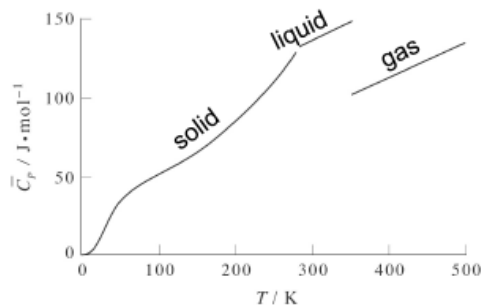


## Review of L5-L7

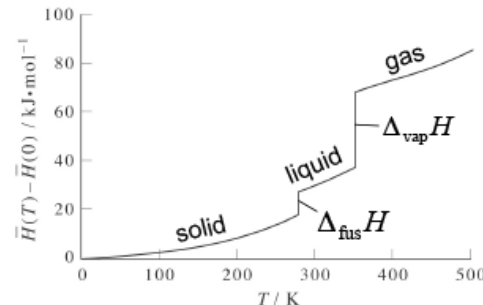
- The First Law of Thermodynamics states that energy is conserved; mathematically  $dU = \delta q + \delta w$  where  $U$  is internal energy,  $q$  is heat, and  $w$  is work; by convention, heat is positive when it is absorbed by the system, work is positive when it is done *on* the system, and vice versa in both cases
- Internal Energy ( $U$ ) is a state function, while heat ( $q$ ) and work ( $w$ ) are path functions
- $\frac{1}{2} m v^2 = \frac{3}{2} K_B T$  (KE is Temperature, ONLY VALID for Kelvin scale)
- The work done by an expanding gas is  $-P_{\text{ext}} dV$  where  $P_{\text{ext}}$  = external pressure against which the gas expands.  
Reversible path work =  $-\int_{V_1}^{V_2} P dV$
- A reversible processes happens in infinitesimally small steps; the maximum work that can be extracted from the isothermal expansion of a gas is the reversible work
- An adiabatic process is one for which  $\delta q = 0$
- A gas cools as it expands adiabatically against external pressure
- Enthalpy  $H$  is defined as  $U + PV$  and  $\Delta H$  for a constant pressure process is equal to the heat transferred  $q_p$
- The constant pressure heat capacity is defined as  $C_p : \left( \frac{\partial H}{\partial T} \right)_P$
- For an ideal gas,  $C_P = C_V + nR$

## Review of L5-L7

- Enthalpy changes with temperature can be determined from heat capacities. Heat capacity can be determined experimentally



