First Law

- **Energy is conserved.**
- **What are the forms of energy? Heat, mechanical, chemical, electrical, etc.**

$$\Delta U = Q - W \text{ or } dU = \delta q - \delta w$$

Internal energy (U) is a state function!

Functions and Perfect Differentials

If ***f*** is a function of x and y and is continuous and differentiable:

$$df = \frac{\partial f(x,y)}{\partial x}dx + \frac{\partial f(x,y)}{\partial y}dy$$

And:

$$\frac{\partial}{\partial y}\left(\frac{\partial f(x,y)}{\partial x}\right) = \frac{\partial}{\partial x}\left(\frac{\partial f(x,y)}{\partial y}\right)$$

And, at each point of the space, ***f*** is unique:

$$f(a,b) - f(a,b) = \int_a^a \int_b^b df = 0$$

Important relations from the First Law

If all work is "***P*** d***V***", it can be shown that:

$$\delta w = P_{ext}\, dV = 0 \quad \Rightarrow \quad dU = dq_v$$

$$\boxed{c_v = \left(\frac{dU}{dT}\right)_v}$$

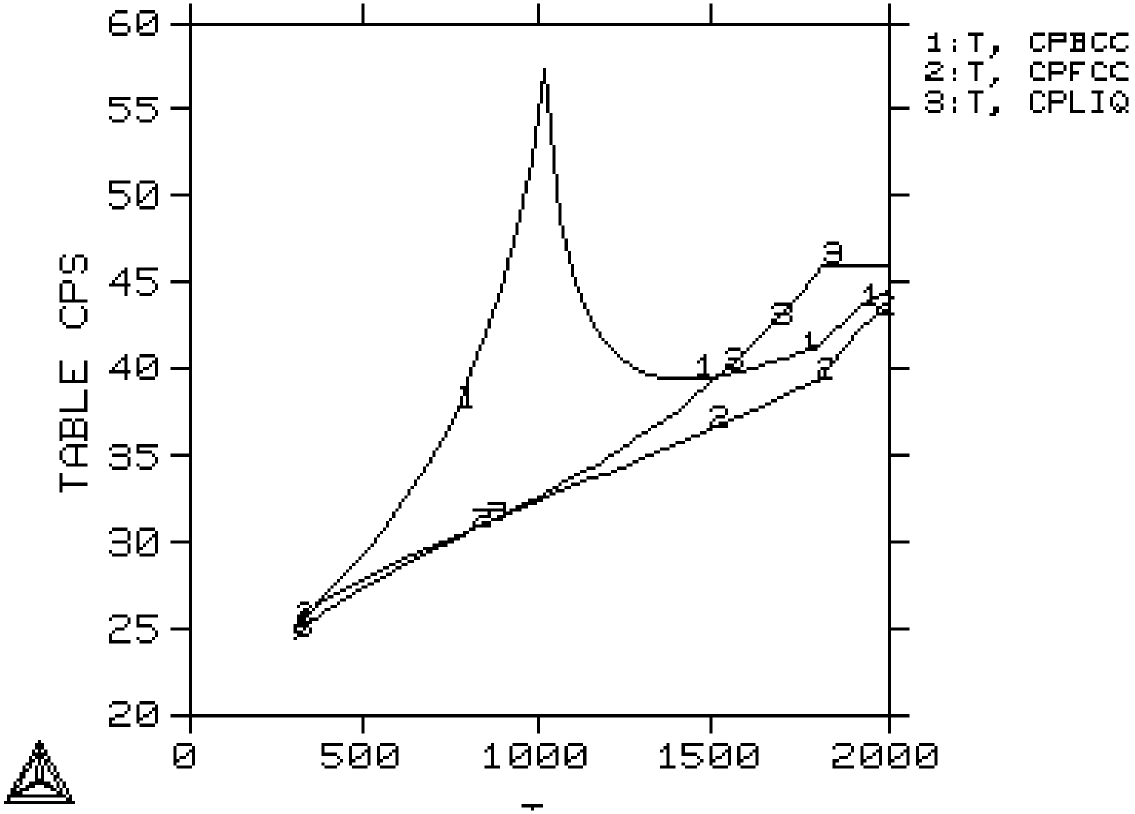
If ***P*** is constant:

$$\delta w = P_{ext} dV \qquad dU = dq_p - P_{ext} dV \qquad dq_p = dU + P_{ext} dV$$

