1 THE NATURE OF THERMODYNAMICS

1] THE BIG PICTURE

1.1) THERMAL PHYSICS

UP UNTIL NOW MOST OF THE PHYSICS YOU HAVE LEARNED DEALS WITH THE TREATMENT OF SINGLE "PARTICLES" (eg BLOCKS, WHEELS, ROCKETS, ELECTRONS, PHOTONS, etc) OR INTERACTIONS BETWEEN THEM (eg COLLISIONS, ELECTRONS & PROTONS IN HYDROGEN ATOM, etc)

THERMAL PHYSICS DEALS WITH LARGE (eg 10^{23}) COLLECTIONS OF PARTICLES. SPECIFICALLY IT FOCUSES UPON THE ENERGY ASSOCIATED WITH THE COLLECTION. THE KINETIC & POTENTIAL ENERGY OF A THROWN BRICK IS NOT PART OF THERMAL PHYSICS; THE CONVERSION OF MASS TO ENERGY THROUGH RADIOACTIVE DECAY IS NOT PART OF THERMAL PHYSICS.

A NON-RADIOACTIVE BRICK SITTING STATIONARY ON THE FLOOR IS STILL A RESERVOIR OF ENERGY. THIS IS COMMONLY THOUGHT OF AS HEAT ENERGY - FROM WHICH "THERMAL PHYSICS" DERIVES ITS NAME.

BUT THERMAL PHYSICS DESCRIBES MUCH MORE THAN HEAT. IT DESCRIBES SALT DIFFUSION, THE CONTACT ANGLE OF A WATER DROP ON A TABLE, THE ALIGNMENT OF DIPOLES IN A MAGNET, etc.

ALL THESE PROCESSES CAN BE DESCRIBED IN TERMS OF AN ENERGY AND THE WAY IT DEPENDS UPON TEMPERATURE, PRESSURE, SALINITY, SURFACE TENSION, etc

1.2) THERMODYNAMICS

THIS USUALLY REFERS TO THE MACROSCOPIC DESCRIPTION OF A COLLECTION OF PARTICLES. OFTEN THROUGH MEASUREMENTS, THEIR PROPERTIES ARE GIVEN IN TERMS OF SUCH EMPIRICAL QUANTITIES AS DENSITY, SPECIFIC HEAT, DIFFUSIVITY, etc

(ANY PHYSICIST WHO SAYS "ONCE WE UNDERSTAND THE MINUTAE THROUGH PARTICLE PHYSICS AND QUANTUM MECHANICS, WE THEN UNDERSTAND EVERYTHING" SHOULD TRY TO PREDICT THE DENSITY OF WATER.)

DESPITE ITS NAME, THERMODYNAMICS USUALLY FOCUSES UPON STATIC PROPERTIES OR PROCESSES THAT CHANGE SO SLOWLY THEY CAN BE TREATED AS STATIC. ADVANCED THERMODYNAMICS DEALS WITH TIME-CHANGING PROCESSES (eg SHOCK WAVES, EXOTHERMAL AND ENDOTHERMAL CHEMICAL REACTIONS, CLOUD FORMATION, etc)

1.3) STATISTICAL MECHANICS

THIS LIES MORE IN THE REALM OF PHYSICS IN THAT IT ATTEMPTS TO PREDICT SOME MACROSCOPIC PROPERTIES THROUGH USING STATISTICS TO PREDICT HOW PARTICLE INTERACTIONS INFLUENCE THE BULK PROPERTIES OF A LARGE COLLECTION (e.g EQUATION OF STATE OF AN IDEAL GAS, SPECIFIC HEAT OF AN "EINSTEIN SOLID" AND PARAMAGNET)

WHEN IT CAN BE APPLIED, IT EXPLAINS <u>WHY</u> THE OBSERVED THERMODYNAMIC PROPERTIES OCCUR.

1.4) ENTROPY

KEY TO LINKING THERMODYNAMICS AND STATISTICAL MECHANICS IS THE NOTION OF ENTROPY, WHICH MEASURES THE DEGREE OF RANDOMNESS OF A COLLECTION OF PARTICLES. IT IS THROUGH ENTROPY THAT WE CAN RELATE TEMPERATURE TO ENERGY IN THE FORM OF HEAT.

