J K}^{-1}$$

PROBABILITY OF  
A 0.1% FLUCTUATION  
IN VOLUME  $\lambda_B^3$

$$= \exp\left(\frac{\Delta S}{k}\right) = \boxed{0.890}$$

CONCLUSION BLUE LIGHT WAVES HAVE A  
SHORTER WAVELENGTH THAN RED WAVES,  
AND ILLUMINATE SMALLER VOLUMES OF  
GAS WHERE FLUCTUATIONS IN DENSITY (AND  
 $\therefore$  REFRACTIVE INDEX) ARE MORE PROBABLE

**➔ MORE BLUE LIGHT IS SCATTERED THAN RED**

SO FAR, WE'VE APPLIED THE MICROSCOPIC INTERPRETATION OF THE ENTROPY TO ISOTHERMAL PROCESSES INVOLVING MOLECULES HAVING THE SAME ENERGY:

- EXPANSION OF IDEAL GASES
- MIXING OF PURE COMPONENTS
- ORIENTATION OF MOLECULES IN CRYSTALS.

WHAT ABOUT THE MORE GENERAL PROBLEM OF THE DISTRIBUTION OF MOLECULES OVER STATES OF DIFFERENT ENERGIES ?

RECALL ...

**BAROMETRIC EQUATION**  
FOR THE DISTRIBUTION OF GAS MOLECULES IN A GRAVITATIONAL FIELD: PROPORTIONAL TO

$$p(\text{height } h) = p(0)e^{-Mgh/RT}$$

$$= p(0)e^{-mgh/kT}$$

$$\exp\left[-\frac{\text{MOLECULAR POTENTIAL ENERGY}}{kT}\right]$$

**MAXWELL EQUATION**  
FOR THE DISTRIBUTION OF MOLECULAR SPEEDS (IN 1 DIMENSION): PROPORTIONAL TO

$$f(v_x) = \sqrt{\frac{m}{2\pi kT}} e^{-\frac{mv_x^2}{2kT}}$$

$$\exp\left[-\frac{\text{MOLECULAR KINETIC ENERGY}}{kT}\right]$$

HOW ARE THESE DISTRIBUTIONS (AND MANY OTHER IMPORTANT DISTRIBUTIONS) EXPLAINED?

**EXAMPLE** (SIMPLE BUT INFORMATIVE!)

SUPPOSE 3 MOLECULES ( $a, b, c$ ) ARE DISTRIBUTED OVER 4 EQUALLY-SPACED ENERGY LEVELS ( $KT, 2KT, 3KT, 4KT$ ) FOR A TOTAL ENERGY OF  $6KT$ .

$4KT$	$c$	—	—	$b$	( $a$ IN LEVEL 1)
$3KT$	—	$c$	$b$	—	
$2KT$	—	$b$	$c$	—	
$1KT$	$ab$	$a$	$a$	$ac$	

$4KT$	—	—	—	<del><math>b</math></del>	( $a$ IN LEVEL 2) $E = KT + 2KT + 4KT$ <del><math>E = 7KT</math></del> TOO MUCH ENERGY
$3KT$	$c$	—	$b$	<del><math>a</math></del>	
$2KT$	$a$	$abc$	$a$	<del><math>c</math></del>	
$1KT$	$b$	—	$c$	—	

$4KT$	—	—	—	<del><math>ab</math></del>	( $a$ IN LEVEL 3)
$3KT$	$a$	$a$	$b$	<del><math>c</math></del>	
$2KT$	$c$	$b$	$c$	—	
$1KT$	$b$	$c$	—	—	

$4KT$	$a$	<del><math>a</math></del>	—	—	( $a$ IN LEVEL 4)
$3KT$	—	—	—	<del><math>b</math></del>	
$2KT$	—	—	—	<del><math>c</math></del>	
$1KT$	$bc$	—	—	—	

AT CONSTANT ENERGY ( $6kT$ ) AND CONSTANT NUMBER OF MOLECULES (3) THERE ARE 10 POSSIBLE CONFIGURATIONS:



NOTICE THAT ONE CONFIGURATION DOMINATES

6 TIMES OUT OF 10 GET  $\rightarrow$   $\left\{ \begin{array}{c} \text{---} \\ \bullet \\ \text{---} \\ \bullet \\ \text{---} \\ \bullet \\ \text{---} \end{array} \right.$

EQUALLY IMPORTANT, THE MOST PROBABLE DISTRIBUTION IS ALSO THE MOST RANDOM (WIDEST SPREAD OF MOLECULES OVER THE ACCESSIBLE ENERGY LEVELS)