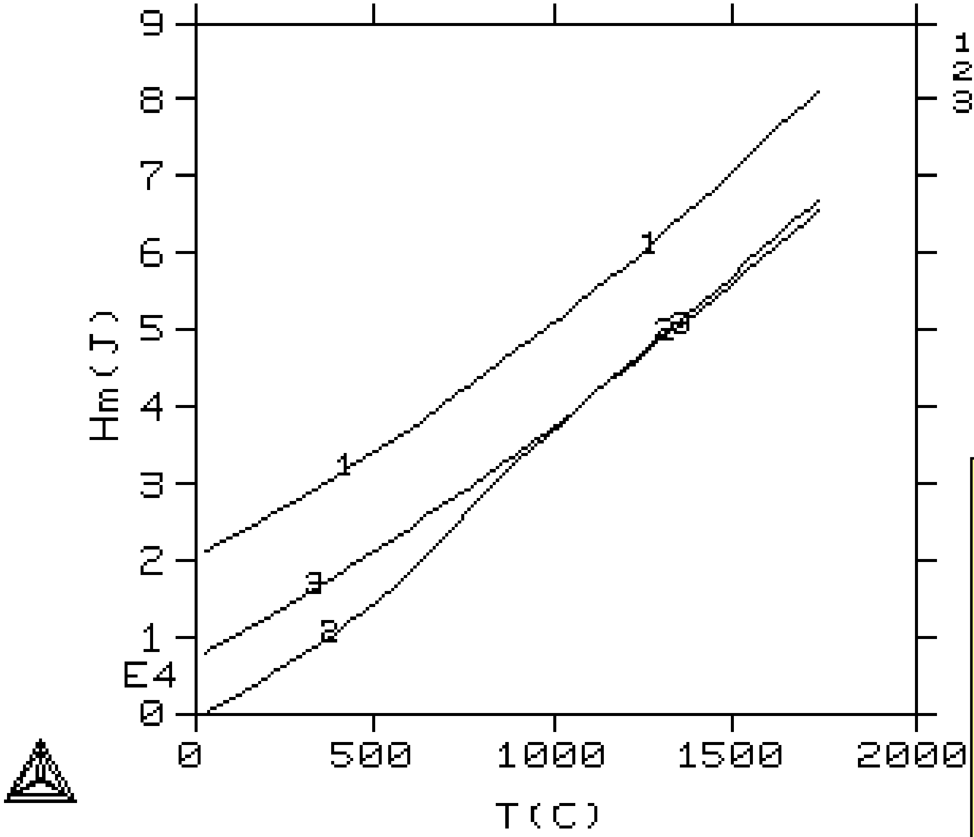
Define Enthalpy as: $H = U + PV$

$$\boxed{c_p = \frac{dq_p}{dT} = \frac{dH}{dT}}$$

Why is C_p important: *C_p can be measured!*



Enthaply can be obtained from C_p measurements



$$c_p = \frac{dH}{dT} \rightarrow H = \int c_p dT$$

$$\int_{T_1}^{T_2} c_p dT = H_2 - H_1$$

How to define the integration constant,
or the "zero" of enthalpy?

