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# Enthalpy and Adiabatic Changes

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Chapter 2 of Atkins: *The First Law: Concepts*

Sections 2.5-2.6 of Atkins (7th, 8th & 9th editions)

## *Enthalpy*

**Definition of Enthalpy**

**Measurement of Enthalpy**

**Variation of Enthalpy with Temperature**

**Relation Between Heat Capacities**

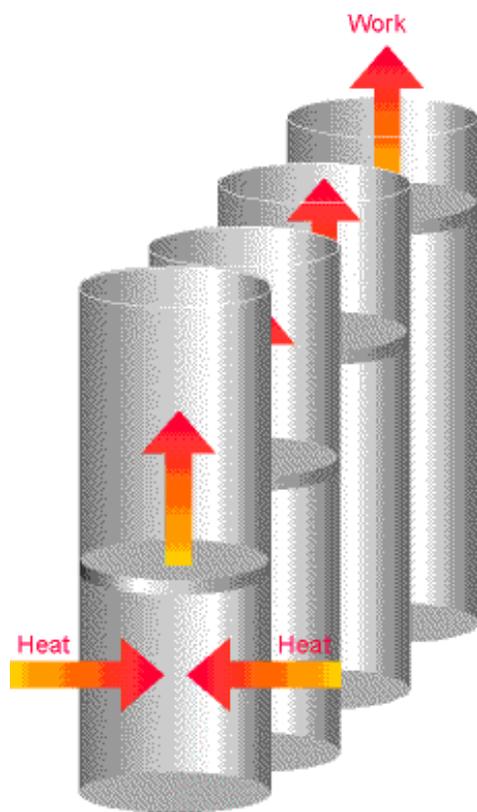
## *Adiabatic Change*

**Work of Adiabatic Change**

**Heat Capacity and Adiabats**

Last updated: Sept. 23, 2012, slide 1, 13 minor edits.

# Enthalpy



For a system that changes volume, the internal energy is not equal to the heat supplied, as for a fixed volume system

Some energy supplied as heat to the system returns to surroundings as expansion work:  
 $dU < dq$ , because  $dU = dq + dw$

When heat is supplied to the system at a constant pressure (e.g., reaction containers open to atmosphere), another thermodynamic *state function* known as **enthalpy**,  $H$ , can be measured accurately:

$$H = U + pV$$

Enthalpy is a convenient state function, since it lumps together changes in energy in the system as well as changes in energy resulting from volume changes.

Change in enthalpy is equal to heat supplied to the system at **constant pressure**

$$dH = dq$$

$$\Delta H = q_p$$

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# Enthalpy: Why does $\Delta H = q_p$ ?

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1. Infinitesimal change in state of system:  $U$  changes to  $U + dU$ ,  $p$  changes to  $p + dp$ ,  $V$  changes to  $V + dV$ , so  $H = U + pV$  becomes

$$\begin{aligned}H + dH &= (U + dU) + (p + dp)(V + dV) \\ &= U + dU + pV + p dV + V dp + dp dV\end{aligned}$$

2. The product of two infinitesimal quantities,  $dp dV$ , disappears. Since  $H = U + pV$ , we write

$$H + dH = H + dU + p dV + V dp$$

$$dH = dU + p dV + V dp$$

3. Substitute in  $dU = dq + dw$

$$dH = dq + dw + p dV + V dp$$

4. System is in mechanical equilibrium with surroundings at pressure  $p$ , so there is only expansion work ( $dw = -pdV$ )