\* THE TOTAL NUMBER OF CONFIGURATIONS (10) IS THE SUM OF THE NUMBER OF WAYS OF PLACING  $N$  MOLECULES INTO LEVELS SO THAT  $N_1$  MOLECULES ARE IN LEVEL 1,  $N_2$  IN LEVEL 2,  $N_3$  IN LEVEL 3,  $N_4$  IN LEVEL 4.

$$\boxed{\text{TOTAL } W = \text{SUM} \left( \frac{N!}{N_1! N_2! N_3! N_4!} \right)} = \frac{3!}{1!1!1!0!} + \frac{3!}{2!0!0!1!} + \frac{3!}{0!3!0!0!}$$

$$= 6 + 3 + 1 = 10$$

**EXAMPLE** 10,000 MOLECULES ARE RANDOMLY DISTRIBUTED OVER 3 EQUALLY-SPACED ENERGY LEVELS:  $1kT$ ,  $2kT$ ,  $3kT$ . THE TOTAL ENERGY IS 15,000  $kT$ .

$N = 10,000 =$  TOTAL NUMBER OF MOLECULES

$N_i =$  NUMBER OF MOLECULES IN LEVEL  $i$

$E_i =$  ENERGY PER MOLECULE IN LEVEL  $i$

(THESE NUMBERS ARE CHOSEN ARBITRARILY!)

$N_1$  MOLECULES ARE IN LEVEL 1 (1kT)  
 $N_2$  MOLECULES ARE IN LEVEL 2 (2kT)  
 $N_3$  MOLECULES ARE IN LEVEL 3 (3kT)

SUM:  $\frac{N}{N}$

$$W = \frac{N!}{N_1! N_2! N_3!} = \text{NUMBER OF CONFIGURATIONS}$$

SUBJECT TO TWO CONSTRAINTS

$$\textcircled{\text{I}} \quad N_1 + N_2 + N_3 = N = 10,000 \quad \left( \begin{array}{l} \text{CONSTANT} \\ \text{NUMBER OF} \\ \text{MOLECULES} \end{array} \right)$$

$$N_1 E_1 + N_2 E_2 + N_3 E_3 = E = N_1 kT + N_2 2kT + N_3 3kT = 15000 kT$$

$$\textcircled{\text{II}} \quad N_1 + 2N_2 + 3N_3 = 15,000 \quad \left( \begin{array}{l} \text{CONSTANT} \\ \text{ENERGY} \end{array} \right)$$



2 EQUATIONS WITH 3 UNKNOWNNS :

GIVEN A VALUE OF  $N_3$ ,

~~10000~~

CALCULATE  $\begin{cases} N_2 = 5000 - 2N_3 \\ N_1 = 10,000 - N_2 - N_3 \end{cases}$

(11-1)

