Lecture 5

Thursday, September 19, 2024 10:00

Midterm Exam : Thursday, October 17

10:00am-11:15am, ~~ANNU 002~~ MacKinnon 318

First Law Continued

Heat transactions

N.B. Thermal energy is to heat as cars are to traffic.

Heat is the flow/transfer of thermal energy.

$$dU = dq + dw$$

both dw_{exp}, expansion work, and dw_{other}, other types of work

$$dU = \boxed{dq} + \cancel{dw_{exp}} + \cancel{dw_{other}}$$

constrain the system so that it does no work

$$dU = dq_V$$

heat transferred at constant volume

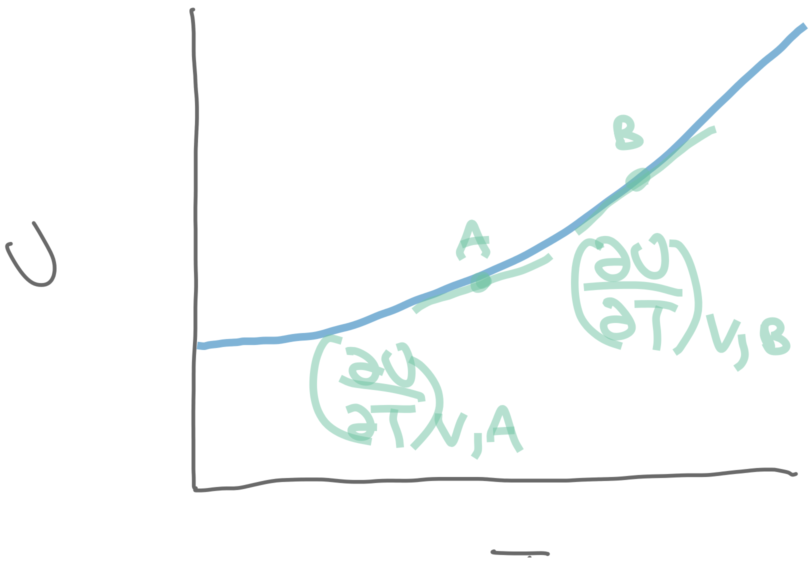
$$\int_i^f dU = \int_i^f dq_V$$

$$\boxed{\underline{\Delta U} = \underline{q_V}}$$

path function

state function

Heat Capacity

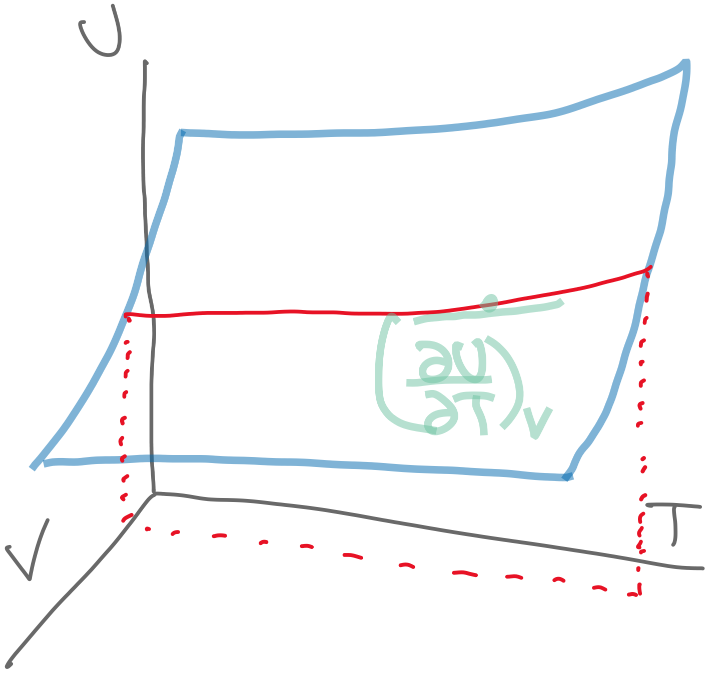


constant volume

over a small range of T, $\left(\frac{\partial U}{\partial T}\right)_V$ is approximately a constant