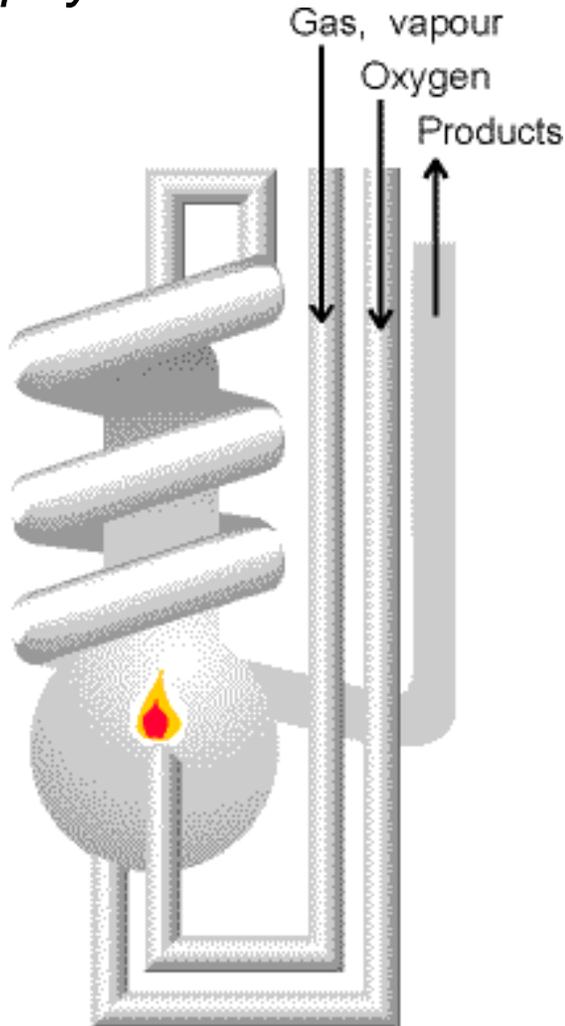
$$dH = dq + V dp$$

5. Impose condition that heating is done at constant pressure, so  $dp = 0$

$$dH = dq \quad (\text{constant } p, w_e = 0)$$

# Measurement of Change in Enthalpy, $\Delta H$

An *adiabatic bomb calorimeter* or an **adiabatic flame calorimeter** can be used to measure  $\Delta H$  by watching the  $\Delta T$  that happens as the result of *physical or chemical changes* occurring at constant pressure.



The adiabatic flame calorimeter measures  $\Delta T$  resulting from combustion of a substance in  $O_2$  (g)

At constant pressure and element is immersed in a  $T$ -controlled water bath - combustion occurs when a known amount of reactant is burned, and  $\Delta T$  is then monitored

The adiabatic bomb calorimeter measures  $\Delta U$  during a change, from which  $\Delta H$  can be calculated (in this case, solids and liquids have such small molar volumes that  $H_m = U_m + pV_m \approx U_m$ )

Processes are accompanied by a very small  $\Delta V$ , so there is negligible work done on surroundings

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# Relation of Internal Energy and Enthalpy<sup>†</sup>

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For a perfect gas, the internal energy and enthalpy can be related by

$$H = U + pV = U + nRT$$

For a measurable change in enthalpy

$$\Delta H = \Delta U + \Delta n_{\text{gas}} RT$$

where  $\Delta n_{\text{gas}}$  is the change of moles of gas in the reaction. For instance



3 mol of gas are replaced by 2 mol of liquid, so at 298 K

$$\Delta H - \Delta U = (-3 \text{ mol}) \times RT \approx -7.5 \text{ kJ}$$

Why is the difference negative?

Heat escapes from system, during reaction, but the system contracts as the liquid is formed (energy is restored from the surroundings)

# Variation of Enthalpy with Temperature

Enthalpy of substance increases as  $T$  is raised - How  $H$  changes is dependent on the conditions, most important being **constant pressure**

