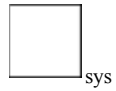


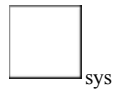
# Chemical Thermodynamics

energy heat work  
 $\Delta E = q + w$  or  $\Delta E = q - w$



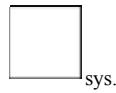
E → surroundings

$\Delta E (-)$   $\Delta E < 0$



← surroundings

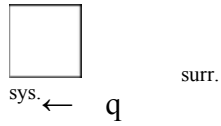
$\Delta E \oplus$   $\Delta E > 0$



q → surroundings

q (-)  $q < 0$

Reaction is exothermic.



$q \oplus$      $q > 0$                   Reaction is endothermic.

If  $w$  is done on the surroundings:

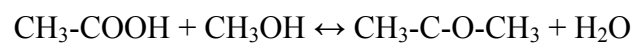
$w (-)$      $w < 0$

If  $w$  is done on the system:

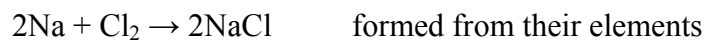
$w \oplus$      $w > 0$

Calculate  $\Delta E$  if 1200 kcal of heat enter a system and 400 kcal of  $w$  is done on the system.

$$\Delta E = 1200 + 400$$



$\Delta H$  Enthalpy – if negative the reaction is exothermic; if positive, then endothermic

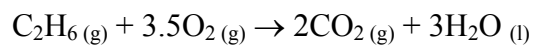


}



$$\Delta H^\circ_r = \sum \Delta H^\circ_f \text{ prod.} - \sum \Delta H^\circ_f \text{ react.}$$

Calculate the  $\Delta H^\circ_r$  for the following reaction using the tables.

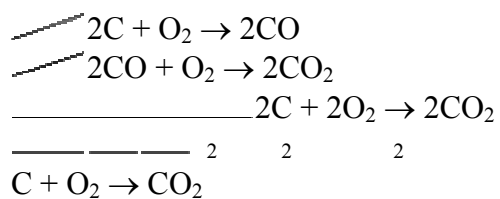


$$\begin{aligned} \Delta H_{\text{r}}^{\circ} &= [(2\Delta H_{\text{f}}^{\circ} \text{CO}_2(\text{g})) + (3\Delta H_{\text{f}}^{\circ} \text{H}_2\text{O}(\text{l}))] - [(\Delta H_{\text{f}}^{\circ} \text{C}_2\text{H}_6(\text{g})) + (3.5\Delta H_{\text{f}}^{\circ} \text{O}_2(\text{g}))] \\ &= [(2 \times -393.5) + (3 \times -285.8)] - [(-84.7)] \\ &= -787.0 - 857.4 + 84.7 \\ &= \mathbf{-1559.7 \text{ kJ/mol}} \end{aligned}$$

$$1 \text{ mol C}_2\text{H}_6 = -1559.7 \text{ kJ}$$

$$30 \text{ g C}_2\text{H}_6 = -1559.7 \text{ kJ}$$

**Hess's Law** – states that the enthalpy of reaction is the same whether the reaction takes place in 1 step or several steps



### Born-Habor Cycle

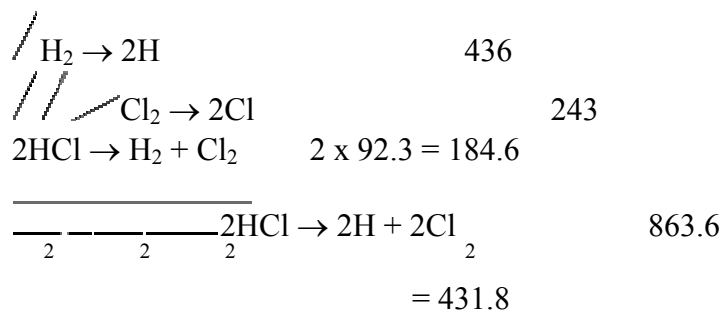
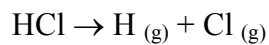
$$-\Delta H_{\text{f}}^{\circ} + \Delta H_{\text{ion}}^{\circ} - \Delta H_{\text{ea}}^{\circ} + \Delta H_{\text{am}}^{\circ}(\text{sub}) + \Delta H_{\text{an}}^{\circ}(\text{dis}) + \Delta H_{\text{x-tal}}^{\circ}$$

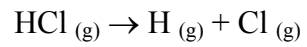
Calculate the  $\Delta H^\circ_{x-tal}$  of NaF using the tables.

$$-(-569) + 495.8 - 327.9 + 107.7 + 78.5 + \Delta H^\circ_{x-tal} = 0$$

$$\Delta H^\circ_{x-tal} = \mathbf{-923.1 \text{ kJ/mol}}$$

Determine the bond association energy of HCl.



