

Lecture Notes B: Thermodynamics I (cont)

1) C_V versus C_P

Heat transferred if volume is held constant

$$q_V = n C_V (T_{\text{final}} - T_{\text{initial}}) = n C_V \Delta T$$

Heat transferred if pressure is held constant

$$q_P = n C_P (T_{\text{final}} - T_{\text{initial}}) = n C_P \Delta T$$

n = number of moles of the substance being heated

C = molar heat capacity

2) Heat transfer at constant volume: Bomb Calorimeter

If you seal some chemical species in a constant volume “bomb”, and measure the heat produced or consumed in a chemical process, you have measured ΔE .

3) Heat transfer at constant pressure: Definition of enthalpy

If you measure the heat produced or consumed in a chemical process at constant pressure, you have measured ΔH , where H is the enthalpy.

4) Relation to C_P and C_V

5) Energy and heat capacities of an ideal gas

$E = \frac{3}{2} n R T$ (for a monatomic ideal gas, Ar, Ne, etc., see Section 4.5 between eqs. [4.10] and [4.11])

C_v

C_p

C_v As you heat, all energy goes to the internal motion of molecules, thereby increasing T

C_p As you heat, the volume increases (gas is doing work). So your heat is being used both to increase T and to do work.

6) State functions (Why have this Enthalpy thing?)

A state function is uniquely determined by the thermodynamic state of a system (P,V,T).

Your altitude above sea level is a state function: it does not matter how you got to Pittsburgh.

The amount of gas in your car is not a state function: it depends on how you got here.

$$\Delta E = q + w$$

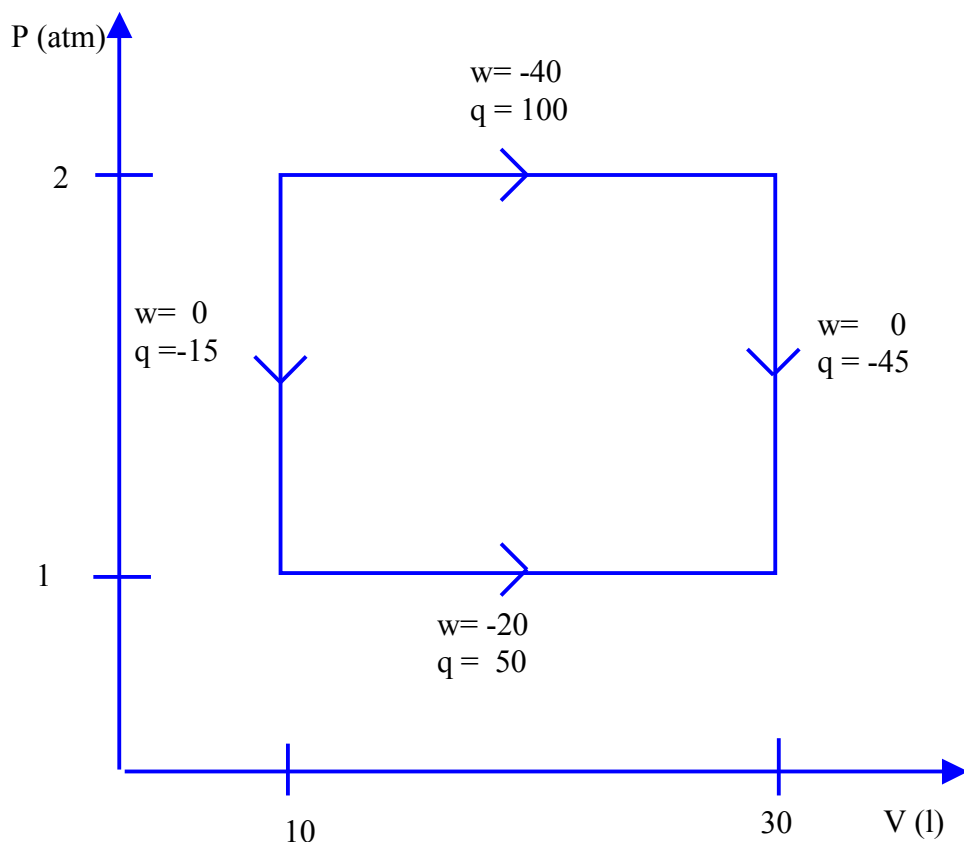
E and H are state functions, q and w are not.

You can't say something "has" a certain amount of heat, but you can say it has a certain amount of energy or enthalpy.

You can extract the energy or enthalpy as either heat or work.

Enthalpy is a great concept, because you typically work at constant pressure. If no work is done, the change in enthalpy is the change in heat for a constant pressure process. This is why the "change in enthalpy" for a chemical reaction is often called the "heat of reaction" (see section 7 of these notes).

From Textbook (page 219) for 1 mole of an monatomic ideal gas



All units are
liter-atm

7) Enthalpy of reaction (also called heat of reaction)

Consider burning acetylene: $\text{C}_2\text{H}_2(\text{g}) + 3/2 \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \quad \Delta\text{H} = -1301.1 \text{ kJ}$

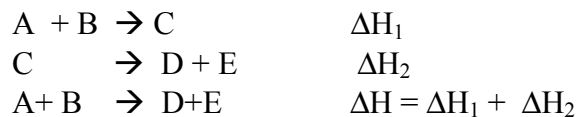
exothermic:	reactants	\rightarrow products + heat	ΔH negative
endothermic:	reactants + heat	\rightarrow products	ΔH positive

Problem: Calculate the change in enthalpy when 5.00 grams of acetylene is burned.

Concept

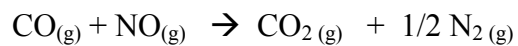
What is ΔH for the reaction: $2\text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{C}_2\text{H}_2(\text{g}) + 3 \text{O}_2(\text{g})$

(a) $\Delta\text{H} = -2602.2 \text{ kJ}$ (b) $\Delta\text{H} = -1301.1 \text{ kJ}$ (c) $\Delta\text{H} = 1301.1 \text{ kJ}$ (d) $\Delta\text{H} = 2602.2 \text{ kJ}$

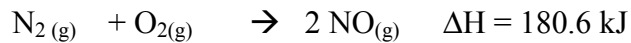
8) Hess's law

Problem

Two gaseous pollutants that form in auto exhaust are CO and NO. An elegant way to eliminate these is through the reaction:



Calculate ΔH and ΔE for the above reaction given the following (all values are for 25°C),



9) Phase changes**Concept**

What are the correct signs for enthalpy's of the above reactions?

- a) $\Delta H_{\text{fus}} = 6.007 \text{ kJ}$, $\Delta H_{\text{vap}} = 40.7 \text{ kJ}$
- b) $\Delta H_{\text{fus}} = 6.007 \text{ kJ}$, $\Delta H_{\text{vap}} = -40.7 \text{ kJ}$
- c) $\Delta H_{\text{fus}} = -6.007 \text{ kJ}$, $\Delta H_{\text{vap}} = 40.7 \text{ kJ}$
- d) $\Delta H_{\text{fus}} = -6.007 \text{ kJ}$, $\Delta H_{\text{vap}} = -40.7 \text{ kJ}$

Problem

How many grams of ice (at 0°C) is needed to cool 1 liter of water from 25°C to 0°C?