ENTROPY IS ESSENTIAL IN THE FORMULATION OF THE 3 LAWS OF THERMODYNAMICS. COLLOQUIALLY, THESE ARE

1. THE ENERGY OF A SYSTEM IS THE SUM OF HEAT AND WORK
2. SYSTEMS MOVE TOWARD THE MOST PROBABLE STATE
3. ONLY ONE SUCH STATE EXISTS AT ABSOLUTE ZERO TEMPERATURE

THESE ARE SOMETIMES LOOSELY PARAPHRASED AS

1. YOU CAN'T WIN
2. THE BEST YOU CAN DO IS BREAK EVEN
3. YOU CAN'T EVEN DO THAT

1.5) TEMPERATURE

TEMPERATURE IS RELATED TO HEAT, BUT THE CONNECTION IS NOT STRAIGHTFORWARD: YOU CAN STICK YOUR HEAD IN A 400°F (200°C) OVEN, BUT YOU WOULDN'T STICK YOUR HAND IN BOILING WATER

WHAT CAN BE SAID ABOUT TEMPERATURE IS THIS! IF TWO SYSTEMS (eg YOUR HAND AND WATER) ARE IN CONTACT SUCH THAT HEAT CAN PASS BETWEEN THEM, THEN BOTH SYSTEMS WILL EVENTUALLY HAVE THE SAME TEMPERATURE.

THIS IS AN IMPLICIT DEFINITION OF TEMPERATURE. A RIGOROUS DEFINITION MUST WAIT UNTIL NEAR THE END OF THE COURSE.

2] THERMODYNAMIC VARIABLES

2.1) PROPERTIES

THE OBSERVABLE (MACROSCOPIC) CHARACTERISTICS OF A SYSTEM – A LARGE COLLECTION OF PARTICLES – ARE CALLED PROPERTIES. (eg. DENSITY, VOLUME, TEMPERATURE, PRESSURE, etc)

AN "EXTENSIVE PROPERTY" IS PROPORTIONAL TO THE MASS (eg VOLUME: IF THE VOLUME DOUBLES THE MASS DOUBLES, ASSUMING FIXED DENSITY)

AN "INTENSIVE PROPERTY" IS NOT AFFECTED BY CHANGE IN MASS (eg TEMPERATURE, PRESSURE, DENSITY. ... CUT A SYSTEM IN HALF AND THESE DON'T CHANGE

AN EXTENSIVE PROPERTY CAN BE CONVERTED TO AN INTENSIVE ONE BY DIVIDING BY MASS. THIS IS CALLED A SPECIFIC VALUE (eg. THE SPECIFIC HEAT (CAPACITY) IS THE HEAT CAPACITY DIVIDED BY MASS.)

2.2) STATE OF A SYSTEM

THIS IS THE CONDITION UNIQUELY SPECIFIED BY A SET OF PROPERTIES. TYPICALLY ONE SPECIFIES THE MINIMUM NUMBER OF INDEPENDENT PROPERTIES THAT DESCRIBE THE SYSTEM.

Eg ① GIVEN DENSITY AND VOLUME, ONE DOESN'T NEED MASS

② FOR DRY AIR, ITS STATE CAN BE DESCRIBED BY PRESSURE, VOLUME AND TEMPERATURE (OR PRESURE, DENSITY AND TEMPERATURE). FOR MOIST AIR MUST ADDITIONALLY SPECIFY THE AMOUNT OF WATER VAPOUR (THROUGH MASS FRACTION OR "PARTIAL PRESSURE")