$$\boxed{C_V = \left(\frac{\partial U}{\partial T}\right)_V}$$

heat capacity at constant volume



$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT$$

by definition

$$dU = C_V dT$$

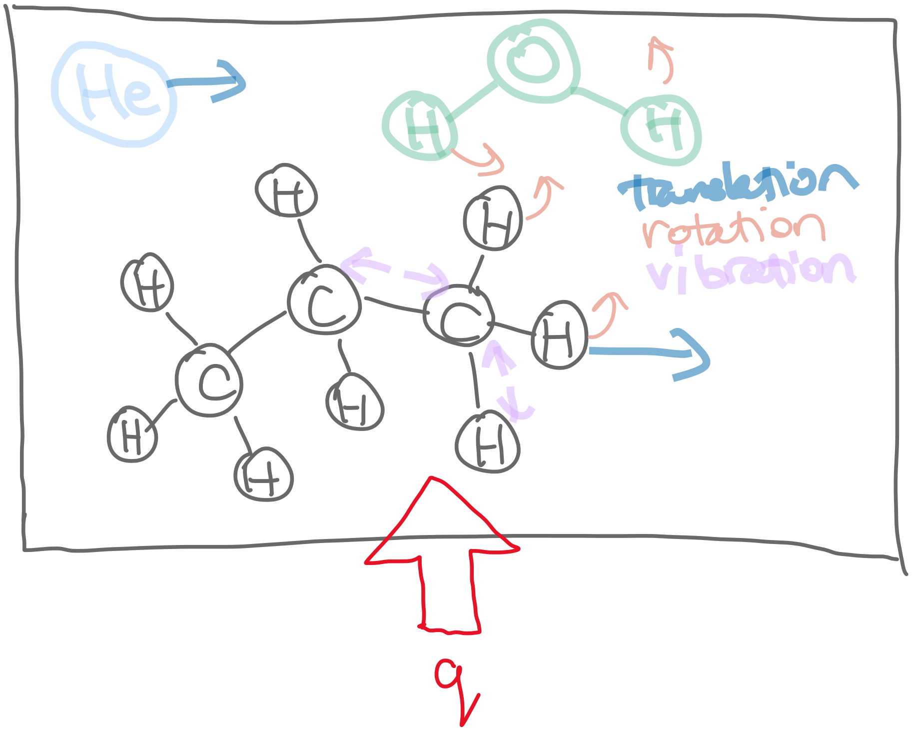
$$\int_i^f dU = \int_{T_i}^{T_f} C_V dT$$

$$\Delta U = C_V \int_{T_i}^{T_f} dT$$

$$\boxed{\Delta U = C_V \Delta T}$$

Experimentally, can obtain C_V by e.g. electrical heating where ΔU is known, and measuring ΔT.

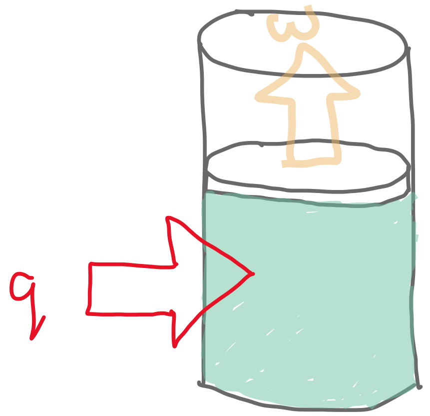
Large C_V: a lot of energy is needed for a change in T.



on a molecular level: generally larger molecules have larger C_V

also, stronger intermolecular interactions imply larger C_V

Topic 2B: Enthalpy



$\Delta U < q$

$$\boxed{H = U + pV}$$

because U, p, and V are all state functions, H is also a state function

How is H related to q?