*Measuring the heat capacity,  
temperature by temperature*

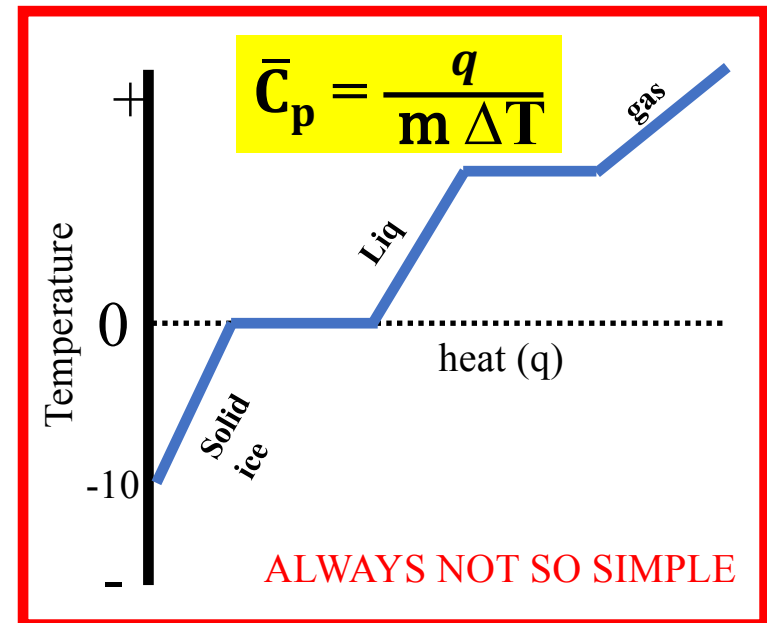


*Integrating the heat capacity,  
adding phase changes*

For  $T > T_{\text{vap}}$ ,

**Benzene:  $T_{\text{fus}}=278.7 \text{ K}$ ,  $T_{\text{vap}}=353.2 \text{ K}$**

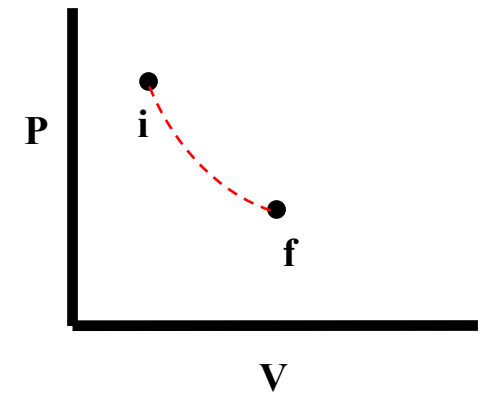
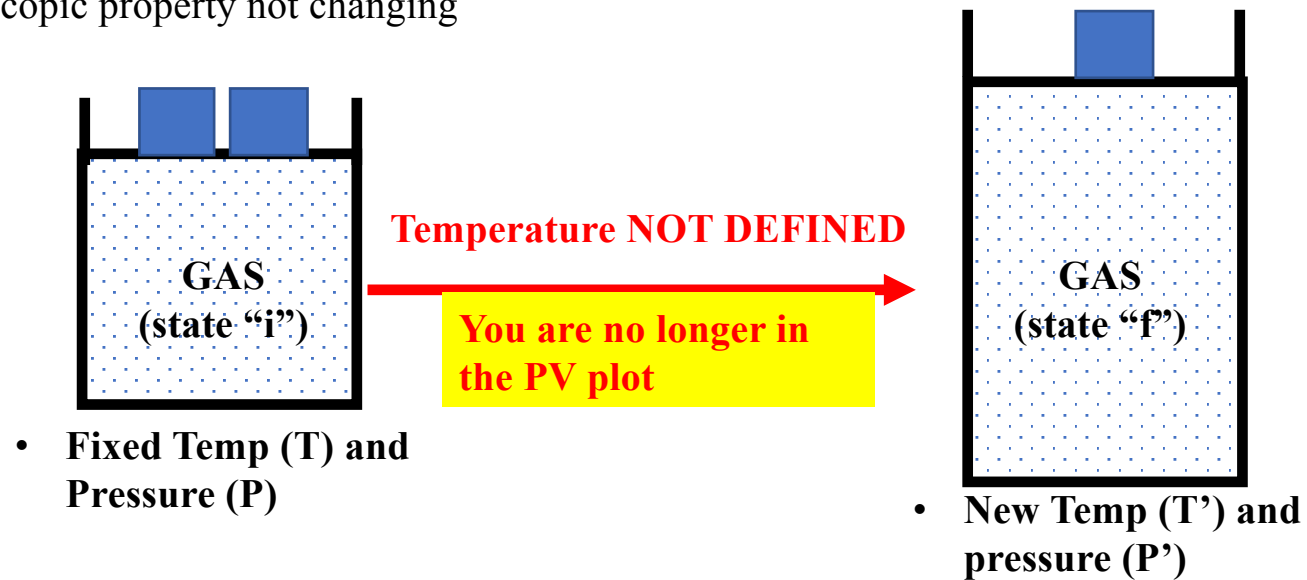
$$H(T) - H(0) = \int_0^{T_{\text{fus}}} C_P^s(T') dT' + \Delta_{\text{fus}}H + \int_{T_{\text{fus}}}^{T_{\text{vap}}} C_P^l(T') dT' + \Delta_{\text{vap}}H + \int_{T_{\text{vap}}}^T C_P^g(T') dT$$



