ΔU and ΔH for Physical Changes

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ΔU and ΔH for Temperature Change

- **Variational Statement of the 2nd Law:**
  - **energy flow is from the hot body to cold body**

    $$T^{(1)} > T^{(2)} \rightarrow \Delta E^{(1)} < 0$$

    $$T^{(1)} < T^{(2)} \rightarrow \Delta E^{(1)} > 0$$

  - **at equilibrium**

    $$T^{(1)} = T^{(2)}$$

- **Therefore, when temperature rises, *U* and *H* increase.**

- **From the definition, ΔH and ΔU differ in that ΔH includes the work needed to push back the atmosphere as the material heats up and expands.**
  - **At constant *V*: $\Delta U = n\int C_v \, dT$**
  - **At constant *P*: $\Delta H = n\int C_p \, dT$**
- **For liquids and solids the volume change is very small, hence, $\Delta H \approx \Delta U$**

1kg material from 20 to 30 °C

At 1 atm	$\Delta(PV) = \Delta H - \Delta U$	ΔH J/kg	ΔU J/kg
air	2850 J/kg	7170	10020
water	0.1 J/kg	41840	41840
iron	0.004 J/kg	4494	4994

ΔU and ΔH for Phase Change

- **Liquid to gas**
  - **Energy to make the molecules to active and energetic so that they fly apart from each other: ΔU**
  - **Energy has to be added to push the atmosphere back and make room for the volume increase: $\Delta(PV)$**
- **Called latent heat of vaporization**

H_{lg} J/kg

ΔU and ΔH for Phase Change

- Latent heat of vaporization is also a function of temperature
  - When the molecules of liquid are cold, it takes more energy to tear them away from their neighbors to form vapor.
  - Water: 2454.1, 893.4 kJ/kg at 20^{o}C, 350^{o}C
- Liquid to solid: heat of fusion
  - The volume change is very small

Preparing a cup of tea

- Pour 1 liter of water at 20°C into a thermally insulated electrically heated teapot.
- After I plug in, how long will I have to wait for the pot to whistle?
- Data the metal of the teapot is equivalent to 200 cm^3 of water, and the label on the teapot tells that its heater is rated at 1250 W

Solution

- **Let the kettle and its contents be the system.**
- **At constant *P*: $\Delta H = n\int Cp\, dT$**
  - $\Delta H = Q - W_{sh}$
  - $\Delta H = -W_{sh} = n\, Cp\Delta T$ **Sensible Heat**

$$(1.2lit)\left(\frac{1kg}{1lit}\right)\left(4184\frac{J}{kg^{o}C}\right)\left(100^{o}C-20^{o}C\right)$$
$$=401664J$$
$$time\ needed=\frac{401664J}{1250J/s}=321s$$

Sensible Heat

Heat transfer to a system in which there are no phase transitions, no chemical reactions, and no changes in composition causes the temperature of the system to change. Only the relationship between the quantity of heat transferred and the resulting temperature change.

The maddening whistle

- **How long will the shrill whistling ?**
- **Assuming no one is around, the whistling only stops when all the water boils away.**
  - $\Delta H = -W_{sh} = nH_{lg}$ **Latent Heat**

$$\left(1lit\right)\left(\frac{1kg}{1lit}\right)\left(2255\frac{KJ}{kg}\right)=2255kJ$$

$$time\ needed=\frac{2255000J}{1250J/s}=1841s$$

Latent Heat

- **When a pure substance is liquefied from the solid state or vaporized from the liquid at constant pressure, no change in temperature occurs; however, the process requires the transfer of a finite amount of heat to the substance.**
- **These are heats of transition accompanying the change of a substance from one solid state to another.**

The thermodynamics of a spectacular crash

- **Avocado and puce colored 1923 Hupmobile sedan deluxe, 200km/hr**

- **1996 Ford Thunderbird 32 cylinder super, 200km/hr**

Hupmobile sedan deluxe

1987 NASCAR version of the Thunderbird

The fastest lap in stock car history,
44.998 sec, 212.809 mph (342.483 km/h)
at Talladega Superspeedway, a record that still stands

Quiz III

- **Head on crash. What is the temperature rise, and what are ΔU and ΔH for this catastrophic event?**