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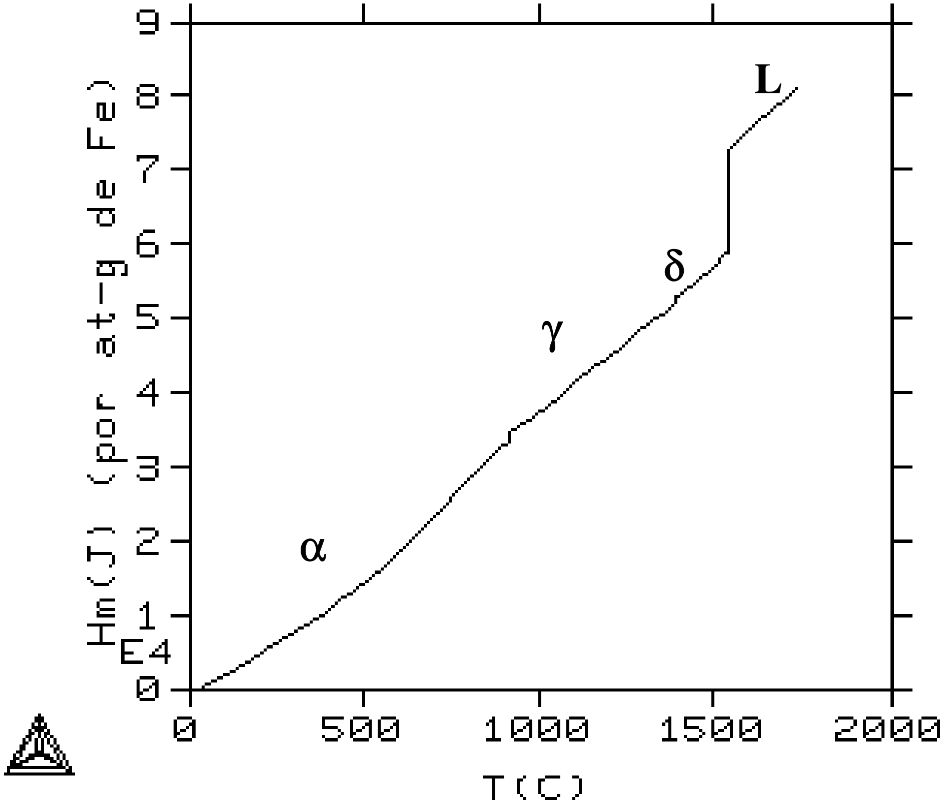
Standard Element Reference

- For each element, define Enthalpy of the stable phase at 1 atm, 298.15K as 0.
- This is called SER, Standard Element Refence

$$H_{Fe}^{SER} = H_{Fe}^{BCC,298.15K,1atm} = 0$$

Enthalpy of stable phases



Enthalpies- a macro

```
go data
switch-data tcfe
define-element fe
reject phase *
restore phase bcc fcc liq
get data
go p-3
set-condition t=300 n=1 p=1e5
compute-equilibrium
set-axis-variable 1 T 298 2000,,,,
step
separate phase
post
set-diagram-axis x T
set-diagram-axis y hm(*),,,,
set-label-curve d
plot,,,
back
set-inter
```

Enthapies – Stable phases

```
go data
switch-data tcfe
define-element fe
reject phase *
restore phase bcc fcc liq
get data
go p-3
set-condition t=300 n=1 p=1e5
compute-equilibrium
set-axis-variable 1 T 298 2000,,,,
step
normal
post
set-diagram-axis x T
set-diagram-axis y hm,,,,
set-label-curve b
plot,,,
back
set-inter
```

Cp curves- a macro

```
go data
sw-d ssol
@@ sw-d tcfe
@@ sw-d bin
@@ these lines are for choosing your database
define-element fe
reject phase *
restore phase bcc fcc liq
get data
go p-3
set-condition t=300 n=1 p=1e5
compute-equilibrium
enter function cpbcc=hm(bcc).t;
enter function cpfcc=hm(fcc).t;
enter function cpliq=hm(liq).t;
set-axis-variable 1 T 298 2000,,,,
step evaluate cpbcc,cpfcc,cpliq
post
enter table cps=cpbcc, cpfcc, cpliq;
set-diagram-axis x T
set-diagram-axis y cps,,,,
set-label-curve d,,,
plot,,,
back
set-inter
```