**given:**  $N_3 = 1,000$  @  $3kT = 3,000 kT$

**EXAMPLE**  $N_2 = 3,000$  @  $2kT = 6,000 kT$

**calc:**  $N_1 = 6,000$  @  $1kT = 6,000 kT$

**CHECK:**  $\underline{\underline{N = 10,000}}$   $\underline{\underline{E = 15,000 kT}}$

FOR EACH VALUE OF  $N_3$ , CALCULATE

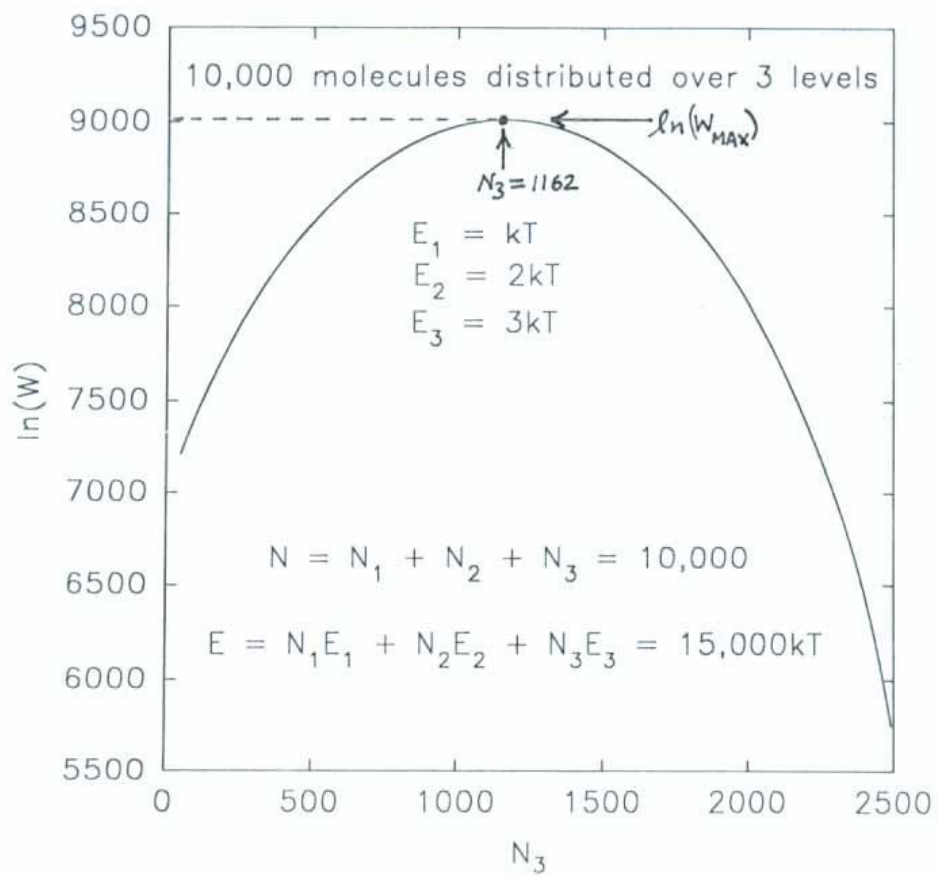
$N_1$ ,  $N_2$  AND USE STIRLING'S APPROXIMATION

$$(\ln N_i! = N_i \ln N_i - N_i)$$

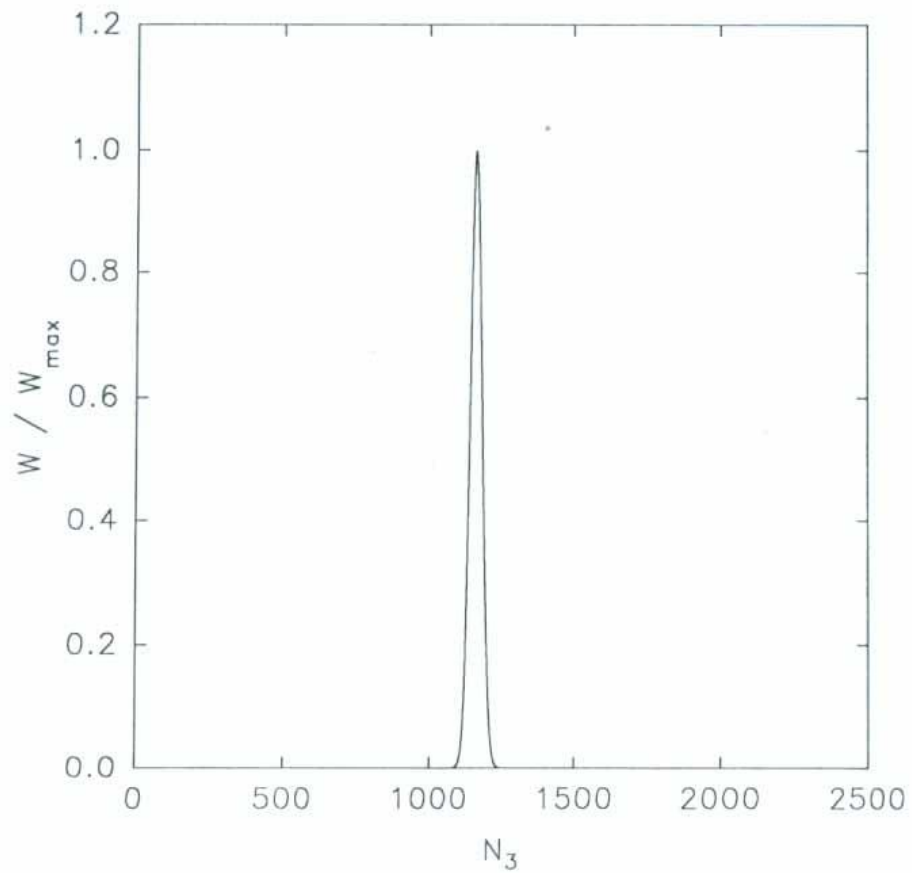
TO CALCULATE THE LOGARITHM OF

THE NUMBER OF POSSIBLE CONFIGURATIONS.

$$\ln W = \ln \left( \frac{N!}{N_1! N_2! N_3!} \right) = \ln N! - \ln N_1! - \ln N_2! - \ln N_3!$$



