

Thermodynamics and Kinetics

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What is the energy we calculated?

- You used GAMESS to calculate the internal (ground state) electronic energy for various molecules under the Born-Oppenheimer approximation.



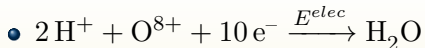
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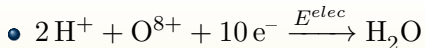
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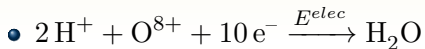
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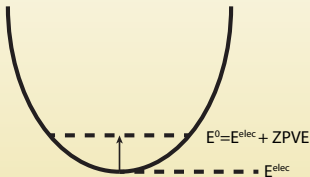
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What is the energy of a molecule?

- E^0 is the minimum energy of a molecule.
- Higher energies are possible through electronic or vibrational excitations as well as translational and rotational motion. If we assume these contributions are separable

$$E = E^0 + E^{elec'} + E^{vib} + E^{rot} + E^{trans}$$

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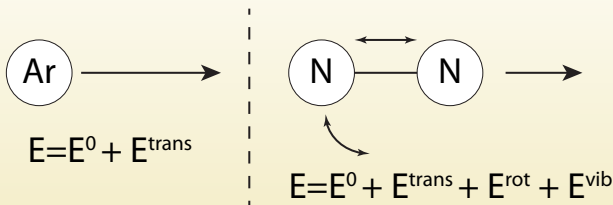
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- We need to specify these quantities to describe the microscopic state of the molecule.

- Macroscopically we want the average value of these quantities over all possible states of an ensemble of molecules at some specified externally imposed set of thermodynamic conditions. (ensemble average)
- This is the domain of statistical mechanics.
- The relative probability of a molecule being in a state with energy E_i above E^0 is given by the Boltzmann factor

$$P_i \propto e^{-E_i\beta}, \quad \beta = \frac{1}{k_B T}$$

- Sum over all states is the (in this canonical, N, V, T free variables) partition function

$$Q(N, V, T) = \sum_i e^{-E_i\beta}$$

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- All thermodynamic quantities can be derived from Q

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$$U = - \left. \frac{\partial \ln Q}{\partial \beta} \right|_{NV}$$

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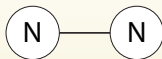
$$G = -\frac{\ln Q}{\beta} + \frac{V}{\beta} \left. \frac{\partial \ln Q}{\partial V} \right|_{NT}$$

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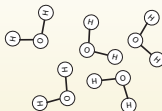
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Ideal Gas



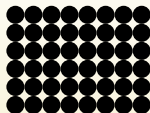
No intermolecular interactions
Only sum over states
of individual molecule

Bulk Liquid



Need all inter/intramolecular
states, MC/MD to get thermo-
dynamic quantities

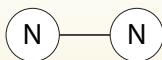
Macroscopic Solid



No rotation or translation.
Sum over vibrational modes

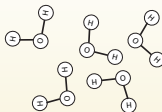
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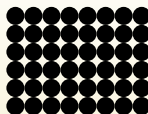
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- Here we will focus on an ideal gas.

- For an ideal gas of N indistinguishable molecules

$$Q = \frac{q^N(V, T)}{N!}$$

- Once again assuming decoupling the molecular partition function is

$$q = q_{trans} q_{vib} q_{rot} q_{elec}$$

- We can treat each of these pieces with models you have seen before. GAMESS chooses 298.15 K by default.

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- Translation: Particle in a 3-D box (have to choose a standard state pressure, GAMESS chooses 1 atm)
- Rotation: Rigid Rotor
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- Typical values

$$q_{trans} \approx 10^{30} \quad q_{rot} \approx 100 \quad q_{vib} \approx 1 \quad q_{elec} \approx g_0$$

- GAMESS will give you these values making the key assumptions on the previous slide after a frequency calculation.
- Lets look at Argon

Ideal Gas Example

- Ar gas

THERMOCHEMISTRY AT T= 298.15 K

USING IDEAL GAS, RIGID ROTOR, HARMONIC NORMAL MODE APPROXIMATIONS.