## Review of L5-L7

### EQUILIBRIUM:

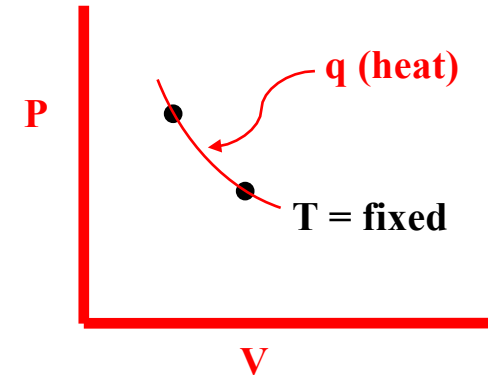
Macroscopic property not changing



## Paths of PV Work (IDEAL GAS)

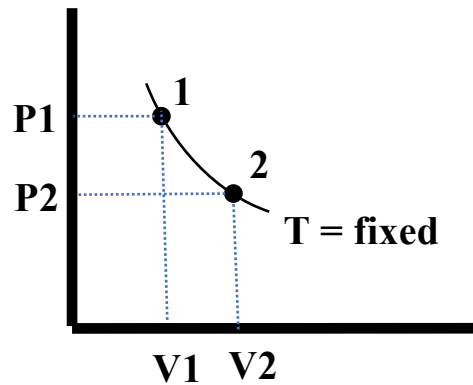
## HEAT RESERVOIR (T)