Enthalpy changes in Reactions

aA + bB= A_aB_b

$$\Delta H^T_{reaction} = H^T_{A_aB_b} - aH^T_A - bH^T_B$$

$$\Delta H^{298.15}_{reaction} = H^{298.15}_{A_aB_b} - aH^{298.15}_A - bH^{298.15T}_B$$

$$if \quad H^{298.15}_A = H^{SER}_A = 0 \; and \; H^{298.15T}_B = H^{SER}_b = 0$$

$$\Delta H^{298.15}_{reaction} = H^{298.15}_{A_aB_b}$$

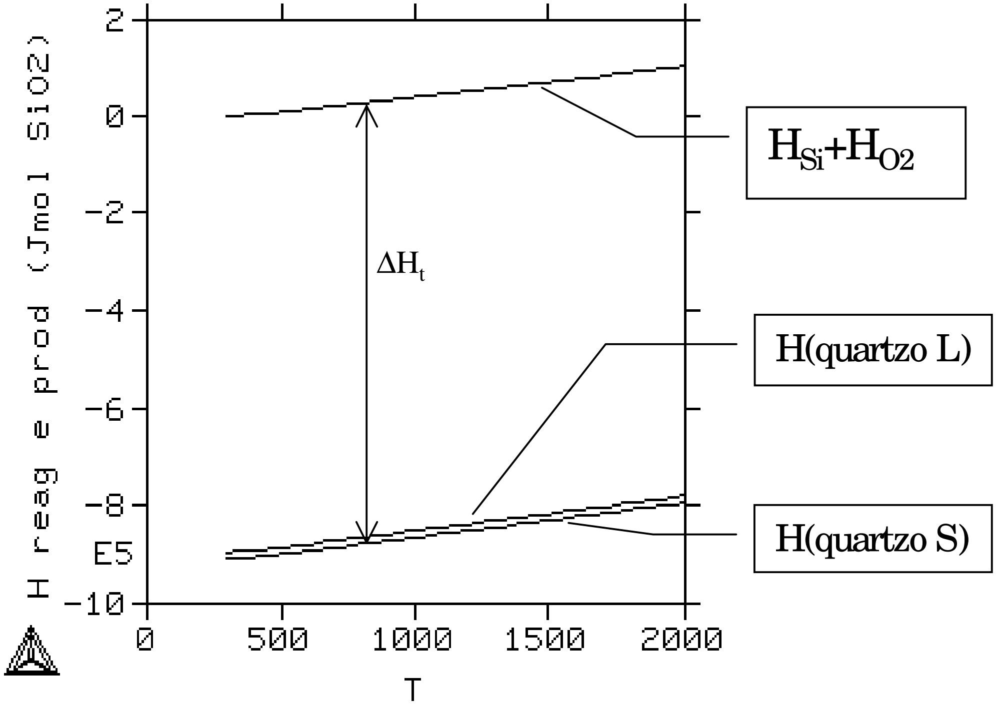
A practical Rule (Neuman Koop)

$$\Delta H_{reacao}^{T} - \Delta H_{reacao}^{298.15} = \int_{298.15}^{T} c_p^{A_aB_b}\, dT - a \int_{298.15}^{T} c_p^{A}\, dT - b \int_{298.15}^{T} c_p^{B}\, dT = \int_{298.15}^{T} \Delta c_p^{reacao}\, dT$$