P= 1.01325E+05 PASCAL.

ALL FREQUENCIES ARE SCALED BY 1.00000

| | Q | LN Q |
|--------|-------------|-----------|
| ELEC. | 1.00000E+00 | 0.000000 |
| TRANS. | 9.92422E+06 | 16.110489 |
| ROT. | 1.00000E+00 | 0.000000 |
| VIB. | 1.00000E+00 | 0.000000 |
| TOT. | 9.92422E+06 | 16.110489 |

| | E | H | G | CV | CP | S |
|---|--------|--------|---------|---------|---------|-------------|
| | KJ/MOL | KJ/MOL | KJ/MOL | J/MOL-K | J/MOL-K | J/MOL-K |
| ELEC. | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| TRANS. | 3.718 | 6.197 | -39.937 | 12.472 | 20.786 | 154.735 |
| ROT. | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| VIB. | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| TOTAL | 3.718 | 6.197 | -39.937 | 12.472 | 20.786 | 154.735 |
| VIB. THERMAL CORRECTION E(T)-E(0) = H(T)-H(0) = | | | | | | 0.000 J/MOL |

- Note: GAMESS scales q_{trans} by 2.46×10^{25}

Ideal Gas Example

• Now N₂

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THE MOMENTS **OF** INERTIA ARE (**IN** AMU*BOHR**2)

0.00000 30.68954 30.68954

THE ROTATIONAL SYMMETRY NUMBER **IS** 2.0

THE ROTATIONAL CONSTANTS ARE (**IN** GHZ)

0.00000 58.75254 58.75254

THE HARMONIC ZERO POINT ENERGY **IS** (SCALED BY 1.000)

0.006598 HARTREE/MOLECULE 1448.038767 CM**2/MOLECULE

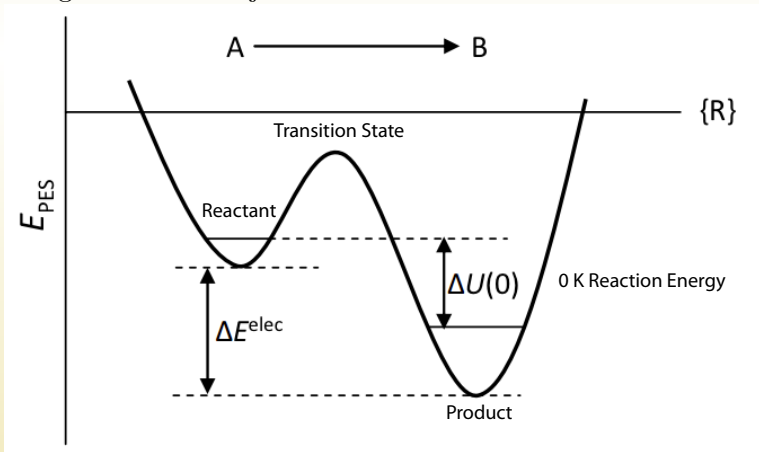
4.140155 KCAL/MOL 17.322407 KJ/MOL

| | Q | LN Q |
|--------|-------------|-----------|
| ELEC. | 1.00000E+00 | 0.000000 |
| TRANS. | 5.82551E+06 | 15.577756 |
| ROT. | 5.28208E+01 | 3.966904 |
| VIB. | 1.00000E+00 | 0.000001 |
| TOT. | 3.07708E+08 | 19.544662 |