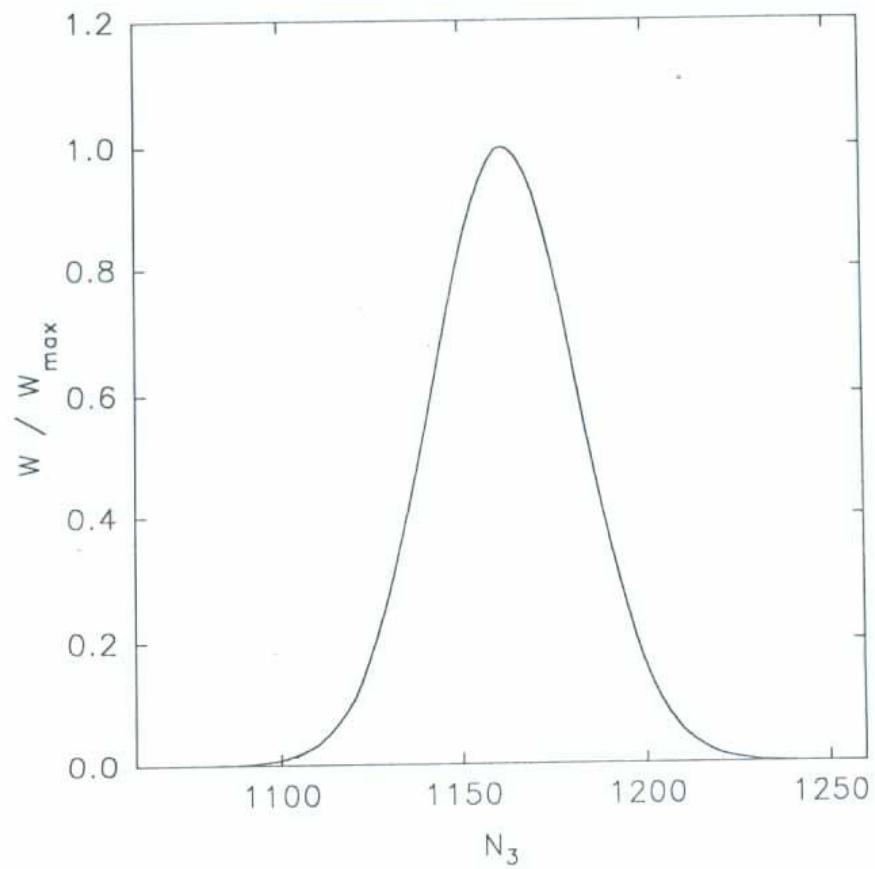
$$\ln(W_{MAX}) = 9012.347 \quad \text{at} \quad N_3 = 1162$$



$0 \leq N_3 \leq 2,500$  POSSIBLE

\* BUT ONLY A NARROW RANGE OF  $N_3$  VALUES IS PROBABLE

$\approx 1170 \pm 100$



GAUSSIAN DISTRIBUTION OF  $N_3$  VALUES !

**\* IMPORTANT (AND UNEXPECTED!) RESULT \***

A WIDE RANGE OF  $N_1, N_2, N_3$  VALUES ARE POSSIBLE,

BUT ONLY A NARROW RANGE OF VALUES IS PROBABLE:

$$\begin{aligned} N_1 &= 6160 \pm 100 \quad (\text{LOWEST ENERGY}) \\ N_2 &= 2670 \pm 200 \\ N_3 &= 1170 \pm 100 \quad (\text{HIGHEST ENERGY}) \end{aligned}$$

CORRESPONDING TO  $N_1, N_2, N_3$  PRODUCING THE LARGEST NUMBER OF CONFIGURATIONS.

THE LARGEST NUMBER OF CONFIGURATIONS IS PRODUCED BY

$$\left. \begin{aligned} N_1 &= 6162 \\ N_2 &= 2676 \\ N_3 &= 1162 \end{aligned} \right\} \ln W_{\text{MAX}} = \ln \left( \frac{10,000!}{N_1! N_2! N_3!} \right) = 9012.347$$

OTHER VALUES OF  $N_1, N_2, N_3$  PRODUCE FEWER CONFIGURATIONS AND ARE MUCH LESS PROBABLE.

