Definitions

Work $đW = -P_{ext}\, dV \rightarrow$ Joules

Heat $đq = C\, dT \rightarrow$ Joules

Heat is a form of energy!

$\Rightarrow$ FIRST LAW

$$dU = đq + đW$$

$$U \equiv q + W$$ Internal Energy

Conditions

Since we have an equation of state not all the observables are independent

$P\ V\ T$

so we can hold one or more observables fixed.

$T =$ const Isothermal Process.
$P =$ const Isobaric
$V =$ const Isocoric

We can also control the flux of heat

IDEAL GAS

$P_1V_1^{\gamma} = P_2V_2^{\gamma}$ $dq = 0 \Rightarrow$ Adiabatic Process $\gamma = \bar{C}_P/\bar{C}_V$

$dT = 0$ Isothermall Expansion

Reversible vs Irreversible

A REV PROCESS IS ONE IN which THE SYSTEM THROUGHOUT THE PROCESS IS NEVER MORE THAN INFINITESIMALLY REMOVED FROM A STATE OF THERMODYNAMIC EQUILIBRIUM

$$P_{ext} \doteq P_{gas} - \delta P$$

SINCE THE SYS. IS AT EQUILIBRIUM

$$P_{ext} = P_{sys} = P(V,T)$$

②

$$dU = C\,dT - P_{ext}\,dV$$

a) Constant V

$$dU = C_V\,dT$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

$$\Delta U = q_V$$

Measured heat at constant Vol gives us ΔU

AT CONSTANT VOLUME

$$đw = 0$$

$$\boxed{\Delta U = q_V}$$

MEASURED HEAT AT CONSTANT VOLUME GIVES US ΔU

AT CONSTANT PRESSURE (EXTERNAL)