Ideal gas,  $PV = nRT = \text{constant}$

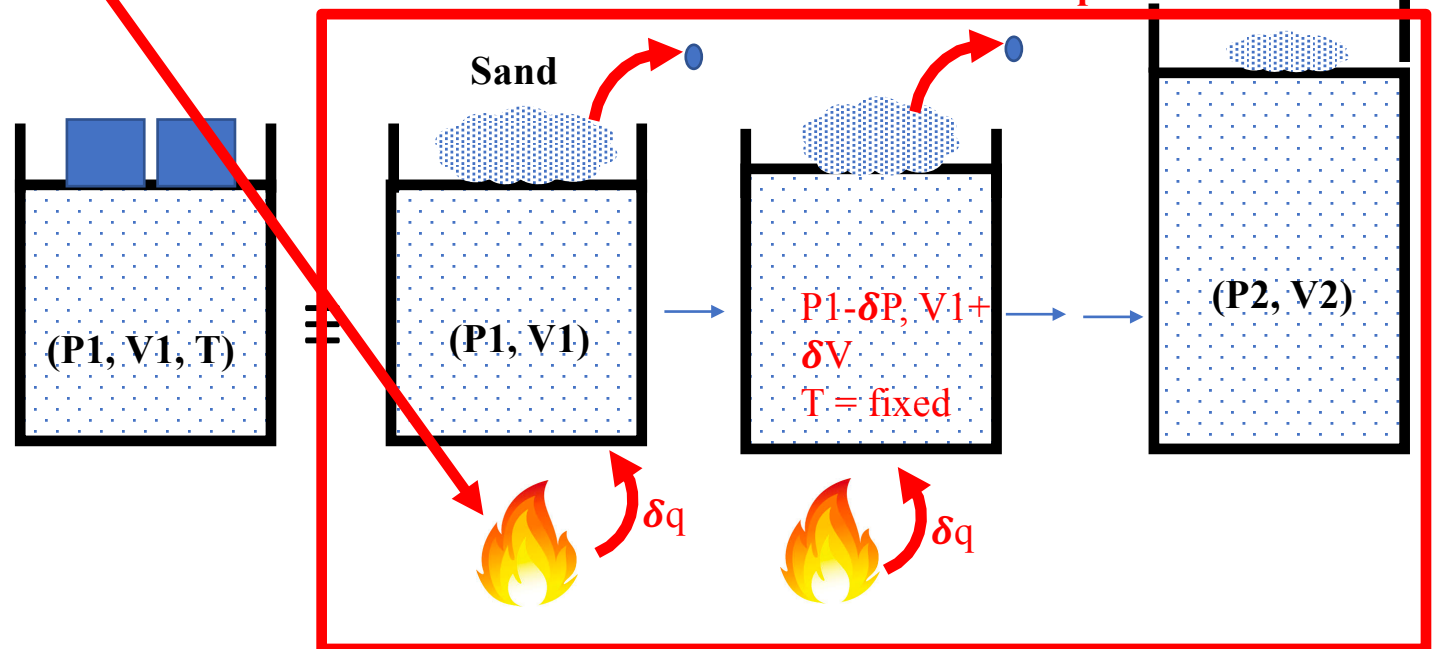


## Reversible Isothermal Expansion

## Reversible Isothermal Expansion ??

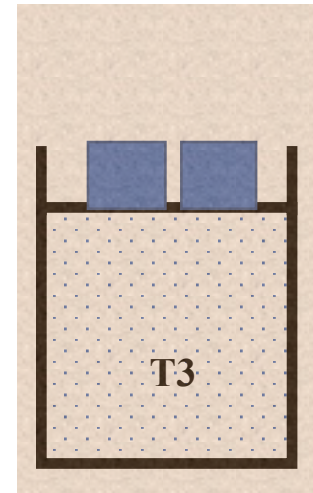
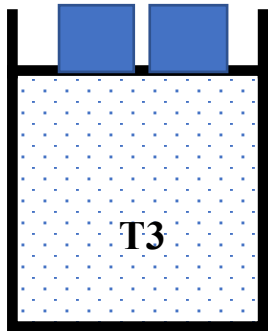
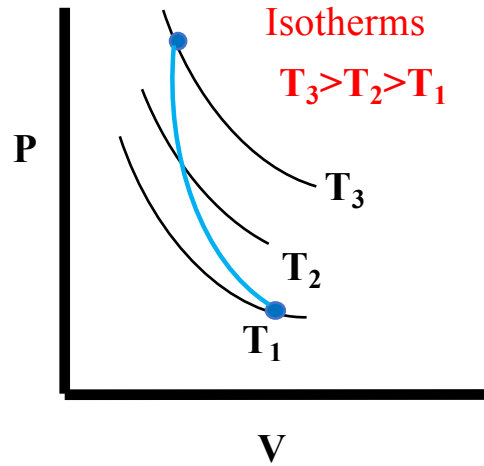


## Isothermal Expansion

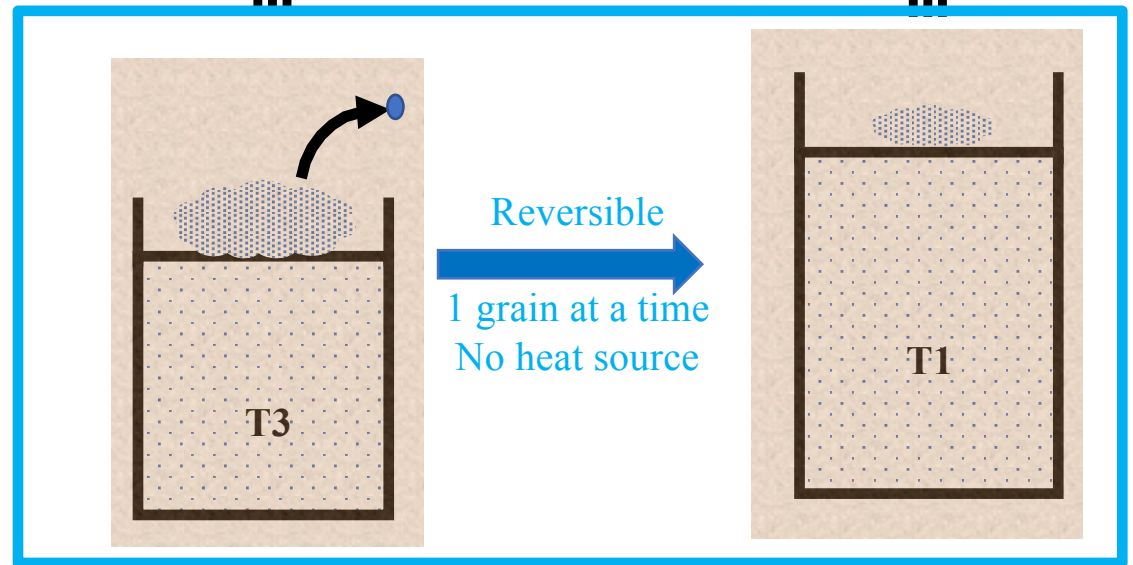
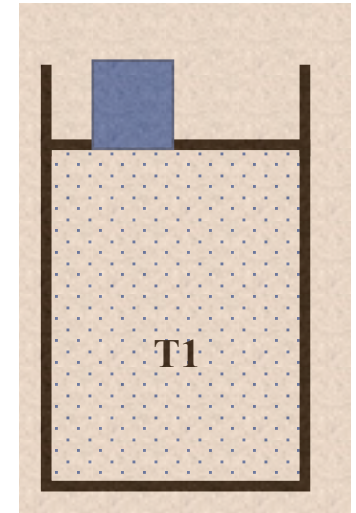