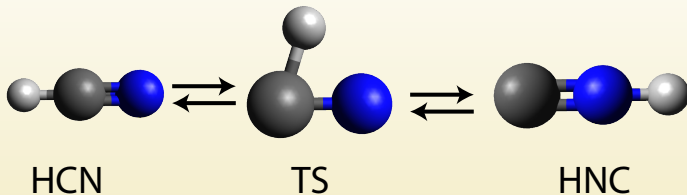
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|---|--------|--------|---------|---------|---------|---------|
| | KJ/MOL | KJ/MOL | KJ/MOL | J/MOL-K | J/MOL-K | J/MOL-K |
| ELEC. | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| TRANS. | 3.718 | 6.197 | -38.616 | 12.472 | 20.786 | 150.306 |
| ROT. | 2.479 | 2.479 | -9.834 | 8.314 | 8.314 | 41.297 |
| VIB. | 17.322 | 17.322 | 17.322 | 0.001 | 0.001 | 0.000 |
| TOTAL | 23.520 | 25.999 | -31.128 | 20.787 | 29.102 | 191.603 |
| VIB. THERMAL CORRECTION E(T)-E(0) = H(T)-H(0) = | | | | | 0.030 | J/MOL |

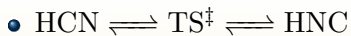
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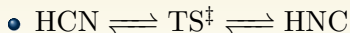
- Now we can use this information to calculate reaction energies. First lets just start with 0 K
- $\text{HCN} \rightleftharpoons \text{TS}^\ddagger \rightleftharpoons \text{HNC}$



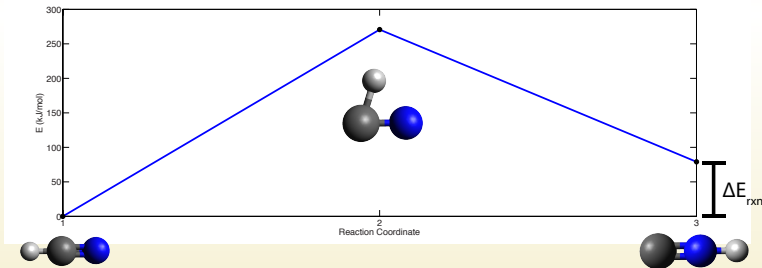


$$\Delta E_{rxn} = \sum E_{products} - \sum E_{reactants}$$

Chemical Reactions



$$\Delta E_{\text{rxn}} = \sum E_{\text{products}} - \sum E_{\text{reactants}}$$

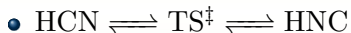


- We can do thermodynamic quantities

$$\Delta H_{\text{rxn}}^{\circ}(T) = \Delta E^{\text{elec}} + \Delta ZPVE + \Delta H^{\circ}(T)_{\text{trans}} + \Delta H^{\circ}(T)_{\text{rot}} + \Delta H^{\circ}(T)_{\text{vib}}$$

Here the Δ is product(s) minus reactant(s).

- $\Delta H_{\text{rxn}}^{\circ} = +77.65 \text{ kJ/mol}$, endothermic reaction



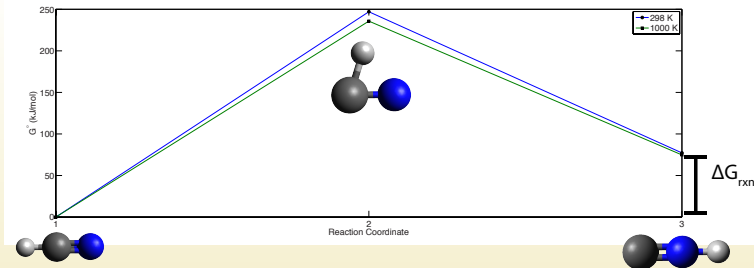
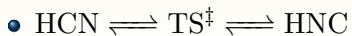
| | E (kJ/mol) | ZPVE | $G_{tot}^\circ(298K)$ | $G_{tot}^\circ(1000\text{ K})$ |
|-----|--------------|---------|-----------------------|--------------------------------|
| HCN | -240693.2 | 50.0165 | -0.76 | -160.462 |
| HNC | -240612.4 | 48.2648 | -2.593 | -164.758 |
| TS | -240403.5 | 30.9667 | -24.35 | -195.324 |

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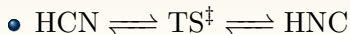
- Here $G_{tot}^\circ(T)$ is the Gibbs free energy contribution from translation, rotation, and vibration at the specified temperature and standard state.