The **heat capacity at constant pressure** is an extensive property, defined as

$$C_p = \left( \frac{\partial H}{\partial T} \right)_p$$

For infinitesimal changes in **temperature**

$$dH = C_p dT \quad (\text{at constant pressure})$$

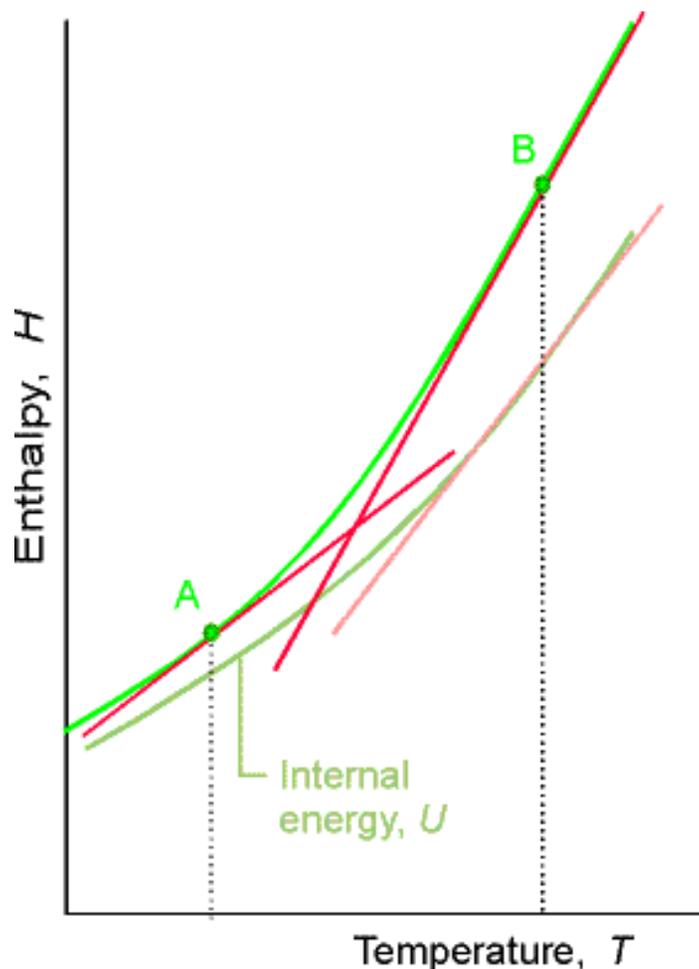
and for measurable changes

$$\Delta H = C_p \Delta T \quad (\text{at constant pressure})$$

and heat at constant pressure

$$q_p = C_p \Delta T$$

Also: intensive property of molar heat capacity at constant pressure,  $C_{p,m}$



# Variations and Relations of Heat Capacities†

Variation of heat capacity is negligible for small temperature ranges - good for noble gases - however, if accurate treatment is necessary

$$C_{p,m} = a + bT + \frac{c}{T^2}$$

where  $a$ ,  $b$  and  $c$  are empirical parameters independent of  $T$

	$a$	$b/(10^{-3}K^{-1})$	$c/(10^5K^2)$
Graphite	16.86	4.77	-8.54
CO <sub>2</sub> (g)	44.22	8.79	-8.62
H <sub>2</sub> O(l)	75.29	0	0
N <sub>2</sub> (g)	28.58	3.77	-0.50

At constant pressure, most systems expand **when heated**, and do work on the surroundings while losing internal energy, with some energy supplied as heat leaking back into the surroundings.

Temperature of a system rises less **when heating at a constant pressure** than when heating at constant volume, implying larger heat capacity:  
*Heat capacity of a system at constant pressure is larger than its heat capacity at constant volume*

$$C_p - C_V = nR$$

# Adiabatic Changes\*

What changes occur when a gas expands *adiabatically*?