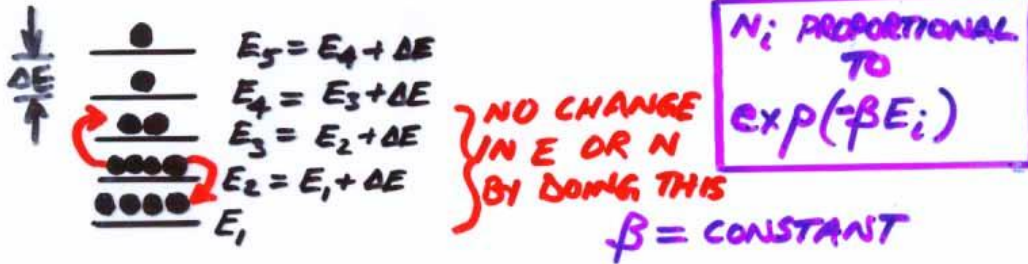
**\* NOTICE THAT THE MOST PROBABLE  $N_1, N_2, N_3$  FOLLOW A GEOMETRIC PROGRESSION.**

$$\frac{N_2}{N_1} = \frac{2676}{6162} = 0.434$$

$$\frac{N_3}{N_2} = \frac{1162}{2676} = 0.434$$

SUGGESTS AN EXPONENTIAL RELATION BETWEEN  $N_i$  AND  $E_i$

**JUSTIFICATION** SHOW THAT THE MOST PROBABLE DISTRIBUTION OF MOLECULES OVER EQUALLY-SPACED ENERGY LEVELS  $E_1, E_2, E_3, \dots$  IS EXPONENTIAL



THE MOST PROBABLE ENERGY LEVEL POPULATION NUMBERS  $N_1, N_2, N_3, \dots$  MAXIMIZES THE NUMBER OF CONFIGURATIONS

$$\ln W_{\text{MAX}} = \ln \left( \frac{N!}{N_1! N_2! N_3! \dots} \right)$$

SINCE  $W_{\text{MAX}}$  IS MAXIMIZED, THE SMALL VARIATION

$$\ln W = \ln \left( \frac{N!}{(N_1+1)! (N_2-2)! (N_3+1)! \dots} \right) \quad \left( \begin{array}{l} \text{CONSISTENT} \\ \text{WITH CONSTANT} \\ N, E \end{array} \right)$$

PRODUCES NEGLIGIBLE CHANGE IN  $W$

$$1 \approx \frac{W_{\text{MAX}}}{W} = \frac{\cancel{N!} (N_1+1)! (N_2-2)! (N_3+1)!}{\cancel{N!} N_1! N_2! N_3!} = \frac{(N_1+1)(N_3+1)}{N_2(N_2-1)}$$

negligible

$$1 \approx \frac{N_1}{N_2} \frac{N_3}{N_2}$$

FOR LARGE VALUES OF  $N_1, N_2, N_3$

$$\frac{N_1}{N_2} \approx \frac{N_2}{N_3}$$

REPEAT FOR OTHER ENERGY LEVELS ...

$$1 = \frac{N_2}{N_3} \frac{N_4}{N_3} \quad 1 = \frac{N_3}{N_4} \frac{N_5}{N_4} \dots$$

TRUE ONLY IF

$$\frac{N_2}{N_1} = \frac{N_3}{N_2} = \frac{N_4}{N_3} \dots = \text{CONSTANT}$$

$$\frac{N_3}{N_1} = \frac{N_3}{N_2} \frac{N_2}{N_1} = (\text{CONSTANT})^2$$

$$\frac{N_4}{N_1} = \frac{N_4}{N_3} \frac{N_3}{N_2} \frac{N_2}{N_1} = (\text{CONSTANT})^3$$

CONCLUSION :  $\ln\left(\frac{N_i}{N_j}\right) = (i-j) \ln(\text{CONSTANT})$

$$i-j = \frac{E_i - E_j}{\Delta E}$$

so  $\ln\left(\frac{N_i}{N_j}\right)$  IS PROPORTIONAL TO  $E_i - E_j$

$$\ln\left(\frac{N_i}{N_j}\right) = -\beta(E_i - E_j) \Rightarrow \boxed{\frac{N_i}{N_j} = \exp[-\beta(E_i - E_j)] = \frac{\exp(-\beta E_i)}{\exp(-\beta E_j)}}$$

**BOLTZMANN DISTRIBUTION — THE MOST PROBABLE  
POPULATION OF DIFFERENT ENERGY LEVELS**

FIND THE NUMBER OF MOLECULES  $N_1, N_2, N_3, \dots$   
IN ENERGY LEVELS  $E_1, E_2, E_3, \dots$  (MAY OR  
MAY NOT BE EQUALLY-SPACED) THAT  
MAXIMIZES:

$$\ln W = \ln \left( \frac{N!}{N_1! N_2! N_3! N_4! \dots} \right)$$

SUBJECT TO THE CONSTRAINTS:

$$N = N_1 + N_2 + N_3 + N_4 + \dots \quad \left( \begin{array}{l} \text{TOTAL NUMBER OF} \\ \text{MOLECULES (N)} \\ \text{IS CONSTANT} \end{array} \right)$$

$$E = N_1 E_1 + N_2 E_2 + N_3 E_3 + N_4 E_4 + \dots \quad \left( \begin{array}{l} \text{TOTAL ENERGY (E)} \\ \text{IS CONSTANT} \end{array} \right)$$