Gibbs Free Energy



- $\text{HCN} \rightleftharpoons \text{TS}^\ddagger \rightleftharpoons \text{HNC}$
- Can calculate Equilibrium constant

$$K = \frac{q_{\text{HNC}}}{q_{\text{HCN}}} e^{-\Delta E_{\text{rxn}}/k_B T} = e^{-\Delta G_{\text{rxn}}^\circ(T)/k_B T}$$



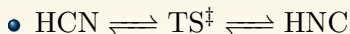
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- We did calculations at two Temperatures we could have also used the Van't Hoff Equation if the temperature range is small enough that $\Delta H_{\text{rxn}}^\circ \approx \text{constant}$

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$$\ln \frac{K(T_2)}{K(T_1)} = -\frac{\Delta H_{\text{rxn}}^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$



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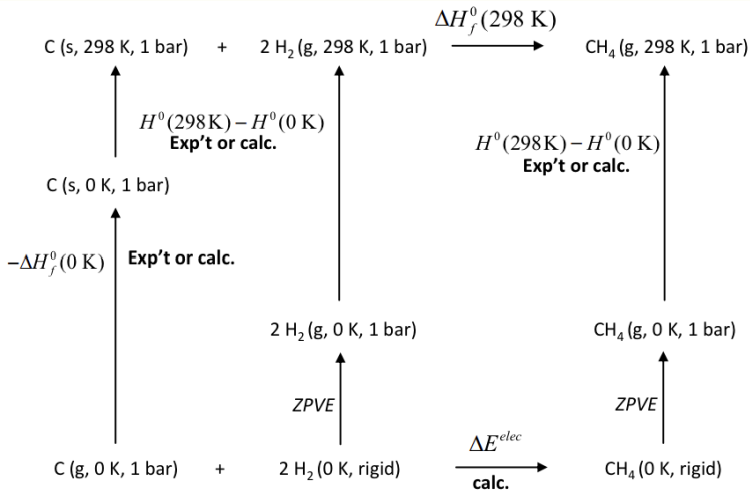
$$\ln \frac{K(T_2)}{K(T_1)} = -\frac{\Delta H_{\text{rxn}}^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

- For arbitrary activities (or pressures assuming Raoult's Law)

$$\Delta G_{\text{rxn}} = \Delta G_{\text{rxn}}^\circ + RT \ln \frac{a_{\text{HNC}}}{a_{\text{HCN}}}$$

Thermodynamic Cycle

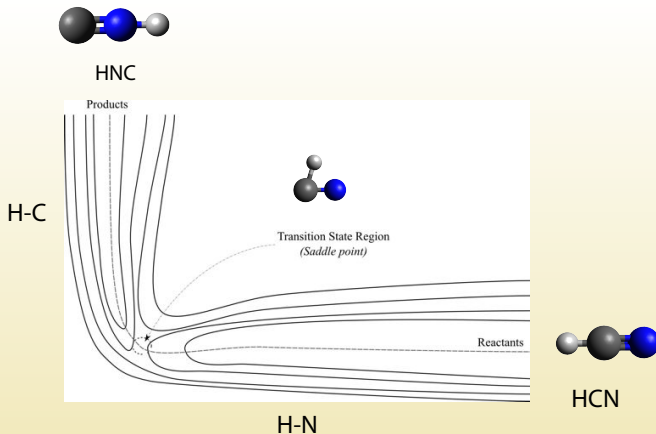
- We can use this approach to calculate all sorts of thermodynamic properties under all different kinds of conditions, for example the heat of formation of methane:



Transition State Theory

Transition state theory assumes

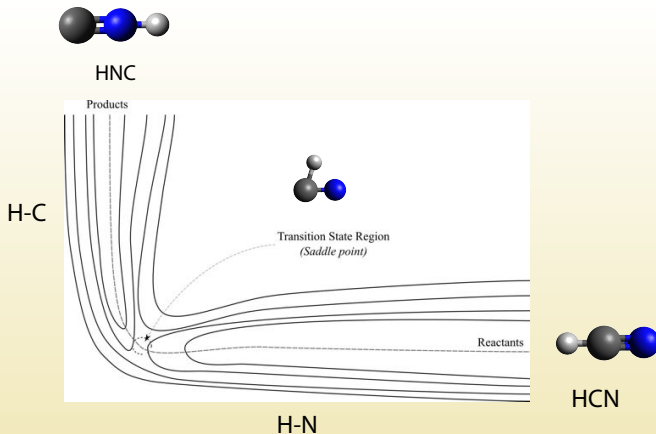
- 1 Existence of a potential energy surface.
- 2 Existence of a dividing surface, point of no return.
- 3 Existence of a critical TS point on that surface.
- 4 Quasi-equilibrium between reactants and TS
- 5 Harmonic PES near the TS



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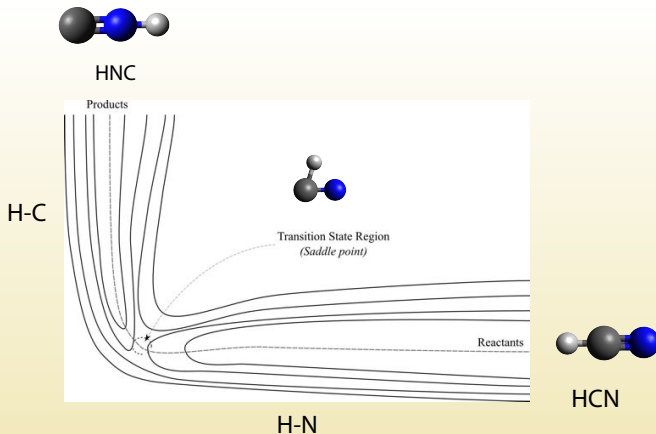
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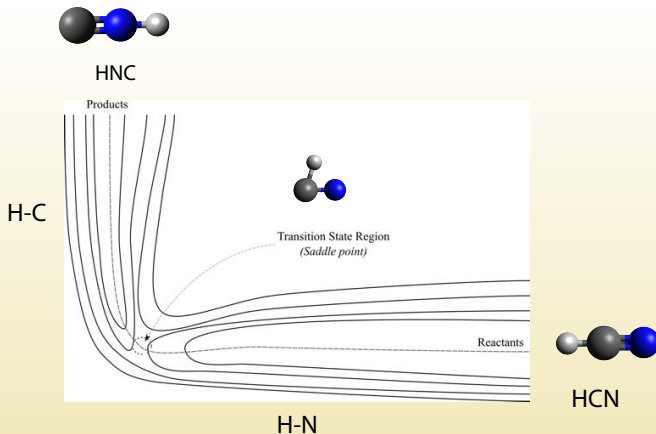
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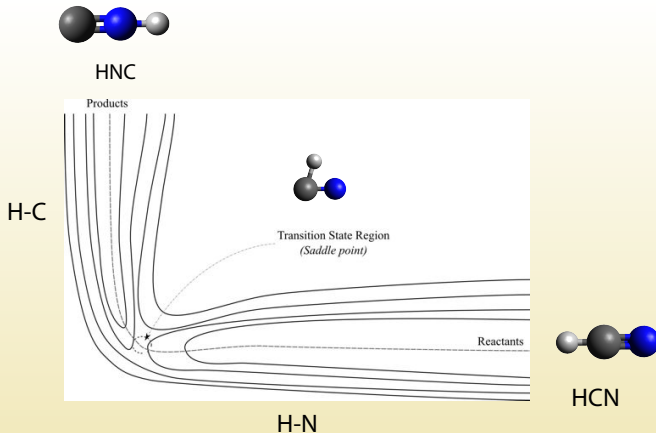
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- Under these assumptions one can show (Δn is change in moles)

$$k_f(T) = \frac{k_B T}{h} \frac{q_{\ddagger}}{q_{\text{reactants}}} (P/RT)^{\Delta n} e^{-\Delta E_a/k_B T}$$