For solid products and reactants, $\Delta C_p = 0$

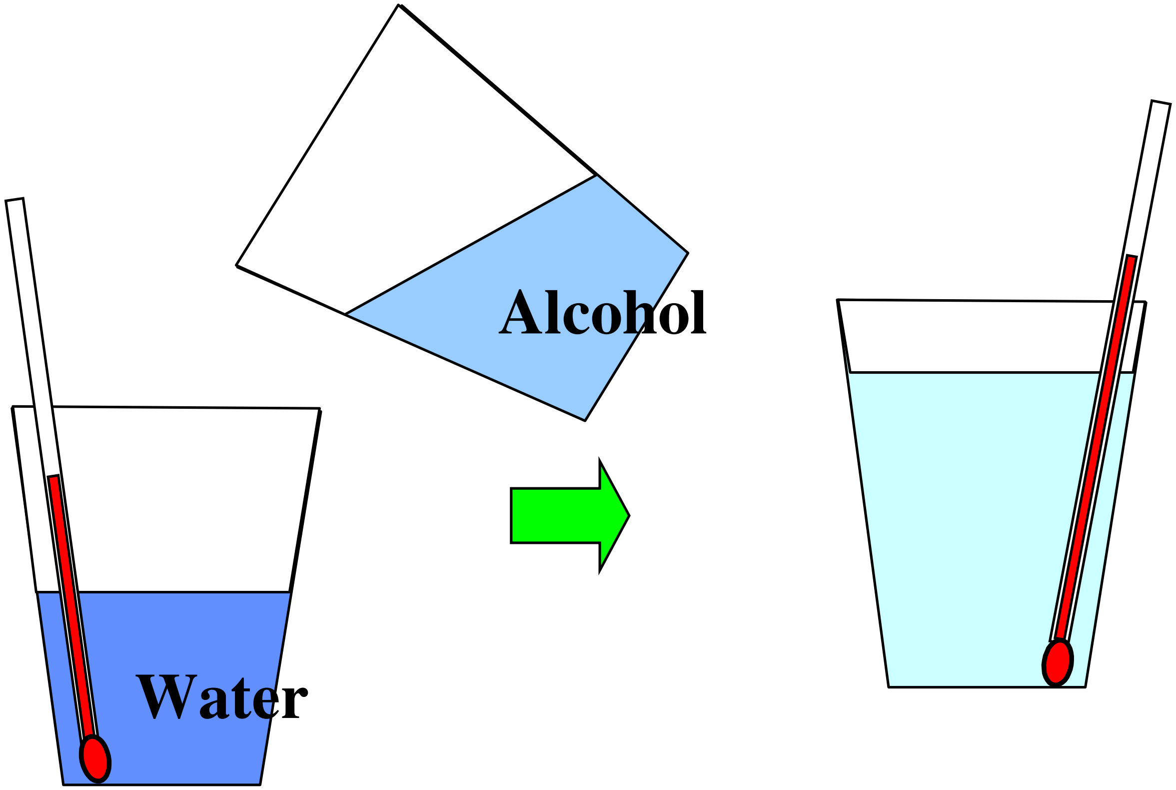
$$\boxed{\Delta H_{A_aB_b,f}^{298.15} = H_{A_aB_b}^{298.15} = \Delta H_{A_aB_b,f}^{O,298.15K}}$$

An example (formation of SiO_2)

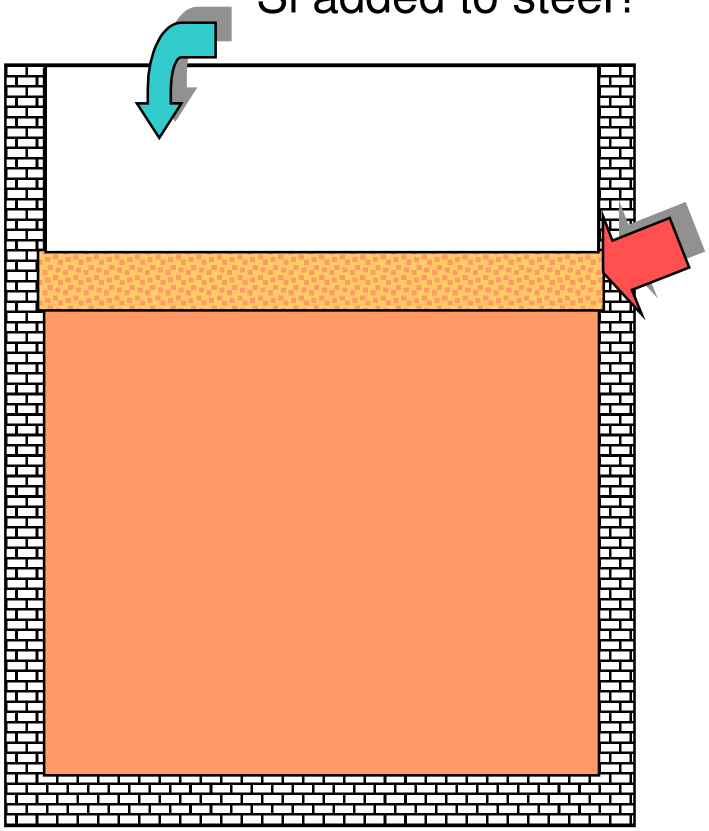


Examples:

Mixing can be exothermic (solution.tcm)



“Heat” of mixing



Si added to steel?

Refractories can dissolve in Slag

Examples

SHS,
Thermite reaction...

Other adiabatic transformations (actually all heat balances assume H=constant