- **Data each car weights 2 tons and has an average C_p of 0.5 kJ/kg/K**

ΔU and ΔH for Chemical Reaction

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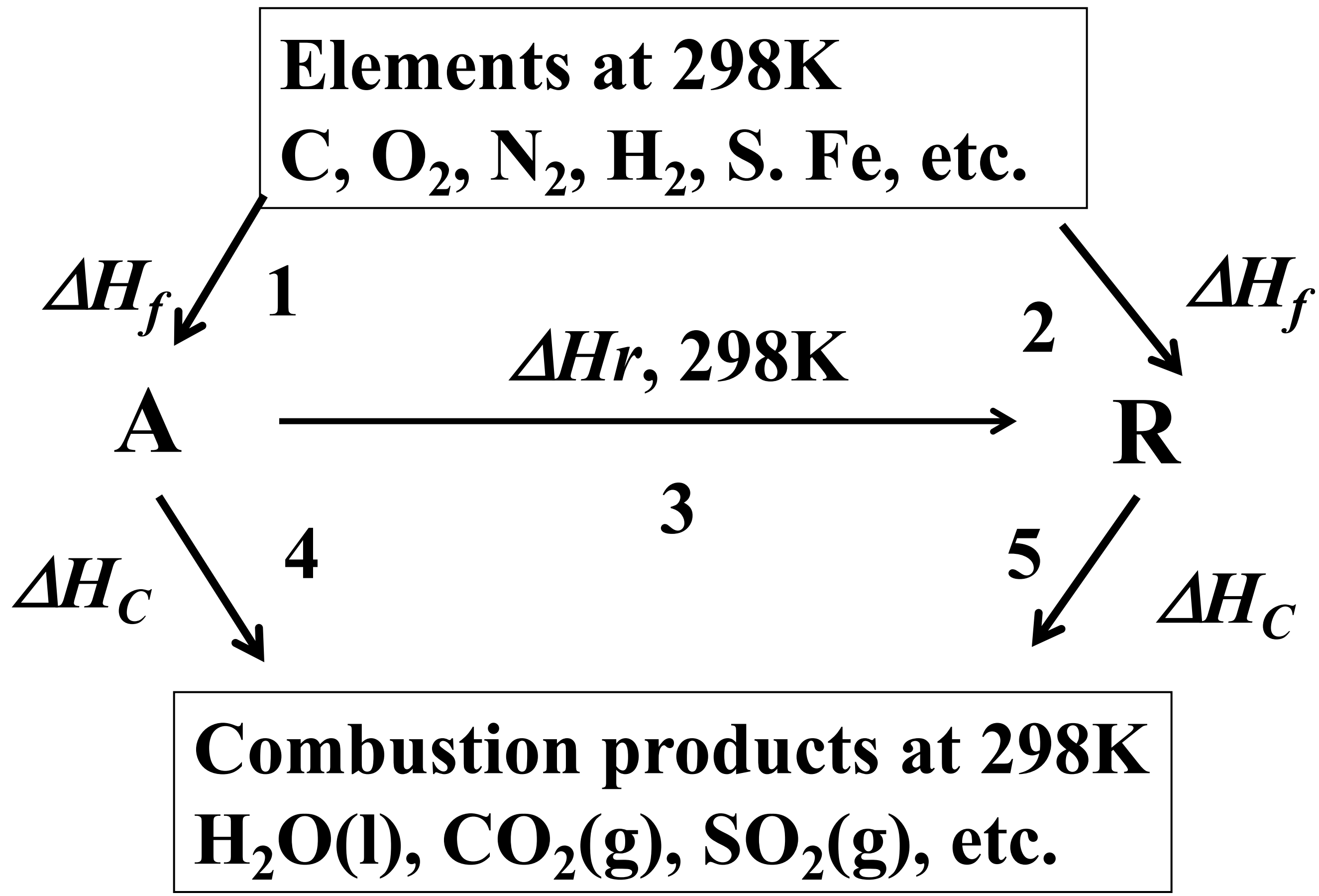
- **At constant *V*: $\Delta U_r = Q - W$**
- **At constant *P*: $\Delta H_r = Q - W$**
- **For liquids and solids $\Delta(pV) \approx 0$**
- $\Delta H_r = \Delta U_r + \Delta(pV)$
- ***For ideal gases only, at temperature T and pressure p,***
- $\Delta H_r = \Delta U_r + (\Delta n)RT$
- ***If no change of moles** $\Delta H_r = \Delta U_r$*