# Review of L5-L7

## Adiabatic Processes



Fly off PV plane  
 Irreversible



**Interesting (Supercritical fluid)**

<https://www.youtube.com/watch?v=-5oq5CZlY8k>

## **Review of L5-L7**

**Equations for work done.**

**How to tabulate Enthalpy of a reaction ?**

**Need to know “Standard Enthalpy”**

Many Slides taken: Prof. Cris Cramer, University of Minnesota



## STANDARD ENTHALPY OF REACTION

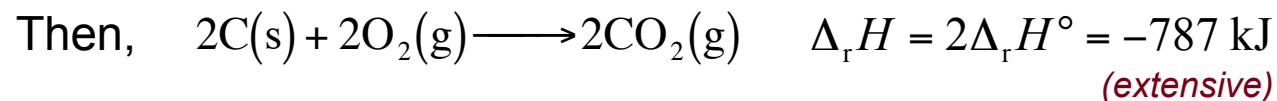
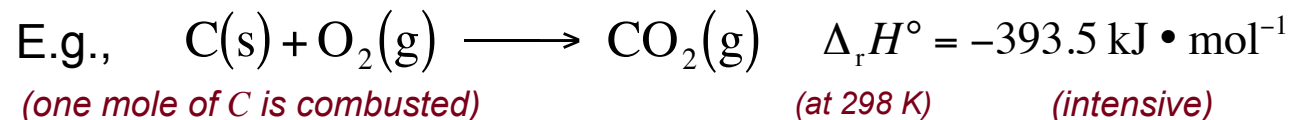
$\Delta_r H$  is *extensive*; its value depends on the number of moles of the reacting species

To facilitate tabulation, the International Union of Pure and Applied Chemistry created the *standard enthalpy of reaction*, which is *intensive*

$$\Delta_r H^\circ$$

$^\circ$  implies *one mole of a specified reagent and all reactants and products in their standard states at a given temperature.*

*(standard states are chosen by convention, for example, for a gas it is a pressure of one bar)*

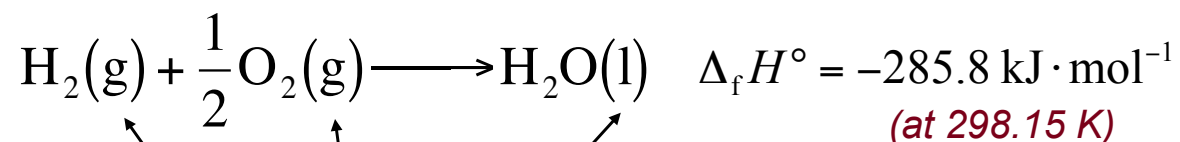


## STANDARD MOLAR ENTHALPY OF FORMATION

The standard enthalpy of reaction to form one mole of a substance from its constituent elements in their naturally occurring elemental forms defines the intensive *standard molar enthalpy of formation*,

$$\Delta_{\text{f}} H^{\circ}$$

indicates all reactants and products in their conventional standard states



Standard-state phases at 1 bar and 298.15 K

*One mole of  $\text{H}_2\text{O}(\text{l})$  is 285.8 kJ downhill in enthalpy from its constituent elements*

## ELEMENTAL HEATS OF FORMATION

To assign specific values for  $\Delta_f H^\circ$ , the values of  $\Delta_f H^\circ$  for *pure elements* in their *most stable forms* at *one bar* and the *temperature of interest* is set to *zero*.

