Enthalpy and Adiabatic Changes

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

Sections 2.5- 2.6 of Atkins

Exercises 2.15(a), 2.16(a), 2.18(a), 2.28(a);
Problem 2.10
Problem from Last Time

A sample of 70. mmol of Kr(g) expands reversibly and isothermally at 373 K from 5.25 cm$^3$ to 6.29 cm$^3$. The internal energy of the sample is known to increase by 83.5 J. Using the virial equation of state up to the second virial coefficient (B = -28.7 cm$^3$ mol$^{-1}$), calculate $w$, $q$, and $\Delta H$ for this process.
Enthalpy and Adiabatic Changes

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

Sections 2.5- 2.6 of Atkins

*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
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:

\[ dU < dq \]

When heat is supplied to the system at a constant pressure, there is a change in another thermodynamic state function known as enthalpy, \( H \).

Mathematically, enthalpy is

\[ H = U + pV \]

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

\[ dH = dq \quad (\text{const } p) \quad \Delta H = q_p \]
Enthalpy: Why does $\Delta H = q_p$?

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

$$H + dH = (U + dU) + (p + dp)(V + dV)$$

$$= U + dU + pV + pdV + Vdp + dpdV$$

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

$$H + dH = H + dU + pdV + Vdp$$

$$dH = dU + pdV + Vdp$$

3. Substitute in $dU = dq + dw$

$$dH = dq + dw + pdV + Vdp$$

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

$$dH = dq + Vdp$$

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 an element is immersed in a $T$-controlled water bath - combustion occurs when a known amount of reactant is burned, and $T$ 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 $H_m = U_m + pV_m \approx U_m$)

In the case of liquids and solids, processes are accompanied by a very small $\Delta V$, so there is negligible work done on surroundings
Relation of Internal Energy and Enthalpy

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

\[ 3 \text{ NO(g)} \rightarrow \text{N}_2\text{O(g)} + \text{NO}_2 \text{(g)} \]

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

\[ \Delta H = \Delta U + (-1 \text{ mol})RT \quad \text{or} \quad \Delta H - \Delta U = -2.5 \text{ kJ} \]

Why is the difference negative? (The change in \( H \) is less than the change in internal energy)

The system contracts as the number of moles of gas decreases (energy is moved to the system 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 \textit{constant pressure}

The \textbf{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 pressure

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

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

\[
C_{p,m}/(\text{J K}^{-1} \text{ mol}^{-1}) = a + bT + \frac{c}{T^2}
\]

Where \(a\), \(b\) and \(c\) are empirical parameters independent of \(T\)

At constant pressure, most systems expand when heated, and do work on the surroundings while losing internal energy. Therefore, some energy supplied as heat returns back to the surroundings as expansion work.

Temperature of a system rises less 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 (to be derived in Chapter 3)

\[
C_p - C_v = nR
\]

<table>
<thead>
<tr>
<th></th>
<th>(a)</th>
<th>(b/(10^{-3}\text{ K}^{-1}))</th>
<th>(c/(10^5\text{ K}^2))</th>
</tr>
</thead>
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<tr>
<td>Graphite</td>
<td>16.86</td>
<td>4.77</td>
<td>-8.54</td>
</tr>
<tr>
<td>(\text{CO}_2) (g)</td>
<td>44.22</td>
<td>8.79</td>
<td>-8.62</td>
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<tr>
<td>(\text{H}_2\text{O}) (l)</td>
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<td>0</td>
</tr>
<tr>
<td>(\text{N}_2) (g)</td>
<td>28.58</td>
<td>3.77</td>
<td>-0.50</td>
</tr>
</tbody>
</table>
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

\[ \Delta U \text{ of ideal gas with } \Delta T \text{ and } \Delta V \text{ expressed in two steps – } \Delta U \text{ results solely from the second step, if } C_V \text{ is indep. of } T, \text{ so:} \]

\[ \Delta U = C_V \left( T_f - T_i \right) = C_V \Delta T \]

Adiabatic expansion, \( q = 0 \), and \( \Delta U = w_{ad} \)

\[ w_{ad} = C_V \Delta T \]

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

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). Consider a reversible case, $p = p_{\text{ext}}$ at all times, so as a gas adiabatically ($q = 0$) expands by $dV$, and the work done is $dw = -p \, dV$

Perfect gas: $dU = C_V \, dT$. Now, since $dU = dw$ for adiabatic changes,

$$C_V dT = -pdV$$

Integrate for measurable changes, after subbing in $p = nRT/V$

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

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

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

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Lecture 7 - 11
Adiabatic Changes

\[ q = 0 \]

\[ \Delta U = C_V (T_f - T_i) = C_V \Delta T \]

\[ V_f T_f^c = V_i T_i^c \quad \text{where} \quad c = \frac{C_{V,m}}{R} \]

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

At left, the variation in \( T \) is shown for reversible adiabatic expanding gas for different values of \( c \) - falls steeply for low \( C_{V,m} \)
Reversible Adiabatic Changes II

