I. Calculate $\Delta G^{\ddagger}$ at 298 K for the reaction 2N + H ----> N_2 + H.

Consider $E_a = 5.4 \, kJ \, mol^{-1}$ and $\Delta S^{\ddagger} = 32.6 \, J \, K^{-1} mol^{-1}$

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$$
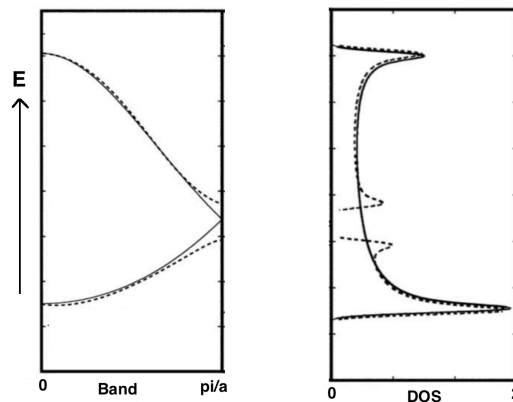
$$E_a = \Delta H^{\ddagger} + pV$$

$$E_a = \Delta H^{\ddagger} + nRT$$

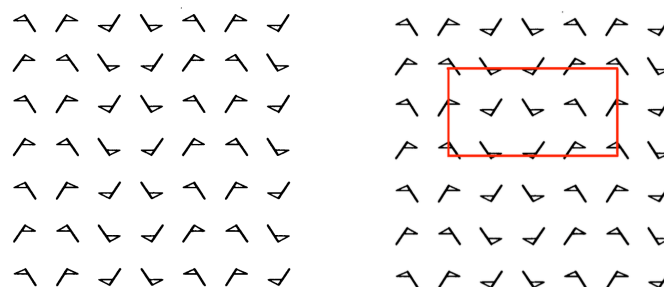Implies that $\Delta H^{\ddagger} = E_a - 3RT$

$$\Delta H^{\ddagger} = -2033 \, J \, mol^{-1}$$

$$\Delta G^{\ddagger} = -2033 - (298)(32.6) \, J \, mol^{-1} = -11.8 \, kJ \, mol^{-1}$$

II. For the band dispersion spectra given below, sketch a schematic density of states (DOS).


III. From the schematic representation of the periodic two-dimensional tiling pattern that is shown below, calculate the total number of basis required to construct a unit cell. Mark the unit cell that was found.


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IV. In the spirit of one electron picture and frontier molecular orbital energy levels diagram, the interaction of a molecule (for example N_2) with iron metal surface has been depicted below. Each one of these interactions indicated involve in charge transfer are labeled with numeric digits. Explain the cases in which interactions

(a) The molecule is donor or acceptor and like-wise the surface is donor or acceptor.

(b) Which interactions are repulsive and attractive? Offer schematic energy level diagrams indicating the features of repulsive and attractive interactions for diagram shown below.

Molecule   Solid Surface
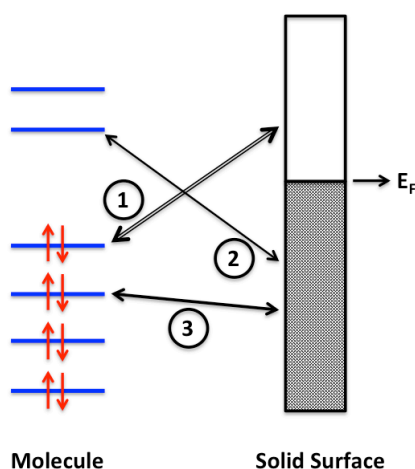
In the case of interaction **1** the molecule is donor and the surface is acceptor (easy) and the interaction **2** is opposite to **1**.

Interaction **3** is an important one in where one would see the interaction between two filled levels between the molecule and solid surface that may lead to a repulsive interaction. However, a stabilizing interaction could be possible for which the schematic energy levels diagrams are shown below.


Repulsive case   Attractive case
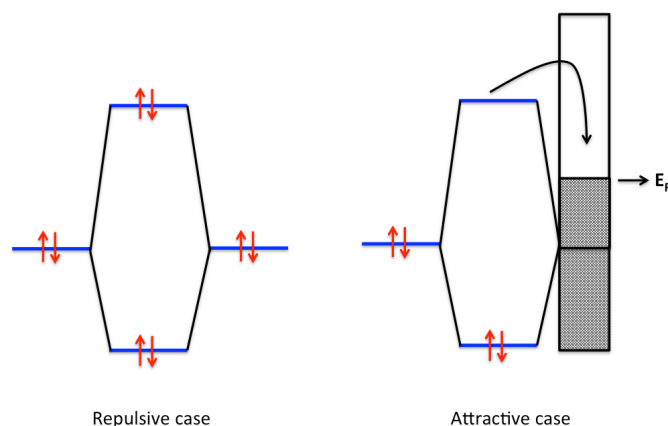
V. Graphically illustrate the Brønsted(Bell)–Evans–Polanyi (BEP) principle for a series of similar chemical reactions in both endothermic and exothermic cases. For illustrating the evolution of enthalpies consider at-least 5 reaction profiles. The schematic graph must be appropriately labeled with all the components depicting the BEP.

Solution: The BEP states that the reaction enthalpy and the rate (activation energy) of similar reactions are linearly correlated. In other words, within the same reaction family, the reaction barriers are linearly correlated to enthalpy of the reactions, that is lower the reaction enthalpy, the lower its activation energy will be. In simple terms, the proportionality may be written as

$$E_a = \alpha(\Delta H)$$

Where E_a is the activation energy and ΔH is the reaction enthalpy with respect to the reference system. The proportionality constant (α) characterizes the location of the transition states along the reaction coordinate.

Reaction coordinate
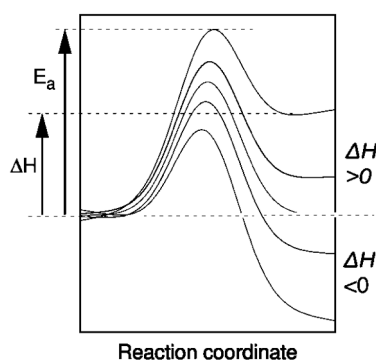
VI. A schematic potential energy surface (PES) is shown below represents a transition between two minima X and Y. The dashed (Red color) line defines the energy reference. Let's say the E^{TS} be a set of energies describing the energy needed to move between the two minima on the PES for a set of different catalysts. For this, construct a functional form that describes the Bronsted/Bell-Evans-Polanyi (BEP) BEP relation.
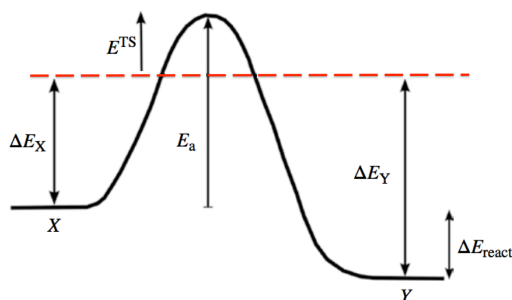
-- Let ΔE_i be a set of adsorption/binding energies (like N_2 binding to the Fe metallic solid surface) for the chemical process moving between the two

minima. If it is, one can define a functional of the form $E^{TS}(\Delta E_i)$, and then according to BEP, the E^{TS} can be written as linear combination of ΔE_i

$$E^{TS} = \sum_i \gamma_i \Delta E_i + \xi$$

where γ is the BEP coefficient and ξ is the slope intercept (refer the lecture notes for more details). See also the question above that would further meaning to such functional defined as above.

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