298 K:       $\text{H}_2(\text{g}) \quad \Delta_f H^\circ = 0 \text{ kJ} \cdot \text{mol}^{-1}$

$\text{O}_2(\text{g}) \quad \Delta_f H^\circ = 0 \text{ kJ} \cdot \text{mol}^{-1}$

$\text{Cl}_2(\text{g}) \quad \Delta_f H^\circ = 0 \text{ kJ} \cdot \text{mol}^{-1}$

$\text{Br}_2(\text{g}) \quad \Delta_f H^\circ = 30.907 \text{ kJ} \cdot \text{mol}^{-1}$

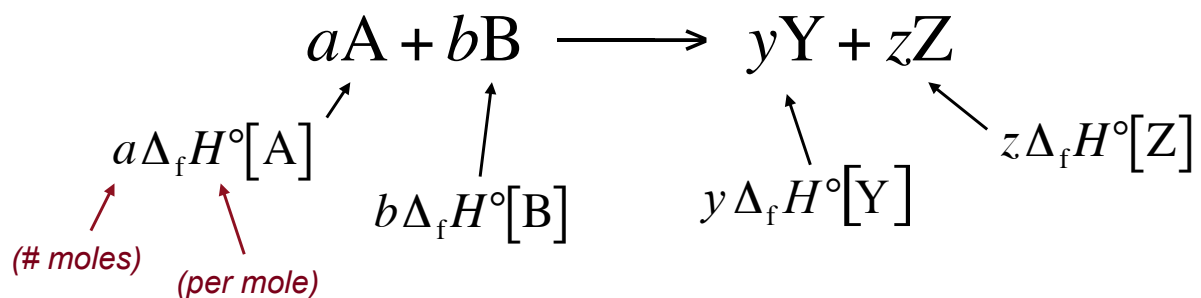
$\text{I}_2(\text{g}) \quad \Delta_f H^\circ = 62.438 \text{ kJ} \cdot \text{mol}^{-1}$

$\text{C}(\text{diamond}) \quad \Delta_f H^\circ = 1.897 \text{ kJ} \cdot \text{mol}^{-1}$

} *pure elements, but  
not in their most  
stable forms at 1  
bar and 298 K*

## USING $\Delta_f H^\circ$ TO GET $\Delta_r H$

One can use Hess' law, together with the standard enthalpies of formation for each of the reactants and products, to compute a heat of reaction at a temperature of interest, e.g., 298 K:

