(3) THE FIRST LAW OF THERMODYNAMICS

1] A REVIEW OF DIFFERENTIALS

FOR A FUNCTION OF 2 VARIABLES, $h(x,y)$ [THINK HEIGHT],
THE TOTAL DIFFERENTIAL IS $dh = \left(\frac{\partial h}{\partial x}\right) dx + \left(\frac{\partial h}{\partial y}\right) dy \equiv \nabla h \cdot d\underline{x}$
[eg. THIS IS CHANGE IN ELEVATION BY MOVING BY MOVING A SMALL DISTANCE dx IN x-DIRECTION AND SMALL DISTANCE dy IN y-DIRECTION]

IF YOU WALK A PATH $\mathcal{C}$ STARTING AT (x_1,y_1) GOING TO (x_2,y_2), THE TOTAL CHANGE IN HEIGHT IS $h(x_2,y_2) - h(x_1,y_1) = \int_{\mathcal{C}} dh = \int_{\mathcal{C}} \nabla h \cdot d\underline{x}$.
THIS IS THE "FUNDAMENTAL THEOREM OF CALCULUS".

IMPORTANTLY, THE CHANGE IN HEIGHT IS ALWAYS THE SAME NO MATTER WHAT PATH YOU TAKE AS LONG AS YOU START AT (x_1,y_1) AND END AT (x_2,y_2). IN PARTICULAR, IF YOU FOLLOW A LOOP TRAIL ENDING WHERE YOU STARTED, THEN $\mathcal{C}$ IS A CLOSED PATH AND THE INTEGRAL IS WRITTEN $\oint_{\mathcal{C}} \nabla h \cdot d\underline{x} = 0$
THAT IS TO SAY, THE PROCESS IS "REVERSIBLE"

IN THERMODYNAMICS, LAWS ARE OFTEN WRITTEN INVOLVING DIFFERENTIALS: $\delta f = a\,dx + b\,dy$, WHERE $a \equiv a(x,y)$, $b = b(x,y)$.
BUT δf ITSELF IS NOT NECESSARILY AT TOTAL ('EXACT') DIFFERENTIAL.
IT IS ONLY THE CASE IF ONE CAN WRITE $a = \left(\frac{\partial f}{\partial x}\right)$ AND $b = \left(\frac{\partial f}{\partial y}\right)$.
ONE CAN TEST IF THIS IS POSSIBLE BY CHECKING IF a & b SATISFY

$$\frac{\partial a}{\partial y} = \frac{\partial b}{\partial x} \qquad (1)$$

(IF INDEED $a = \frac{\partial f}{\partial x}$ AND $b = \frac{\partial f}{\partial y}$, (1) CONFIRMS $\frac{\partial^2 f}{\partial y \partial x} = \frac{\partial^2 f}{\partial x \partial y}$)

EXAMPLE: $\delta f = x\,dx + y\,dy$.

CHECK $\frac{\partial(x)}{\partial x} = \frac{\partial(y)}{\partial y} = 1$ ✓.

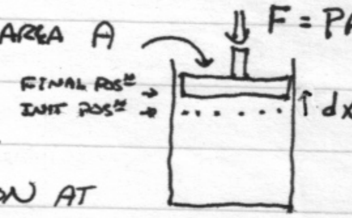
TO FIND f: $\frac{\partial f}{\partial x} = x \Rightarrow f = \frac{1}{2}x^2 + g(y)$

BUT $y = \frac{\partial f}{\partial y} = \frac{dg}{dy} \Rightarrow g(y) = \frac{1}{2}y^2 + \mathcal{C}$ ← CONSTANT

SO $f = \frac{1}{2}x^2 + \frac{1}{2}y^2 + \mathcal{C}$. $\mathcal{C}$ IS ARBITRARY SO OFTEN SET TO ZERO

2] (CONFIGURATION) WORK

THIS IS WORK PERFORMED BY FORCES ACTING ON A SYSTEM OR BY A SYSTEM EXERTING FORCES ON ITS ENVIRONMENT. IMPORTANTLY, CONFIGURATION WORK IS <u>REVERSIBLE</u>: IF A FORCE DOES WORK ON A SYSTEM, THE SYSTEM CAN EXERT FORCE BACK ON ITS ENVIROMENT RESTORING IT TO ITS ORIGINAL STATE.