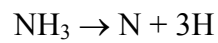


$$\Delta H^\circ_{\text{dis}} = (\Delta H^\circ_f \text{H}_{\text{atom}} + \Delta H^\circ_f \text{Cl}_{\text{atom}}) - \Delta H^\circ_f \text{HCl}$$

$$= (218.5 + 121.3) - (-92.3)$$

$$= 218.5 + 121.3 + 92.3$$

$$= 432.1$$



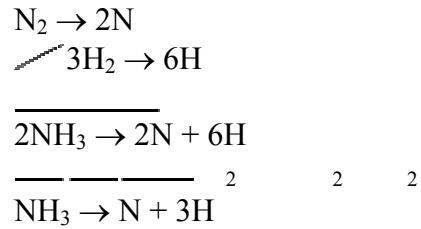
$$\Delta H^\circ_{\text{dis}} = (\Delta H^\circ_f \text{N} + 3 \times \Delta H^\circ_f \text{H}) - (\Delta H^\circ_f \text{NH}_3)$$

$$= (472.6 + 3 \times 218.5) - (-46.11)$$

$$= 1174.21$$

$$\frac{\quad}{3} = 391.40$$



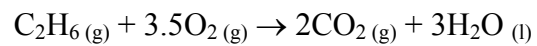


$\Delta G$  Gibbs free energy – allows us to determine if a reaction is spontaneous or not (if  $\Delta G$  is negative then the reaction is spontaneous; if positive then it is not)

$\Delta S$  entropy – measure of disorder

$$\Delta G = \Delta H - T\Delta S$$

Calculate the free energy for the following reaction:



$$\Delta G^\circ_r = \sum \Delta G^\circ_f \text{ prod.} - \sum \Delta G^\circ_f \text{ react.}$$

$$= [(2\Delta G^\circ_f \text{CO}_2(\text{g})) + (3\Delta G^\circ_f \text{H}_2\text{O}(\text{l}))] - [\Delta G^\circ_f \text{C}_2\text{H}_6]$$

$$= [2(-394.4) + 3(-237.2)] - (-32)$$

= -1467.44 so reaction is spontaneous

$$\Delta H^\circ_r = -1559 \text{ exothermic}$$

$$\Delta G^\circ_r = -1467 \text{ spontaneous}$$

$$\Delta S = [S_{\text{prod}} - S_{\text{react}}]$$

$$= [(2S \text{CO}_2) + (3S \text{H}_2\text{O}(\text{l}))] - [(S \text{C}_2\text{H}_6) + (3.5S \text{O}_2)]$$

$$= [(2 \times .2137) + (3 \times .06991)] - [(.2295) + (3.5 \times .205)]$$

$$= -.3099$$

$$\Delta G = \Delta H - T\Delta S$$

$$-1467 = -1560 - 298\Delta S$$

$$298\Delta S = 1467 - 1560$$

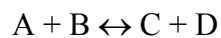
$$\Delta S = \frac{1467 - 1560}{298}$$



$$= -.3121$$

### 3 Laws of Thermodynamics

1. Energy cannot be created or destroyed but changes from one form to another.
2. In a spontaneous reaction the entropy of the universe (the system i.e. a reaction) increases.
3. The entropy of a perfect crystal is at 0 K.



$$k = \frac{[C][D]}{[A][B]} = 3 \times 10^5 \text{ (for example)}$$

$$\Delta G = -RT \ln k \text{ (where R is } 8.364 \text{ J/}^\circ\text{K and T is in } ^\circ\text{K)}$$

$$\Delta G = -2.3RT \log k$$

$$= (-2.3)(8.364 \text{ J/}^\circ\text{K})(298 \text{ }^\circ\text{K}) \log 3 \times 10^5$$

Given  $\Delta G$  is -14.500 at 0 K:

$$-14.500 = (-2.3)(8.314)(273)\log k$$