9/15/99

Note: $\ominus$ sign. In an expansion, System does work on surroundings!

Last time we saw irreversible expansion at constant P

$$w = -\int P\,dV = -P\int dV = -P(V_2 - V_1)$$

Now take a reversible expansion where P slowly decreases.

$$w = -\int P\,dV$$ but at each point along the way $P = \frac{nRT}{V}$

So $w_T = -\int \frac{nRT}{V}\,dV$ if isothermal (T = constant)

then $w_T = -nRT \int_{V_1}^{V_2} \frac{dV}{V}$

$$w_T = -nRT \ln V_2/V_1$$ At const T, $P \propto \frac{1}{V}$

$$w_T = -nRT \ln P_1/P_2$$

For an ideal (isothermal) gas, the heat absorbed by the gas is equal to minus the work done $q_T = w_T$

Gas does work on surroundings (energy → surroundings) ∴ 1st law says than energy (heat) must go into the gas

$$\therefore \quad q_T = nRT \ln V_2/V_1 = nRT \ln P_1/P_2$$

Path Independence

What is $E_2 - E_1$ for $(P_1\ T_1\ V_1) \rightarrow (P_2\ T_2\ V_2)$?

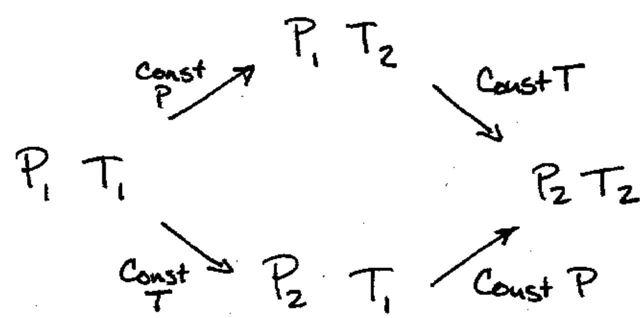
Note that if no exchange of mass with the surroundings, then

$$\frac{P_1 V_1}{T_1} = nR = \frac{P_2 V_2}{T_2}$$

So if we know P and T, then we know V

Reduces to $(P_1\ T_1) \rightarrow (P_2\ T_2)$

Simple paths



$$P_1 T_1 \xrightarrow[\underbrace{\qquad}_{q_P\ \ w_P}]{\text{Const } P} P_1 T_2 \xrightarrow[\underbrace{\qquad}_{q_T\ \ w_T}]{\text{isothermal}} P_2 T_2$$

So total change is: $q_P + w_P + q_T + w_T = E_2 - E_1$

Just saw that for isothermal expansion of ideal gas

$$q_T = -w_T \qquad q_T + w_T = 0$$

$$w_p = -P(V_2 - V_1) = -nR(T_2 - T_1)$$

$$E_2 - E_1 = 0 + q_p + w_p$$

$$= C_p(T_2 - T_1) - nR(T_2 - T_1)$$

$$E_2 - E_1 = (C_p - nR)(T_2 - T_1)$$

Remember $H = E + PV$ $\qquad PV = nRT$

<u>So</u> $$H_2 - H_1 = E_2 - E_1 + P_2V_2 - P_1V_1$$

$$= E_2 - E_1 + nRT_2 - nRT_1$$

$$= (E_2 - E_1) + nR(T_2 - T_1)$$

$$= (C_p - nR)(T_2 - T_1) + nR(T_2 - T_1)$$

$$= (C_p - \cancel{nR} + \cancel{nR})(T_2 - T_1)$$

$$= C_p(T_2 - T_1)$$

H is a measure of the heat xferred at const. P

Phase Changes

	Forward	Reverse
Gas → liquid	Condensation	(Boiling) Vaporization
Solid → liquid	Melting	Freezing
Solid → gas	Sublimation	Condensation

In biology, lipid membranes can undergo phase changes
Thought to play a role in protein-protein interactions and perhaps trans-membrane signaling.

A simple example: 1 mol water

$$H_2O\ (s)\ \text{at}\ 0^\circ C \rightarrow H_2O\ (g)\ \text{at}\ 100^\circ C$$

Break down into reversible steps

1) Ice melts (isothermal) $H_2O\ (s)$ at $0^\circ C \rightarrow H_2O(l)$ at $0^\circ C$

Heat absorbed by the system → $q_P = 6.007$ kJ/mol Table 2.2

$(q_P = \Delta H\ !)$

2) Heat (l) water $0^\circ \rightarrow 100^\circ$

$$q = (75.4\ J\ K^{-1} mol^{-1})(100\ K)$$
$$= 7540\ J\ mol = 7.54\ kJ/mol$$

3) Ice vaporizes (boils) at $100^\circ C$ (isothermal) $q_P = 40.66$ kJ/mol