- If ΔH_r >0, *it means the Hafter has to be larger than Hbefore, hence energy must be added, otherwise the system would cool.*
- If ΔH_r <0, *the system must be cooled to keep temperature unchanged.*
- ΔH_r >0, *the reaction is endothermic*
- ΔH_r <0, *the reaction is exothermic*

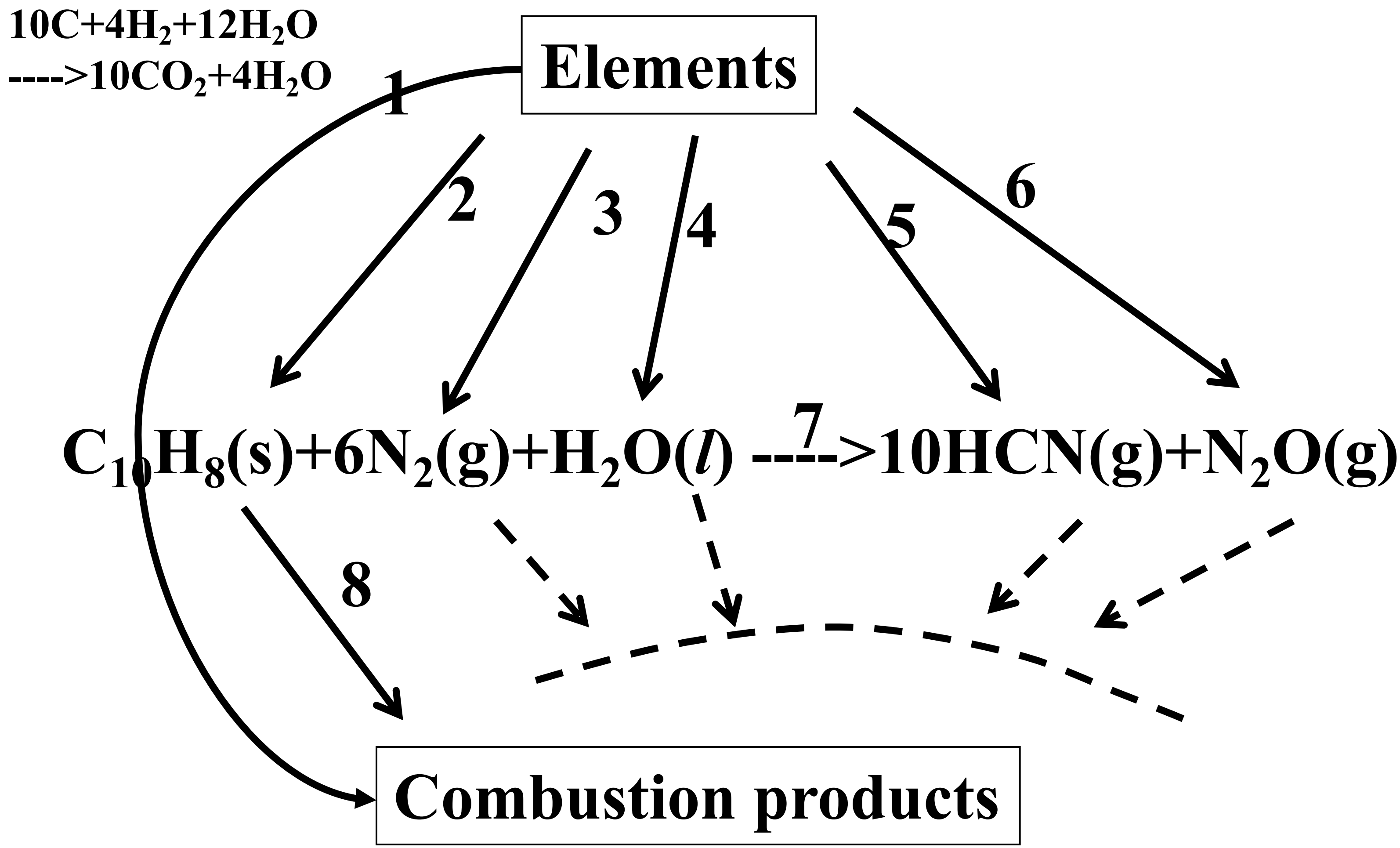
Reaction network at standard conditions, 25°C and 1atm