- Work is done - internal energy falls
- Temperature of the working gas falls
- Kinetic energy of the molecules falls with average speed of the molecules

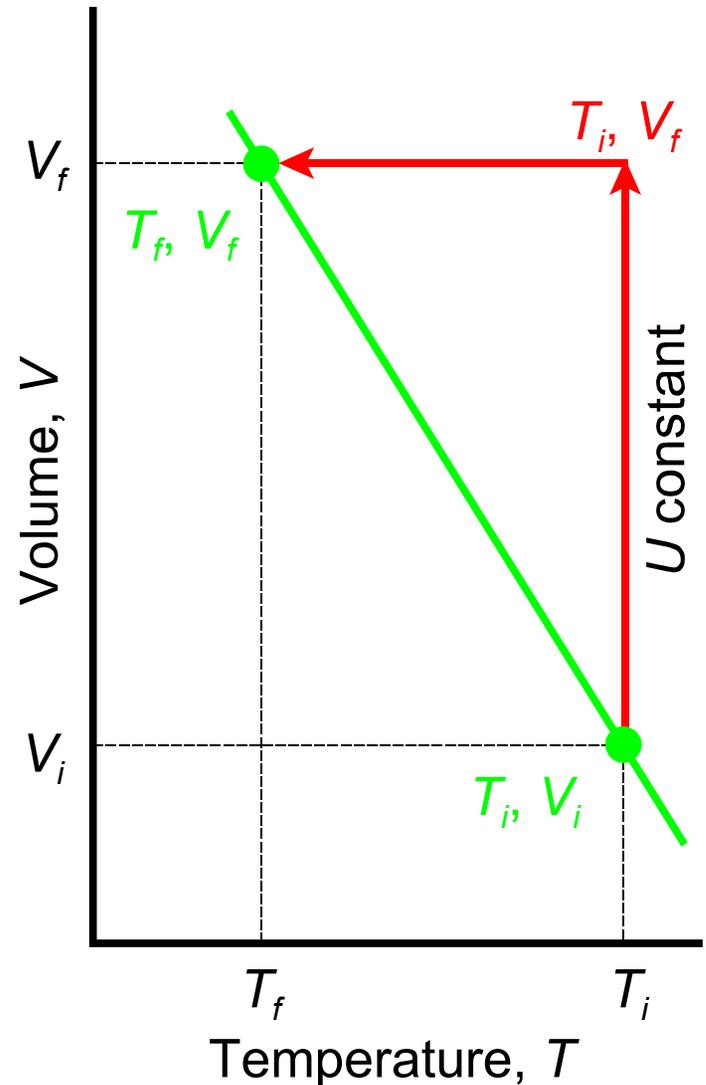
$\Delta U$  of ideal gas with  $\Delta T$  and  $\Delta V$  expressed in two steps -  $\Delta U$  results solely from the second step, if  $C_V$  is indep. of  $T$ , so:

$$\Delta U = C_V(T_f - T_i) = C_V\Delta T$$

Adiabatic expansion,  $q = 0$ , and  $\therefore \Delta U = w_{\text{ad}}$

$$w_{\text{ad}} = C_V\Delta T$$

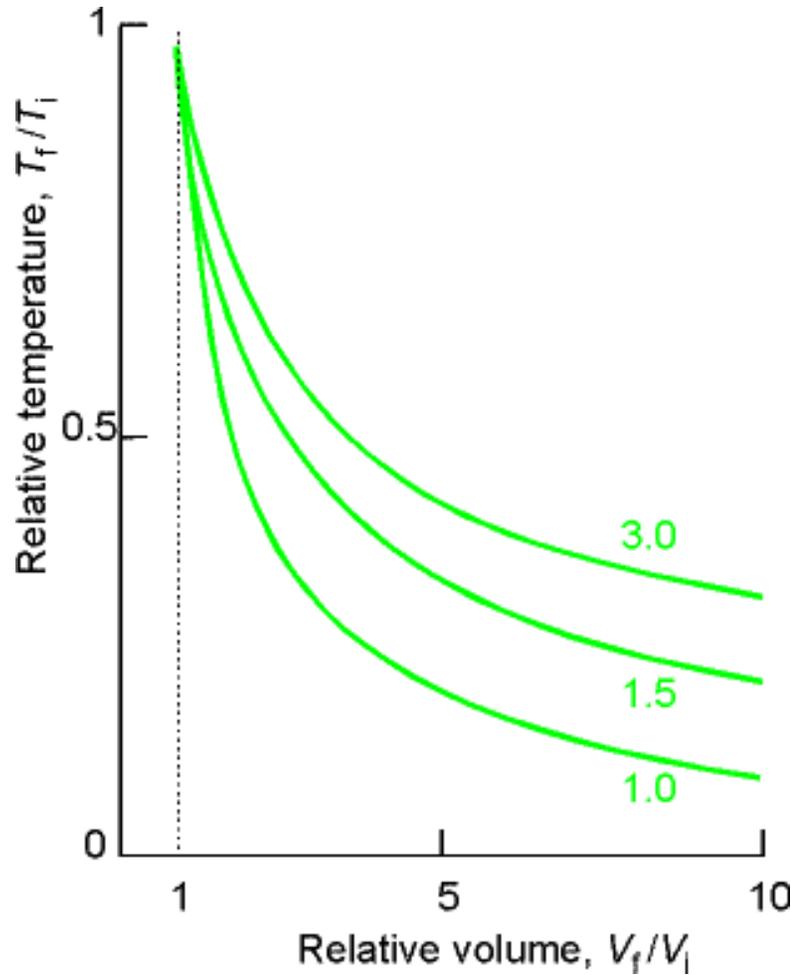
The work done during an adiabatic expansion of a perfect gas is proportional to the temperature difference between the initial and final states (mean  $E_K \propto T$ )



\*pistoncyl

# Adiabatic Changes, continued

To calculate the work done by adiabatic expansion,  $w_{\text{ad}}$ ,  $\Delta T$  must be related to  $\Delta V$  (which we know from the *perfect gas law*)



We will only consider **reversible adiabatic expansion**, where the external and internal pressures are always matched:

$$V_f T_f^c = V_i T_i^c \quad c = \frac{C_{V,m}}{R}$$

From the above relations, the expression for final temperature, which gives us  $\Delta T$ , is

$$T_f = T_i \left( \frac{V_i}{V_f} \right)^{1/c}$$

Variation in  $T$  is shown for reversible adiabatic expanding gas for different values of  $c$  - falls steeply for low  $C_{V,m}$

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# Adiabatic Changes, justification\*

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Consider a case  $p = p_{\text{ext}}$  at all times, so as the gas expands by  $dV$ , the work done is  $w = -p dV$

Perfect gas:  $dU = C_V dT$ . Since  $dU = dw$  for adiabatic change,

$$C_V dT = -p dV \quad \text{or} \quad C_V \frac{dT}{T} = -nR \frac{dV}{V}$$

Integrate for measurable changes

$$C_V \int_{T_i}^{T_f} \frac{dT}{T} = -nR \int_{V_i}^{V_f} \frac{dV}{V}$$
$$C_V \ln \left( \frac{T_f}{T_i} \right) = -nR \ln \left( \frac{V_f}{V_i} \right)$$

With  $c = C_V/nR$ , and identities  $a \ln x = \ln x^a$  and  $-\ln(x/y) = \ln(y/x)$

$$\ln \left( \frac{T_f}{T_i} \right)^c = \ln \left( \frac{V_i}{V_f} \right)$$

# Heat Capacity Ratio and Adiabats<sup>s</sup>

It is shown in Atkins (p.65, 6th; p. 54, 7th) that for an adiabatic reversible expanding gas