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

$$H + dH = U + dU + pV + pdV + Vdp + \underset{\sim 0}{\cancel{dpdV}}$$

$$H + dH = \underline{U + pV} + dU + pdV + Vdp$$

$$\cancel{H} + dH = \cancel{H} + dU + pdV + Vdp$$

$$dH = dU + pdV + Vdp$$

$$dH = \underbrace{dU}_{dq + dw} + pdV + Vdp$$

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

condition 1: the system only does expansion work, $dw = -pdV$

$$dH = dq + (-\cancel{pdV}) + \cancel{pdV} + Vdp$$

condition 2: constant pressure

$$dH = dq_p + \cancel{Vdp}$$

$$dH = dq_p$$

$$\Delta H = \int_i^f q_p$$

$$\boxed{\Delta H = q_p}$$

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

heat capacity at constant pressure

Topic 2C: Thermochemistry

Enthalpy of Reaction

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$

standard state

$\Delta_r H^\ominus = -890\ kJ\cdot mol^{-1}$

reaction

Enthalpy of Formation

$6\,C(s, graphite) + 3H_2(g) \rightarrow C_6H_6(l)$

$\Delta_f H^\ominus = +49.0\ kJ\cdot mol^{-1}$

$N_2(g) \rightarrow N_2(g)$

$\Delta_f H^\ominus = 0\ kJ\cdot mol^{-1}$

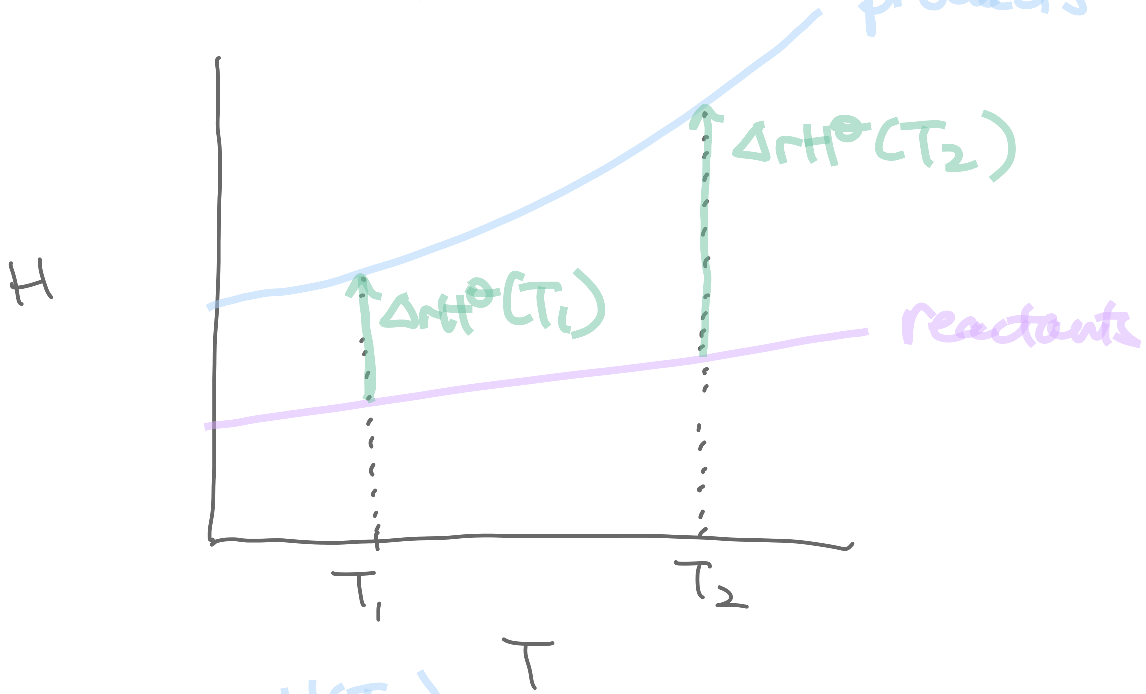
Reference state of an element is its most stable state at the specified temperature and 1 bar.

stoichiometric coefficient

$$\Delta_r H^\ominus = \sum_{products} \boxed{\nu}\,\Delta_f H^\ominus - \sum_{reactants} \boxed{\nu}\,\Delta_f H^\ominus$$

The Temperature Dependence of

Reaction Enthalpies



$\leftarrow H(T_2) - H(T_1)$

$$\Delta H = C_p \Delta T$$

$$\boxed{H(T_2) = H(T_1) + \int_{T_1}^{T_2} C_p \, dT}$$

applies to every species in reaction

$$\Delta_r H^\circ(T_2) = H_B(T_1) + \int_{T_1}^{T_2} C_{p,B} \, dT$$

$$- H_A(T_1) + \int_{T_1}^{T_2} C_{p,A} \, dT$$

$$\boxed{\Delta_r H^\ominus(T_2) = \Delta_r H^\ominus(T_1) + \int_{T_1}^{T_2} \underbrace{\Delta_r C_p^\ominus}\, dT}$$

differential form

$$\Delta_r C_p^\ominus = \sum_{\text{products}} \nu C_{p,m}^\ominus - \sum_{\text{reactants}} \nu C_{p,m}^\ominus$$

$$\boxed{\Delta_r H^\circ(T_2) = \Delta_r H^\circ(T_1) + \Delta_r C_p^\circ (T_2 - T_1)}$$

integrated form

Kirchhoff's Law