Reaction network at standard conditions, 25°C and 1atm

- $\Delta H_{f1} + \Delta H_{r3} = \Delta H_{f2}$
- $\Delta H_{r3} + \Delta H_{c5} = \Delta H_{c4}$
- *In general,*
- $\Delta H_r = \sum \Delta H_f(products) - \sum \Delta H_f(reactants)$
- $\Delta H_r = \sum \Delta H_c(reactants) - \sum \Delta H_c(products)$

$C_{10}H_8(s)+6N_2(g)+H_2O(g)$ ---->$10HCN(g)+N_2O(g)$



- $\Delta H_f(3) = 0$, $\Delta H_f(4) = -285.84$,
- $\Delta H_f(5) = 130.54$, $\Delta H_f(6) = 81.5$
- $\Delta H_c(8) = -5157$
- $\Delta H_{f,\ C10H8} = ?$
- $1 = 2 + 8$, or $2 = 1 - 8$
- $\Delta H_{f,\ C10H8} = [10(\Delta H_{f,\ CO2} + 4(\Delta H_{f,\ H2O(l)})] - \Delta H_{c,\ C10H8}$
- $\Delta H_{f,\ C10H8} = 10(-393.5)+4(-285.84)-(-5157)$

  $= 78.64$ kJ

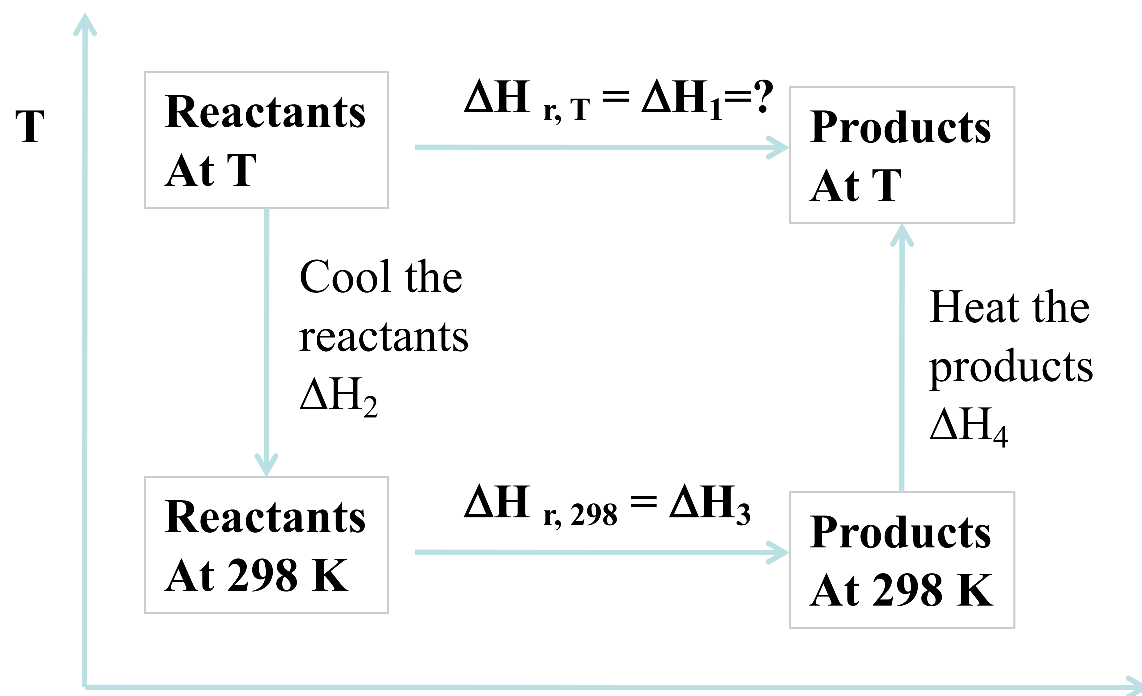
Quiz:

- **Find ΔH_r = ?**

- 2+3+4+7 = 5 +6
- 7 = 5+6-(2+3+4)
- $\Delta H_r = 10(\Delta H_{f,\ HCN}) + \Delta H_{f,\ N2O}$

  $- [\ \Delta H_{f,\ C10H8} + 6\Delta H_{f,\ N2} + \Delta H_{f,\ H2O(l)}]$
- =10(130.54)+81.5-[78.64+0+(-285.84)]
- =1594.10 kJ/mol
- It is a highly endothermic reaction, requiring a considerable heat input.