NEED TO SOLVE:

$$0 = d \ln W = d \ln N! - d \ln N_1! - d \ln N_2! - d \ln N_3! - \dots$$

$$0 = dN = dN_1 + dN_2 + dN_3 + \dots$$

$$0 = E_1 dN_1 + E_2 dN_2 + E_3 dN_3 + \dots$$



## OPTIMIZATION - FINDING A MAXIMUM (OR A MINIMUM) IN A FUNCTION

1000'S OF APPLICATIONS, SUCH AS:

- FINDING THE MAXIMUM YIELD OF CHEMICAL REACTIONS (T? p? COMPOSITION? CATALYST?)
- TIME STOP LIGHTS FOR MAXIMUM TRAFFIC FLOW
- ANALYSIS OF DATA USING LEAST SQUARES, CURVE FITTING, X-RAY STRUCTURE DETERMINATION
- MANUFACTURING → MAX. PRODUCTION, MIN. COST
- LOCATING EQUILIBRIUM STATES OF SYSTEMS.  
MIN.  $G_{T,P}$     MIN.  $A_{T,V}$     MAX.  $S_{U,V}$

SIMPLE EXAMPLE:  $f(x)$     LOCATE THE MAXIMUM IN  
THE FUNCTION  $f(x) = -x^2 + 4x - 3$ .

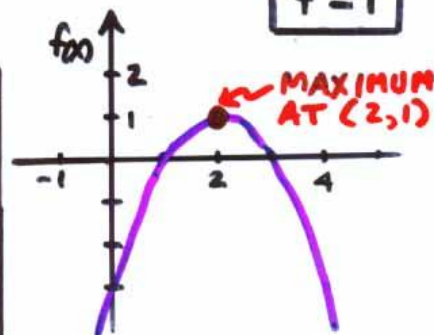
$$\text{SOLVE } \frac{df(x)}{dx} = -2x + 4 = 0 \Rightarrow$$

$$\begin{array}{l} x=2 \\ f=1 \end{array}$$

AT THE MAXIMUM IN  $f(x)$

$$df = \frac{df}{dx} dx = 0$$

FOR ANY INFINITESIMAL  
CHANGE  $dx$



### MAXIMUM (OR MINIMUM) IN $f(x, y)$

FOR ARBITRARY AND INDEPENDENT VALUES OF  $dx, dy$ :

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy = 0$$

SATISFIED ONLY IF

$$\left. \begin{aligned} \left(\frac{\partial f}{\partial x}\right)_y &= 0 \\ \left(\frac{\partial f}{\partial y}\right)_x &= 0 \end{aligned} \right\} \text{SOLVE THESE EQUATIONS} \\ \text{TO LOCATE A} \\ \text{MAXIMUM OR MINIMUM} \\ \text{IN } f(x, y)$$

### CONSTRAINED MAXIMUM (OR MINIMUM) IN $f(x, y)$

PROBLEM: LOCATE A MAXIMUM (OR MINIMUM) IN THE FUNCTION  $f(x, y)$  SUBJECT TO THE RESTRICTION  $g(x, y) = 0$  (e.g. CONSTANT ENERGY)

$$\left. \begin{aligned} df &= \frac{\partial f}{\partial x} dx + \frac{\partial f}{\partial y} dy = 0 \\ dg &= \frac{\partial g}{\partial x} dx + \frac{\partial g}{\partial y} dy = 0 \end{aligned} \right\} \text{TRUE FOR} \\ \text{INDEPENDENT} \\ \text{VALUES} \\ \text{OF } dx, dy$$

$$\left. \begin{aligned} \therefore \frac{\partial g}{\partial x} &\text{ MUST BE PROPORTIONAL TO } \frac{\partial f}{\partial x} \\ \text{AND } \frac{\partial g}{\partial y} &\text{ MUST BE PROPORTIONAL TO } \frac{\partial f}{\partial y} \end{aligned} \right\} \text{WITH THE SAME} \\ \text{PROPORTIONALITY} \\ \text{CONSTANT} \\ \text{(CALL IT } \alpha \text{)}$$