THE COMMON EXAMPLE IS "PdV" WORK.

Eg CONSIDER A GAS IN A VESSEL WITH A PISTON AT ONE END. THE FORCE APPLIED TO THE PISTON IS SPREAD OUT OVER ITS AREA A AND SO IS FELT AS PRESSURE $P = F/A$.

IF THE PISTON MOVES A SMALL DISTANCE dx (>0 IF DECOMPRESSING) THE WORK IS

$$\delta W = F dx \simeq PA dx = + P dV \qquad (1)$$

THE TOTAL WORK IN CHANGING THE VOLUME FROM V_1 TO V_2 IS

$$W = + \int_{V_i}^{V_f} P dV \qquad (2)$$

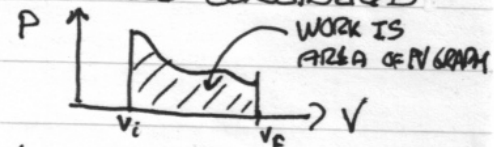
NOTE: WORK IS <u>NEGATIVE</u> IF GAS <u>COMPRESSED</u> (WORK DONE ON SYSTEM)
WORK IS <u>POSITIVE</u> IF GAS <u>EXPANDS</u> (SYSTEM WORKS ON ENVIRONMENT)
[ARGH! OTHER TEXTS EMPLOY THE OPPOSITE CONVENTION]

THOUGH WE WILL USUALLY DEAL WITH PdV WORK, CONFIGURATION WORK IS MANIFEST IN OTHER FORMS:

- σdA (SURFACE TENSION)
- $\mathcal{E} dq$ (ELECTROMOTIVE FORCE ... eg A BATTERY)
- $B dM$ (MAGNETIC FORCE ... eg IN INDUCTION COIL)
- $E dP$ (ELECTRIC FIELD ACROSS DIELECTRIC .. eg CAPACITOR)

3] COMPUTING PdV WORK

AS THE δW NOTATION IN $\boxed{\delta W = P dV}$ SUGGESTS, THE WORK IS NOT INDEPENDENT OF 'PATH'. IT DEPENDS ON HOW P CHANGES AS V CHANGES. TYPICALLY, ONE OF FOUR CIRCUMSTANCES ARE CONSIDERED TO COMPUTE $W = \int_{V_i}^{V_f} P\, dV$



1) ISOCHORIC PROCESS (V - CONSTANT) $\Rightarrow$ $W = 0$
2) ISOBARIC PROCESS (P - CONSTANT) $\Rightarrow$ $W = P(V_f - V_i)$
3) ISOTHERMAL PROCESS (T - CONSTANT)
   FOR IDEAL GAS $W = nRT \int_{V_i}^{V_f} \frac{1}{V}\, dV = nRT \ln(V_f/V_i)$
4) ADIABATIC PROCESS ... HAVE TO WAIT TO NEXT CHAPTER AND BEYOND. EFFECTIVELY THIS IS THE CONDITION THAT ENTROPY, S, IS CONSTANT $\Rightarrow$ NO HEAT LOSS (SEE P. 25 OF NOTES)
   ↳ ALSO "ISENTROPIC"

EXAMPLES

1) WHAT IS THE WORK TO COMPRESS $1\,km^3$ OF AIR BY 1 L ASSUMING THE VOLUME CHANGE IS SO SMALL THAT THE PRESSURE REMAINS AT 1 BAR?

SOL$^{\underline{N}}$ THIS IS AN ISOBARIC PROCESS

$$\Rightarrow W = P(V_f - V_i) = (10^5\,Pa)(-10^{-3}\,m^3) = -100\,J$$ //

2) WHAT IS THE WORK TO COMPRESS 10 L OF AIR BY 1 L ASSUMING THE TEMPERATURE IS 20°C THROUGHOUT AND THE INITIAL PRESSURE IS 1 ATM?