$$dU = đq - P_{ext}\,dV$$

CONSIDER A REVERSIBLE PATH

$$\Rightarrow P_{ext} = P(V)$$

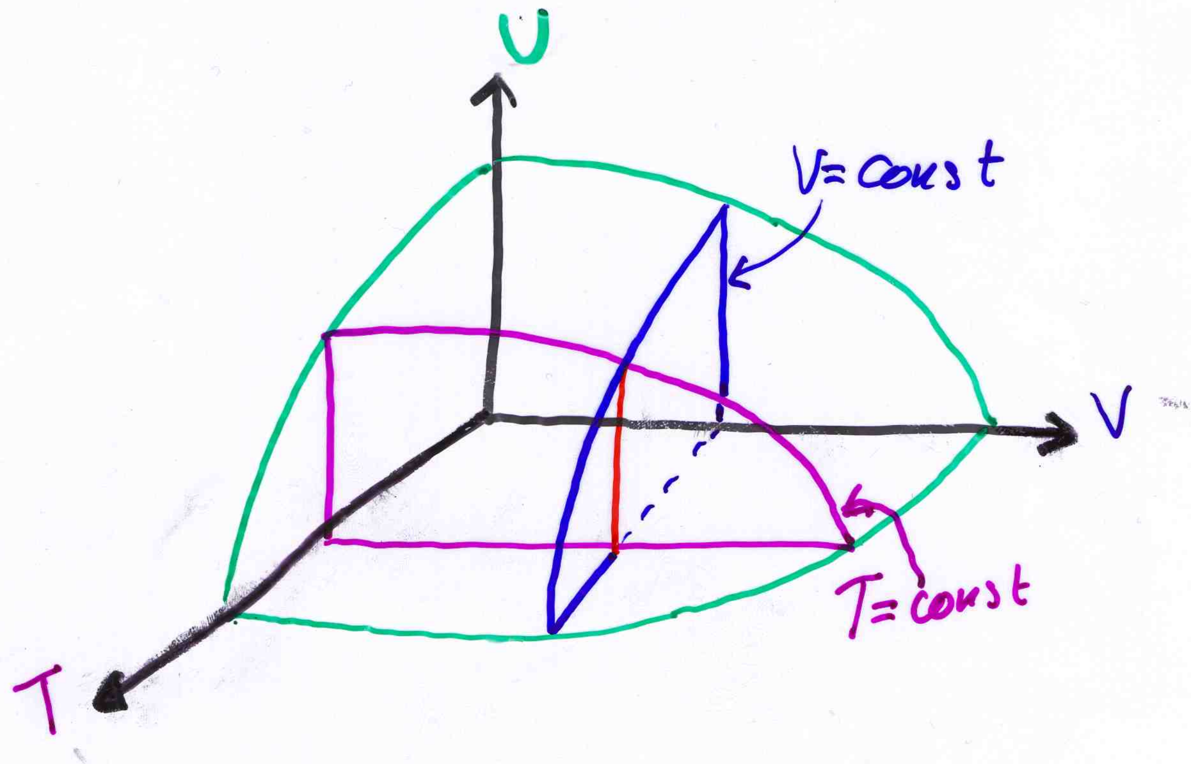
$$dU = đq - P\,dV$$

$$U_f - U_i = q_p - P(V_f - V_i)$$

$$(U_f + PV_f) - (U_i + PV_i) = q_p$$

$$\boxed{\Delta H \equiv q_p}$$

$$\boxed{H = U + PV}$$



U
V=const
V
T=const
T

IF WE HAVE A DIFFERENTIAL EXPRESSION

$$dF = M(V,T)\, dV + N(V,T)\, dT,$$

WE SAY THAT dF IS AN EXACT DIFFERENTIAL IF, AND ONLY IF,

$$\left(\frac{\partial M}{\partial T}\right)_V = \left(\frac{\partial N}{\partial V}\right)_T .$$

FOR $U(T,P)$

$$\left(\frac{\partial}{\partial P}\left(\frac{\partial U}{\partial T}\right)_P\right)_T = \left(\frac{\partial}{\partial T}\left(\frac{\partial U}{\partial P}\right)_T\right)_P$$

LET US CONSIDER TWO MEASURABLE PROPERTIES

i) CONSTANT PRESSURE COEFFICIENT OF THERMAL EXPANSION, α

$$\alpha \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

ii) ISOTHERMAL COMPRESSIBILITY, k

$$k \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T.$$

NOTICE THAT IN THIS EXPRESIONS WE ~~EX~~ CONSIDER ~~TEMP~~ VOLUME AS A FUNCTION OF (P,T) OR

$$V(P,T).$$

REMARK: THE RHS OF α AND k CAN BE MEASURED AND CALCULATED FROM EQ. OF STATE.

BUT WE CONSIDER $T(V,P)$ OR $P(V,T)$.

FIRST WE CONSIDER THE TEMPERATURE AS A FUNCTION OF (V, P). THUS THE DIFFERENTIAL OF TEMPERATURE IS GIVEN BY

$$dT = \left(\frac{\partial T}{\partial V}\right)_P dV + \left(\frac{\partial T}{\partial P}\right)_V dP.$$

BUT WE COULD ALSO CONSIDER THE PRESSURE AS A FUNCTION OF (V, T). THUS

$$dP = \left(\frac{\partial P}{\partial V}\right)_T dV + \left(\frac{\partial P}{\partial T}\right)_V dT.$$

USING THE LATTER EQ (CONST. $P \Rightarrow dP = 0$)

$$dT = -\frac{\left(\frac{\partial P}{\partial V}\right)_T}{\left(\frac{\partial P}{\partial T}\right)_V} dV + \frac{1}{\left(\frac{\partial P}{\partial T}\right)_V} dP.$$

BY COMPARISON WE CONCLUDE

$$\left(\frac{\partial T}{\partial V}\right)_P = -\frac{\left(\frac{\partial P}{\partial V}\right)_T}{\left(\frac{\partial P}{\partial T}\right)_V}$$

$$\left(\frac{\partial T}{\partial P}\right)_V = \frac{1}{\left(\frac{\partial P}{\partial T}\right)_V}.$$

$$\left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial P}{\partial V}\right)_T$$

$$\left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial P}{\partial T}\right)_V \frac{1}{\left(\frac{\partial P}{\partial V}\right)_T} = -1$$

$$\boxed{\left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial P}\right)_T = -1}$$

OR

$$\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V \left(\frac{\partial P}{\partial V}\right)_T = -1$$

$$\left(\frac{\partial P}{\partial T}\right)_V = -\frac{1}{\left(\frac{\partial V}{\partial P}\right)_T}\;\frac{1}{\left(\frac{\partial T}{\partial V}\right)_P}$$

$$= -\frac{\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial P}\right)_T}$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P}{\left(-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T\right)} = \frac{\alpha}{\kappa}$$