

# STATISTICAL MOLECULAR THERMODYNAMICS

*Christopher J. Cramer*

Video 5.10

Standard Enthalpy

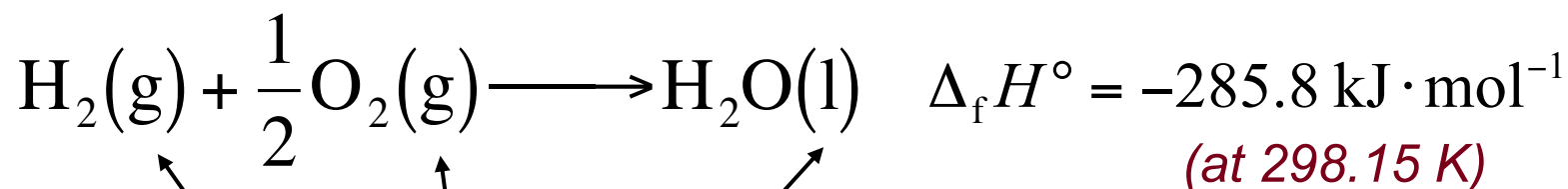


## STANDARD MOLAR ENTHALPY OF FORMATION

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*,



indicates all reactants and products in their conventional standard states



Standard-state phases at 1 bar and 298.15 K

*One mole of H<sub>2</sub>O(l) is 285.8 kJ downhill in enthalpy from its constituent elements*

# THERMOCHEMICAL ABBREVIATIONS

## subscript

## meaning

vap ——— vaporization, evaporation

sub ——— sublimation

fus ——— melting, fusion

trs ——— transition between phases

mix ——— mixing of fluids or gases

ads ——— adsorption

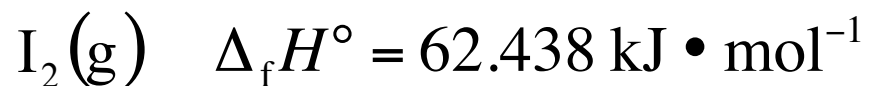
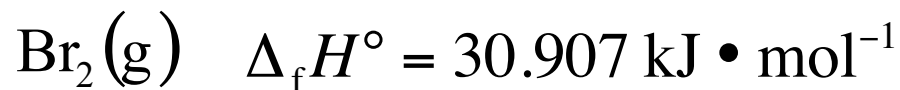
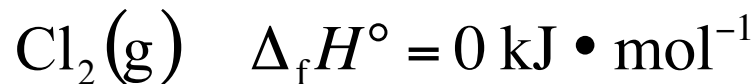
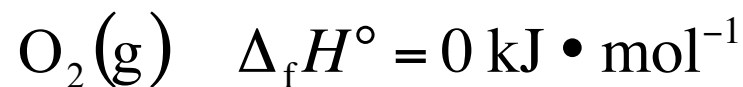
c ——— combustion

f ——— formation

r ——— reaction

# ELEMENTAL HEATS OF FORMATION

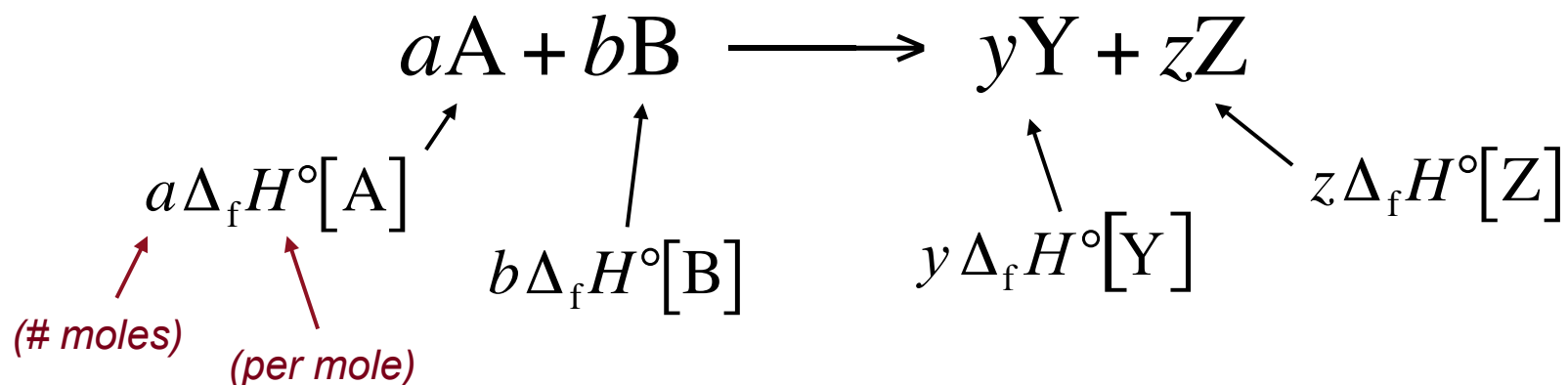
To assign specific values for  $\Delta_f H^\circ$ , the values of  $\Delta_f H^\circ$  for *pure elements* in their *most stable forms* at *one bar* and the *temperature of interest* is set to *zero*.



*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:

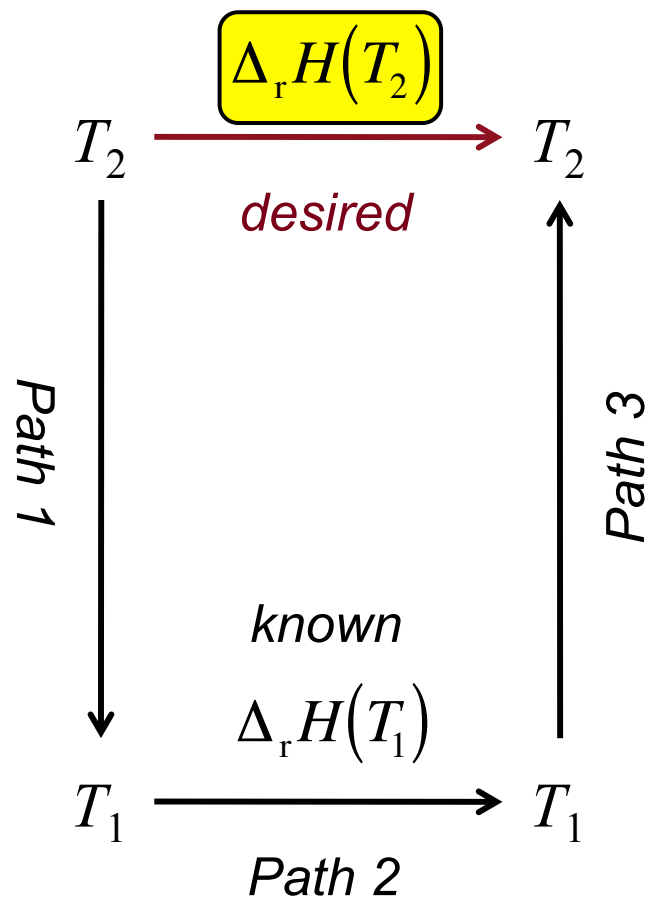


$$\Delta_r H = \Delta_f H^\circ(\text{products}) - \Delta_f H^\circ(\text{reactants})$$

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

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

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



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

(note sign and order of limits)

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

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

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

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