EXAMPLE A

$$\begin{aligned} dx + dy &= 0 &\Rightarrow dx &= -dy \\ dx + 2dy &= 0 &\Rightarrow dx &= -2dy \end{aligned} \left. \begin{array}{l} \text{CANNOT BE} \\ \text{SOLVED FOR} \\ \text{ARBITRARY } dx, dy \\ \text{VALUES} \\ \text{(ONLY } dx = dy = 0) \end{array} \right\}$$

EXAMPLE B

$$\begin{aligned} dx + dy &= 0 &\Rightarrow dx &= -dy \\ 2dx + 2dy &= 0 &\Rightarrow 2dx &= -2dy \end{aligned} \left. \begin{array}{l} \text{TRUE FOR } \underline{\text{ALL}} \\ \text{VALUES OF } dx, dy \\ (\alpha = 2) \end{array} \right\}$$

CONCLUSION TO LOCATE A MAXIMUM OR MINIMUM IN  $f(x, y)$  AND SATISFY THE CONSTRAINT  $g(x, y) = 0$ , SOLVE:

$$\left. \begin{array}{l} \frac{\partial f}{\partial x} = \alpha \frac{\partial g}{\partial x} \\ \frac{\partial f}{\partial y} = \alpha \frac{\partial g}{\partial y} \end{array} \right\} \begin{array}{l} \text{EQUIVALENT} \\ \text{TO} \\ (\alpha \text{ CONSTANT}) \end{array} \left[ \begin{array}{l} \frac{\partial}{\partial x} (f - \alpha g) = 0 \\ \frac{\partial}{\partial y} (f - \alpha g) = 0 \end{array} \right. \begin{array}{l} \text{MORE} \\ \text{DETAILS} \\ \downarrow \end{array}$$

LAGRANGE'S METHOD OF UNDETERMINED MULTIPLIERS

TO FIND A MAXIMUM OR MINIMUM IN  $f(x, y)$  WITH CONSTRAINT  $g(x, y) = 0$ , FIND THE UNCONSTRAINED MAXIMUM OR MINIMUM IN

$$F(x, y) \equiv f(x, y) - \alpha g(x, y)$$

BY SOLVING

$$\frac{\partial F}{\partial x} = 0 \quad \text{AND} \quad \frac{\partial F}{\partial y} = 0 \quad \left( \begin{array}{l} \text{NO} \\ \text{CONSTRAINTS} \\ \text{ON} \\ F(x, y) \end{array} \right)$$

### WHAT IF THERE ARE TWO CONSTRAINTS?

TO MAXIMIZE OR MINIMIZE  $f(x, y)$  AND SATISFY CONSTRAINTS  $g(x, y) = 0$  AND  $h(x, y) = 0$

[E.g. CONSTANT NUMBER OF MOLECULES, CONSTANT ENERGY]

$$\left. \begin{aligned} df &= (\partial f / \partial x)_y dx + (\partial f / \partial y)_x dy = 0 \\ dg &= (\partial g / \partial x)_y dx + (\partial g / \partial y)_x dy = 0 \\ dh &= (\partial h / \partial x)_y dx + (\partial h / \partial y)_x dy = 0 \end{aligned} \right\} \begin{array}{l} \text{FOR} \\ \text{ALL} \\ dx, dy \\ \text{VALUES} \end{array}$$

ONLY IF

$$\begin{aligned} (\partial f / \partial x)_y &= \alpha (\partial g / \partial x)_y = \beta (\partial h / \partial x)_y \\ (\partial f / \partial y)_x &= \alpha (\partial g / \partial y)_x = \beta (\partial h / \partial y)_x \end{aligned} \quad \left( \begin{array}{l} \alpha \text{ AND } \beta \\ \text{ARE} \\ \text{CONSTANTS} \end{array} \right)$$

$\therefore$  FIND THE UNCONSTRAINED MAXIMUM OR MINIMUM IN  $F(x, y) \equiv f(x, y) - \alpha g(x, y) - \beta h(x, y)$

BY SOLVING  $(\partial F / \partial x)_y = 0$  AND  $(\partial F / \partial y)_x = 0$