Initial and final states of an ideal 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

\[ \frac{T_i}{T_f} = \left( \frac{V_f}{V_i} \right)^{\frac{1}{c}} \quad \text{and} \quad \frac{1}{c} = \gamma - 1 \]

\[ \frac{1}{c} = \frac{R}{C_{V,m}} = \frac{R}{C_{V,m}} + \frac{C_{V,m}}{C_{V,m}} - 1 \]

\[ = \frac{R + C_{V,m}}{C_{V,m}} - 1 = \frac{C_{p,m}}{C_{V,m}} - 1 = \gamma - 1 \]

Combine these expressions:

\[ p_i V_i^\gamma = p_f V_f^\gamma \]
So for a reversible adiabatic change
\[ pV^\gamma = \text{constant} \]

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
\[ \gamma = \frac{C_{V,m} + R}{C_{V,m}} = 1 + \frac{R}{C_{V,m}} \]

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!*
Problem 1

Calculate the final T of a sample of CO$_2$ of mass 16.0 g that is expanded reversibly and adiabatically from 500. mL at 298.15 K to 2.00 L.

The value of $C_p,m$ for CO$_2$ is 37.11 J K$^{-1}$ mol$^{-1}$

$$\frac{T_f}{T_i} = (\frac{V_i}{V_f})^{1/c} \text{ where } c = \frac{C_v}{R} = \frac{(C_p - R)}{R}$$

$$T_f = 200 \text{ K}$$

Remember: $C_p$ (J/K) = $C_v$ (J/K) + nR (moles*J/mol-K)

$$C_{p,m} \text{ (J/mol-K)} = C_{v,m} \text{ (J/mol-K)} + R \text{ (J/mol-K)}$$
Problem 2

Calculate the final p of a sample of H₂O(g) of mass 1.4 g that is expanded reversibly and adiabatically from an initial T of 300. K and a volume of 1.0 L to a final volume of 3.0 L.

The value of $\gamma$ for H₂O(g) is 1.3

\[ P_f = P_i (V_i/V_f)^\gamma \]

\[ P_i = \frac{nRT}{V_i} \]

\[ P_f = 0.46 \text{ atm} \]
Problem 3

When 2.0 mol of CO₂ is heated at a constant pressure of 1.25 atm, its temperature increases from 250 K to 277 K. Calculate q, ΔH, and ΔU for this process.

The value of \( C_{p,m} \) for CO₂ is 37.11 J K\(^{-1}\) mol\(^{-1}\)

\[
\Delta H = q_p = C_p \Delta T = 2.0 \times 10^3 \text{ J}
\]

\[
\Delta U = \Delta H - nR \Delta T = 1.6 \times 10^3 \text{ J}
\]
Problem 4

5.0 mol of CO$_2$ is originally confined in a 15.0 L vessel at 280. K and then adiabatically expanded against a constant pressure of 78.5 kPa until the volume has increased by a factor of 4.0.

Calculate $q$, $w$, $\Delta T$, $\Delta H$, and $\Delta U$ for this process.

The value of $C_{p,m}$ for CO$_2$ is 37.11 J K$^{-1}$ mol$^{-1}$

$q = 0$

$w = -P_{\text{ext}} \Delta V = -3.5 \times 10^3$ J

$\Delta U = -3.5 \times 10^3$ J

$\Delta T = \Delta U/C_{v,m} = \Delta U/(C_{p,m} - nR) = -24$ K

$\Delta H = \Delta U + nR \Delta T = -4.5 \times 10^3$ J
Problem 5

One mole of an alkane C\textsubscript{n}H\textsubscript{2n+2} is burned in excess oxygen to form CO\textsubscript{2}(g) and H\textsubscript{2}O(g) at 298.15 K and 1 bar pressure. At constant pressure, the heat released in the process is found to be 2877.04 kJ. It is also found that 20 g of the alkane occupies a volume of 4.210 L at 298.15 K and 2 atm pressure. Determine the standard partial molar enthalpy of the alkene.
Problem 5 - Key

PV = nRT
Mol. Weight = mRT/PV = 58.11 g
Mol Weight = 12.011n + 1.008(2n+2) = 58.11 g
n = 4

\[ \text{C}_4\text{H}_{10(l)} + 6.5 \text{O}_2 (g) \rightarrow 4\text{CO}_2 (g) + 5\text{H}_2\text{O} (l) \]
\[ \Delta H_{\text{comb}} = 4\Delta H_{\text{CO}_2} + 5\Delta H_{\text{H}_2\text{O}} - 6.5\Delta H_{\text{O}_2} - \Delta H_{\text{C}_4\text{H}_{10}} \]

\[ \Delta H_{\text{C}_4\text{H}_{10}} = 4\Delta H_{\text{CO}_2} + 5\Delta H_{\text{H}_2\text{O}} - 6.5\Delta H_{\text{O}_2} - \Delta H_{\text{comb}} \]
\[ = 4(-393.51) + 5(-285.83) - 0 - (-2877.04) \]
\[ = -126.15 \text{ kJ} \]