3] UNITS

3.1) PRESSURE

- THE STANDARD SI UNIT FOR PRESSURE IS THE PASCALE: $\underline{1\,Pa = 1\,N/m^2}$.
- IN ATMOSPHERIC SCIENCE PRESSURE IS MEASURED RELATIVE TO ATMOSPHERIC PRESSURE AT SEA LEVEL AND 20°C: $\underline{1\,ATM = 1.013 \times 10^5\,Pa} = 101.3\,kPa$.
- MORE CONVENIENTLY, FOR THOSE PHYSICS-INCLINED, ONE DEFINES PRESSURE AS $\underline{1\,BAR = 10^5\,Pa}$. SO $1\,ATM = 1.013\,BAR = 1013\,mBAR$.
- CONDENSED MATTER PHYSICS WORKING WITH VACUUMS DEFINE PRESSURE IN TERMS OF THE "TORR": $\underline{1\,TORR = 133\,Pa}$. THIS IS THE PRESSURE THAT RAISES MERCURY BY 1mm. (1 ATM RAISES MERCURY BY 76cm. SO $1\,TORR = \frac{1}{760}\,ATM$).

3.2) TEMPERATURE

IN CANADA, UNLESS WE'RE COOKING, WE MEASURE TEMPERATURE IN CELSIUS. THE SCALE IS SET SO THAT WATER FREEZES AT 1ATM IF THE TEMPERATURE IS 0°C AND IT BOILS AT 1ATM IF $T = 100°C$. CRUDELY THE SCALE IS LINEAR IN THE SENSE THAT DOUBLING THE INPUT OF HEAT DOUBLES THE TEMPERATURE. (WE WILL SEE THIS ISN'T ACCURATE) MORE ACCURATELY, TEMPERATURE SCALES SO THAT THE PRESSURE OF A FIXED VOLUME OF GAS DECREASES LINEARLY WITH TEMPERATURE

NO MATTER WHAT THE GAS OR INITIAL VOLUME (WITH QUALIFICATIONS) THE PRESSURE IS FOUND TO DECREASE TO ZERO, BY EXTRAPOLATION OF A TEMPERATURE-PRESSURE PLOT, AS $T \to -273°C$

THE VALUE $\approx -273°C$ IS CALLED "<u>ABSOLUTE ZERO</u>"

THIS IS USED TO DEFINE THE KELVIN SCALE, WHICH SHIFTS THE ORIGIN OF THE CELSIUS SCALE SO THAT $-273°C = 0K$. ICE WATER IS 273K AND BOILING WATER IS 373K AT 1ATM

3.3) AMOUNT OF "STUFF"

IN TYPICAL SI UNITS, THE NUMBER OF PARTICLES (i.e ATOMS/MOLECULES) IS MEASURED IN MASS: 1 kg (THE MASS OF $10^3\,cm^3$ OF WATER AT 20°C, 1 atm)

CHEMISTS OFTEN PREFER USING "MOLES" FOR WHICH 1 MOL CONTAINS $N_A \simeq 6.02 \times 10^{23}$ PARTICLES WHOSE COMBINED MASS EQUALS THE ATOMIC MASS BUT MEASURED IN GRAMS. THIS IS APPLIED TO MIXTURES OF MOLECULES TOO. (eg FOR AIR (78% N_2, 21% O_2 + OTHER) THE MASS PER MOLE IS $M_a = 28.97$ g/mol).

4] THE ZERO'TH LAW OF THERMODYNAMICS

EFFECTIVELY THIS IS ANOTHER IMPLICIT DEFINITION OF TEMPERATURE
"IF TWO SYSTEMS ARE SEPARATELY IN THERMAL EQUILIBRIUM WITH A THIRD SYSTEM, THEY ARE IN EQUILIBRIUM WITH EACH OTHER"

(IN MATH TERMS, THIS IS AN ASSOCIATIVE LAW: $A = B$ & $A = C \Rightarrow B = C$)

THIS "LAW" IS CENTRAL TO THE FUNCTION OF A THERMOMETER: IF A THERMOMETER IN CONTACT WITH ONE SYSTEM GIVES THE SAME READING AS IT GIVES WHEN IN CONTACT WITH ANOTHER SYSTEM, THEN THE TWO SYSTEMS HAVE THE SAME TEMPERATURE.

[HISTORICAL NOTE: THIS LAW WAS FORMULATED DECADES AFTER THE 1ST, 2ND & 3RD LAWS.]