USE THE LAGRANGE METHOD TO FIND THE MOST PROBABLE (MAXIMUM NUMBER OF CONFIGURATIONS) DISTRIBUTION  $N_1, N_2, N_3, N_4, \dots$  OF MOLECULES OVER ENERGY LEVELS  $E_1, E_2, E_3, E_4, \dots$  WITH CONSTRAINTS

$$\begin{aligned} N_1 + N_2 + N_3 + N_4 + \dots &= N \\ N_1 E_1 + N_2 E_2 + N_3 E_3 + N_4 E_4 + \dots &= E \end{aligned} \quad \left( \begin{array}{l} \text{NUMBER OF MOLECULES} \\ \text{AND THE TOTAL ENERGY} \\ \text{ARE CONSTANT} \end{array} \right)$$

## BOLTZMANN LAW FOR THE MOST PROBABLE DISTRIBUTION OF MOLECULES OVER ENERGY LEVELS

MAXIMIZE THE LOGARITHM OF THE NUMBER OF CONFIGURATIONS

$$\ln W = \ln \left[ \frac{N!}{(N_1! N_2! N_3! N_4! \dots)} \right] \equiv f$$

SUBJECT TO THE CONSTRAINTS

$$N_1 + N_2 + N_3 + N_4 \dots - N = 0 \equiv g \text{ } \left. \vphantom{N_1 + N_2 + N_3 + N_4 \dots - N = 0} \right\} \text{CONSTANT}$$

$$N_1 E_1 + N_2 E_2 + N_3 E_3 + N_4 E_4 \dots - E = 0 \equiv h \text{ } \left. \vphantom{N_1 E_1 + N_2 E_2 + N_3 E_3 + N_4 E_4 \dots - E = 0} \right\} N, E$$

$$\text{SO } \boxed{\frac{\partial f}{\partial N_i} - \alpha \frac{\partial g}{\partial N_i} - \beta \frac{\partial h}{\partial N_i} = 0}$$

$$\frac{\partial f}{\partial N_i} = \frac{\partial}{\partial N_i} \left[ \ln \left( \frac{N!}{(N_1! N_2! N_3! \dots)} \right) \right] = - \frac{\partial \ln N_i!}{\partial N_i}$$

$$\frac{\partial f}{\partial N_i} = \frac{\partial}{\partial N_i} (N_i \ln N_i - N_i) = N_i \left( \frac{1}{N_i} \right) - \ln N_i - 1 = -\ln N_i$$

$$\boxed{\frac{\partial f}{\partial N_i} = -\ln N_i}$$

$$\boxed{\frac{\partial g}{\partial N_i} = 1}$$

$$\boxed{\frac{\partial h}{\partial N_i} = E_i}$$

COMBINING THE BOXED EQUATIONS

$$\ln N_i = -\alpha - \beta E_i$$

$$(A = e^{-\alpha})$$

$$-\ln N_i - \alpha - \beta E_i = 0$$

$$\boxed{N_i = e^{-\alpha} e^{-\beta E_i} = A e^{-\beta E_i}}$$

BUT WHAT ARE THE  $\beta$  AND  $A$  CONSTANTS?

$$\text{TOTAL NUMBER OF MOLECULES} = \sum_{i=1}^{\infty} N_i = A \sum_i e^{-\beta E_i} = N = N_1 + N_2 + N_3 \dots$$

$$A = \frac{N}{\sum_i e^{-\beta E_i}}$$

$N, \beta, A, E_1, E_2, E_3, \dots$   
ARE CONSTANT  
SO...

$$\frac{N_i}{N} = \frac{e^{-\beta E_i}}{\sum_j e^{-\beta E_j}}$$

GIVES THE FRACTION OF THE TOTAL MOLECULES IN LEVEL  $i$

$$\frac{N_i}{N_j} = \frac{N_i/N}{N_j/N} = \frac{e^{-\beta E_i}}{\sum_j e^{-\beta E_j}} \bigg/ \frac{e^{-\beta E_j}}{\sum_j e^{-\beta E_j}} = \frac{e^{-\beta E_i}}{e^{-\beta E_j}}$$

$$N_i/N_j = e^{-\beta(E_i - E_j)}$$

GIVES THE RATIO OF THE NUMBER OF MOLECULES IN LEVELS  $i$  AND  $j$

MAXWELL DISTRIBUTION OF MOLECULES WITH KINETIC ENERGY  $E_i = \frac{1}{2}mv_i^2$

$N_i$  PROPORTIONAL TO  $e^{-\frac{1}{2}mv_i^2/kT}$

BAROMETRIC EQUATION FOR THE DISTRIBUTION OF MOLECULES WITH GRAVITATIONAL POTENTIAL ENERGY  $E_i = mgh_i$

$N_i$  PROPORTIONAL TO  $e^{-mgh_i/kT}$

FIND  $\beta = 1/kT$

$N_i$  PROPORTIONAL TO  $e^{-E_i/kT}$