- Could group all the leading terms into $A(T)$

$$k_f(T) = A(T) e^{-\Delta E_a/k_B T}$$

- Looks familiar right?
- equivalently

$$k_f(T) = \frac{k_B T}{h} e^{\frac{-\Delta^\ddagger G^\circ(T)}{k_B T}}$$

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- Looks familiar right?
- equivalently

$$k_f(T) = \frac{k_B T}{h} e^{\frac{-\Delta^\ddagger G^\circ(T)}{k_B T}}$$

- Apparent activation energy given by

$$E_{app} = RT^2 \frac{\partial \ln k}{\partial T}$$

- Under these assumptions one can show (Δn is change in moles)

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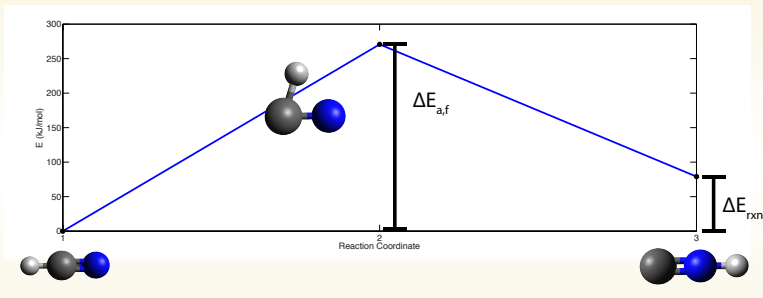
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Kinetics



- $k_r = k_f / K$

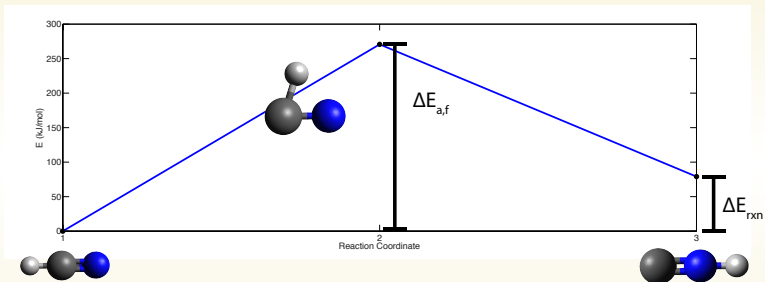
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- Could stick in a mass balance, *e.g.* unsteady CSTR

$$\frac{dC_{HCN}}{dt} = \frac{C_{HCN,0} - C_{HCN}}{\tau} - r$$

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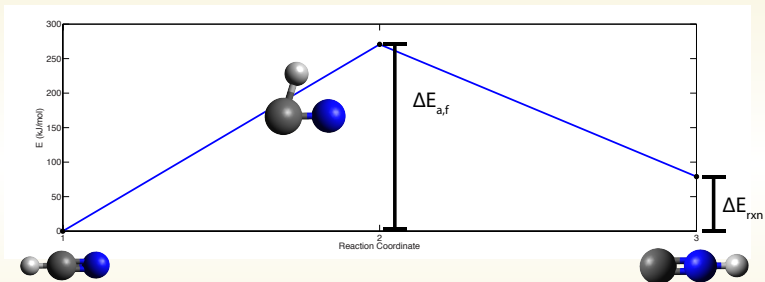
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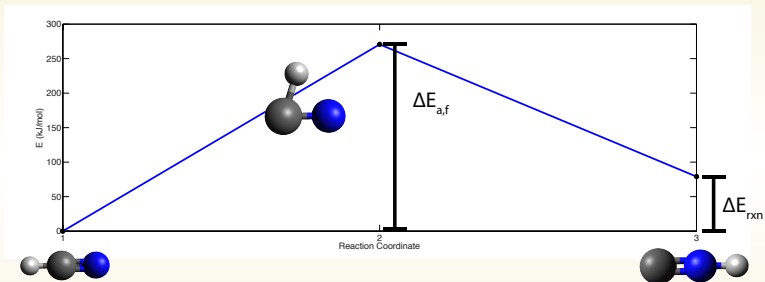
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