$$pV^\gamma = \text{constant}$$

where  $\gamma$  is the **heat capacity ratio** of a substance

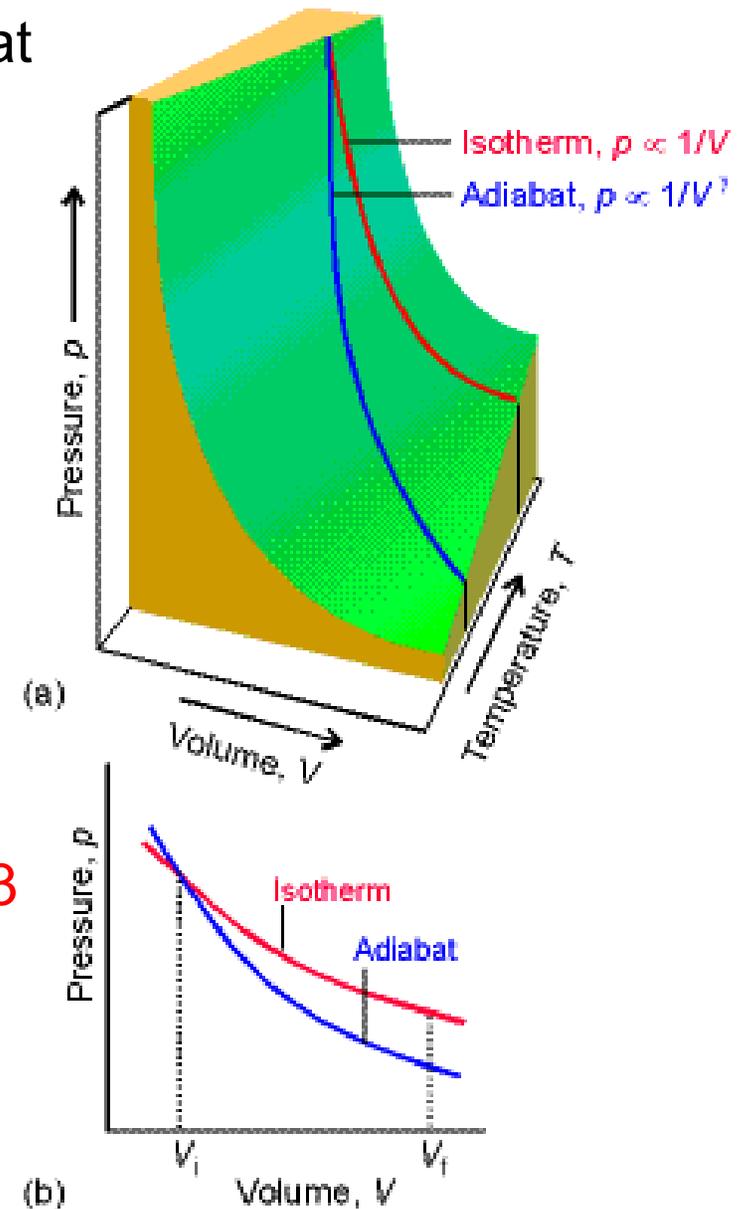
$$\gamma = \frac{C_{p,m}}{C_{V,m}}$$

Heat capacity at constant pressure > heat capacity at constant volume

$$\gamma = \frac{C_{V,m} + R}{C_{V,m}}$$

Monatomic perfect gas,  $C_{V,m} = (3/2)R$ ,  $\gamma = 5/3$   
Polyatomic perfect gas,  $C_{V,m} = 3R$ ,  $\gamma = 4/3$

Pressure declines more steeply for adiabat than for isotherm, because of temperature decrease in the former case



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# Justification

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Initial and final states of a gas satisfy the perfect gas law, no matter what the change of state

$$\frac{p_i V_i}{p_f V_f} = \frac{T_i}{T_f}$$

We have shown that for reversible adiabatic change, the temperature changes, such that

$$\left( \frac{T_i}{T_f} \right) = \left( \frac{V_f}{V_i} \right)^{1/c}$$

Combine the two expressions:

$$p_i V_i^\gamma = p_f V_f^\gamma$$

Thus,  $pV^\gamma = \text{constant}$ , as shown

# Incorrect figure: adiabatic expansion

The figure on the left is incorrect for a reversible adiabatic expansion, since the temperature must drop during an expansion. The figure is wrong in 6th and 7th eds. (left), but modified in the 8th, 9th eds. (right).