SOL$^{\underline{N}}$/ INITIALLY WE HAVE $P_i V_i = nRT$

$$\Rightarrow nR = P_i V_i / T \simeq (1.013 \times 10^5\,Pa)(10^{-2}\,m^3)/(293\,K) \simeq 3.46\,J/K$$

SO, ASSUMING ISOTHERMAL PROCESS,

$$W \simeq (3.46\,J/K)(293\,K) \ln\left(\frac{9L}{10L}\right) \simeq -107\,J$$ //

4] DISSIPATIVE WORK AND HEAT

DISSIPATIVE WORK IS THE THERMODYNAMIC EQUIVALENT OF A BLOCK SKIDDING TO A HALT DUE TO FRICTION. THE WORK IS IRREVERSIBLE : FRICTION ALWAYS DECELERATES (REMOVES KINETIC ENERGY) FROM THE BLOCK.

FOR LIQUIDS AND GASES, THE COUNTERPART OF FRICTION IS VISCOSITY, WHICH SLOWS MOTION AND DISSIPATES ENERGY. TYPICALLY THE ENERGY LOSS/VOLUME/TIME IS $\mu \underline{u} \cdot \nabla^2 \underline{u}$ WHERE μ IS THE MOLECULAR VISCOSITY ($\approx 10^{-3}$ kg/(m·s) FOR WATER AT STP)
IN AN ELECTRIC CIRCUIT, THE COUNTERPART OF FRICTION IS THE RESISTANCE. THE POWER LOST DUE TO A CURRENT I PASSING THROUGH A RESISTOR OF RESISTANCE R IS $P = I^2 R$. SO THE "WORK" LOST IN TIME dt IS $\delta W = -I^2 R\, dt$.

IF ENERGY IS CONSERVED, WHERE DOES THE LOST WORK GO? ANSWER: HEAT. THIS IS DENOTED BY "δQ".

FALL AND YOU MIGHT GET A FRICTION BURN. RESISTORS GET HOT WHEN CURRENTS PASS THROUGH THEM. STIRRING A POT OF WATER IMPARTS KINETIC ENERGY WHICH EVENTUALLY DISSIPATES VIA TURBULENCE TO WARM THE FLUID.

HEAT ITSELF CAN ENTER OR LEAVE A SYSTEM THROUGH VARIOUS PROCESSES

1) CONDUCTION : TRANSFER BY MOLECULAR CONTACT
2) CONVECTION : BULK MOTION USUALLY BY BUOYANCY
3) RADIATION : TRANSFER BY ELECTROMAGNETIC WAVES (eg INFRARED)

<u>HEAT ENERGY ALWAYS FLOWS FROM HOT TO COLD.</u>

5] THE FIRST LAW OF THERMODYNAMICS

THIS IS THE LAW OF CONSERVATION OF ENERGY, INCLUDING HEAT ENERGY:

$$dU = \delta Q + (-\delta W) \qquad (1)$$

- dU: CHANGE OF TOTAL ENERGY OF SYSTEM
- δQ: HEAT INPUT TO SYSTEM
- $-\delta W$: WORK INPUT TO SYSTEM
- δW: WORK PERFORMED BY SYSTEM

U IS CALLED THE "<u>INTERNAL ENERGY</u>" OF THE SYSTEM. IT IS A STATE VARIABLE, MEANING THAT IN A CYCLICAL PROCESS, THE INTERNAL ENERGY IS THE SAME AS AT THE START

$$\oint dU = 0$$

SUPPOSE THE WORK IS DUE ONLY TO PRESSURE: $\delta W = PdV$

SO (1) $\Rightarrow$

$$\boxed{dU = \delta Q - PdV} \qquad (2)$$

IF THE PROCESS IS ISOCHORIC (V - CONSTANT), THEN U CHANGES ONLY DUE TO HEATING OR COOLING THE SYSTEM: $dU = \delta Q$

IF THE SYSTEM IS INSULATED (eg IN A THERMOS), THEN NO HEAT CAN LEAVE OR ENTER THE SYSTEM: $dU = -PdV$

SYSTEMS FOR WHICH $\delta Q = 0$ ARE SAID TO BE "<u>ADIABATIC</u>".

SOMETIMES (2) IS WRITTEN IN TERMS OF INTENSIVE PROPERTIES BY DIVIDING THROUGH BY MASS OR # MOLES. Eg DIVIDING BY MASS:

$$\boxed{du = \delta q - Pd\alpha} \qquad 3$$

WHERE $\alpha = V/\text{MASS} = 1/\rho$, WITH $\rho \equiv$ DENSITY