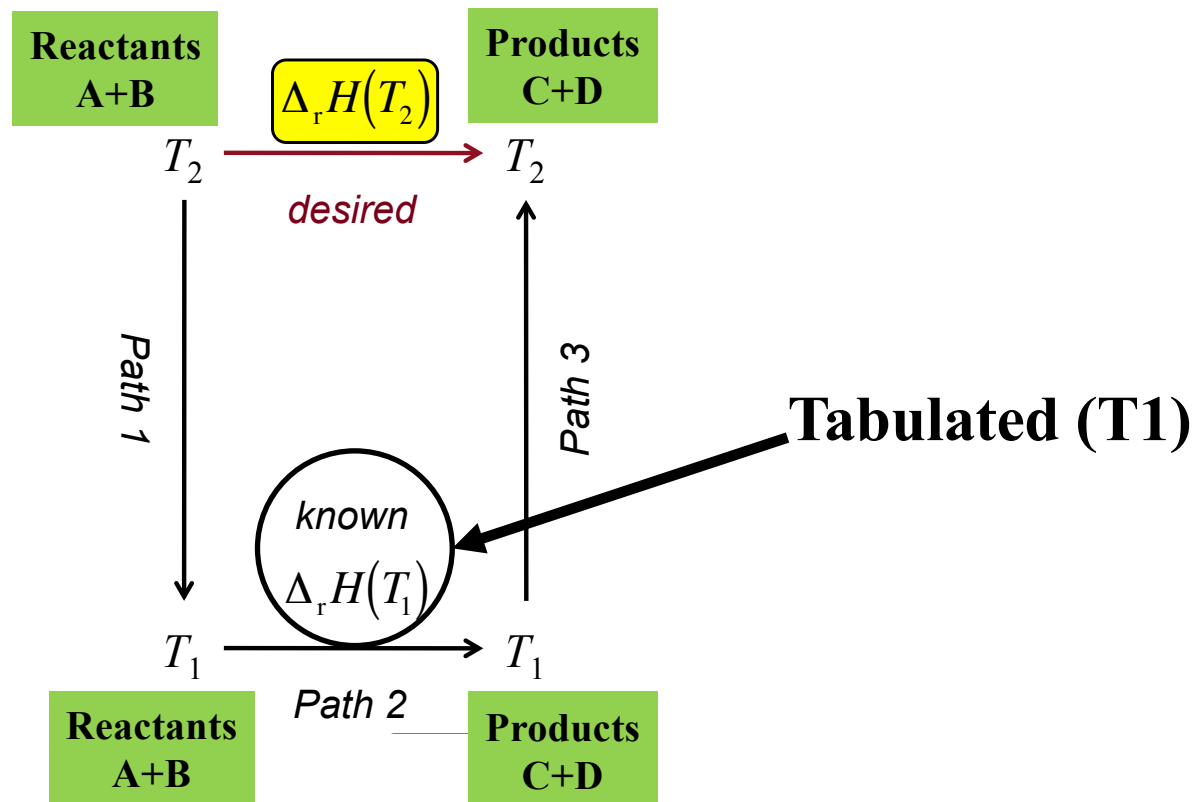


$$\Delta_r H = \Delta_f H^\circ(\text{products}) - \Delta_f H^\circ(\text{reactants})$$

$$\Delta_r H = (y\Delta_f H^\circ[Y] + z\Delta_f H^\circ[Z]) - (a\Delta_f H^\circ[A] + b\Delta_f H^\circ[B])$$

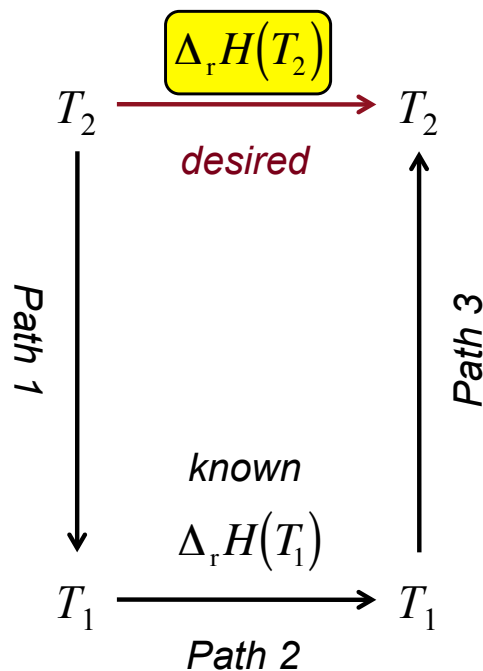
## RELATING $\Delta_r H$ VALUES AT DIFFERENT $T$

To convert  $\Delta_r H$  from  $T_1$  (e.g., 298 K) to  $T_2$  requires  $C_p$



## RELATING $\Delta_r H$ VALUES AT DIFFERENT $T$

To convert  $\Delta_r H$  from  $T_1$  (e.g., 298 K) to  $T_2$  requires  $C_p$



$$\Delta_r H(T_2) = \Delta H_1 + \Delta H_2 + \Delta H_3$$

(note sign and order of limits)

$$\Delta H_1 = - \int_{T_1}^{T_2} C_p(\text{reactants}) dT$$

$$\Delta H_2 = \Delta_r H(T_1)$$

$$\Delta H_3 = \int_{T_1}^{T_2} C_p(\text{products}) dT$$

$$\Delta_r H(T_2) = \Delta_r H(T_1) + \int_{T_1}^{T_2} [C_p(\text{products}) - C_p(\text{reactants})] dT$$



**Next:** solve some problems: Application of 1st Law (close system)