Reactions at other than standard conditions



Reactions at other than standard conditions

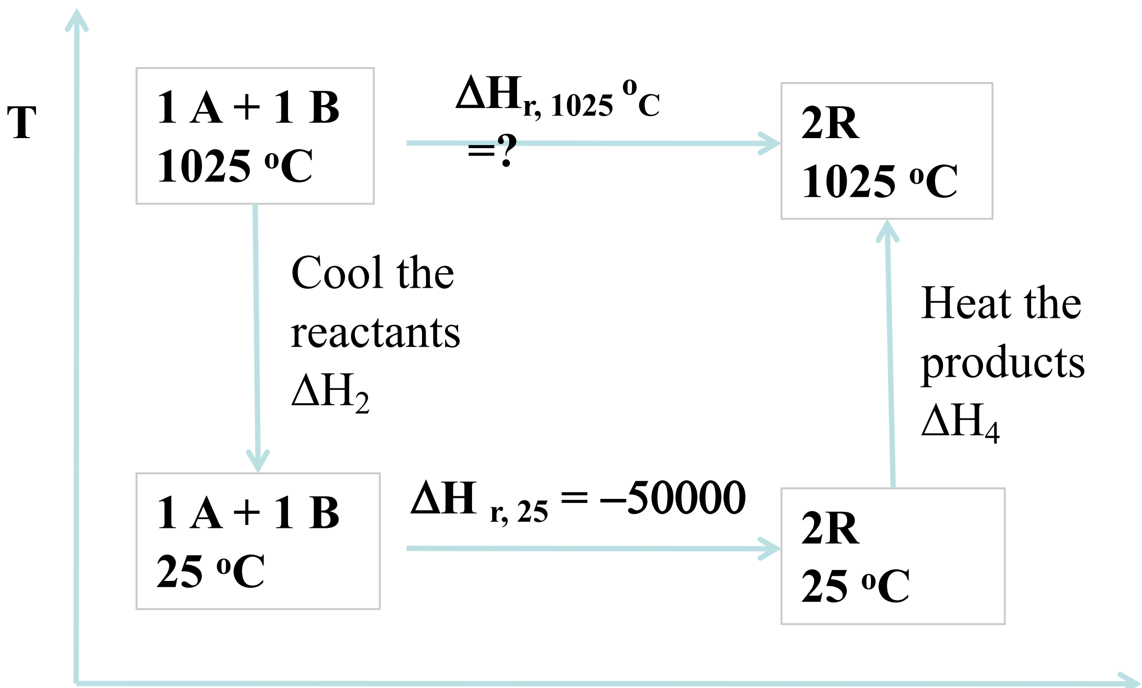
- $\Delta H_1 = \Delta H_2 + \Delta H_3 + \Delta H_4$
- Kowning c_p's and $\Delta H_{r,\ 298}$ will allow you to calculate ΔH_1

Example

- From the ΔH_C and ΔH_f tables, we can calculate the standard heat of gas phase reaction, $A+B \rightarrow 2R$ … $\Delta H_{r,\ 298} = -50$ kJ
- At 25 °C the reaction is strongly exothermic. But that doesn't interest me be cause we plan to run the reaction at 1025 °C.

- What is the ΔH_r at that temperature, and is the reaction still exothermic at that temperature?
- Average C_p :
- $C_{p,A}$ = 35J/mol·K, $C_{p,B}$ = 45J/mol·K
- $C_{p,R}$ = 80J/mol·K

Example


T
1 A + 1 B
1025 °C
ΔH r, 1025 °C =?
2R
1025 °C
Cool the reactants ΔH2
Heat the products ΔH4
1 A + 1 B
25 °C
ΔH r, 25 = –50000
2R
25 °C

Example

- Making an enthalpy balance for 1mol A, 1mol B, and 2mol R,
- $\Delta H_1 = \Delta H_2 + \Delta H_3 + \Delta H_4$
- $=(nc_p\Delta T)_{Reactants} + \mathbf{\Delta H}_{\mathbf{r,\ 25}} \mathbf{+} (nc_p\Delta T)_{Products}$
- $=1(35)(25 - 1025)+1(45)(25 - 1025)+(-50000)+2(80)(25 - 1025)$
- =30kJ endothermic