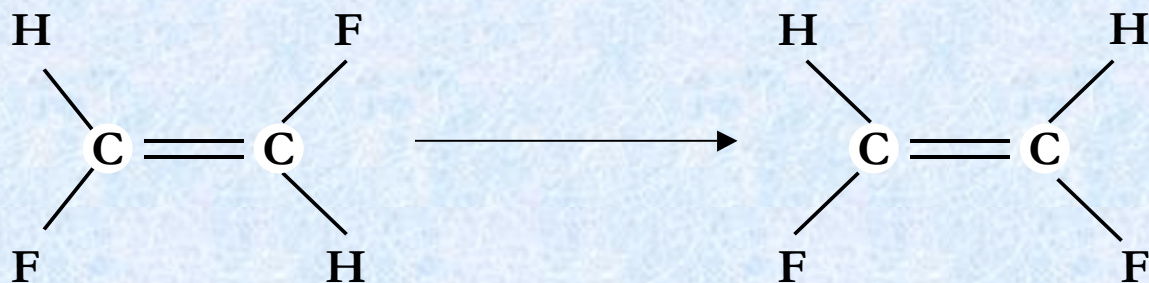


Temperature Dependence of ΔH



trans 1,2 difluoroethylene

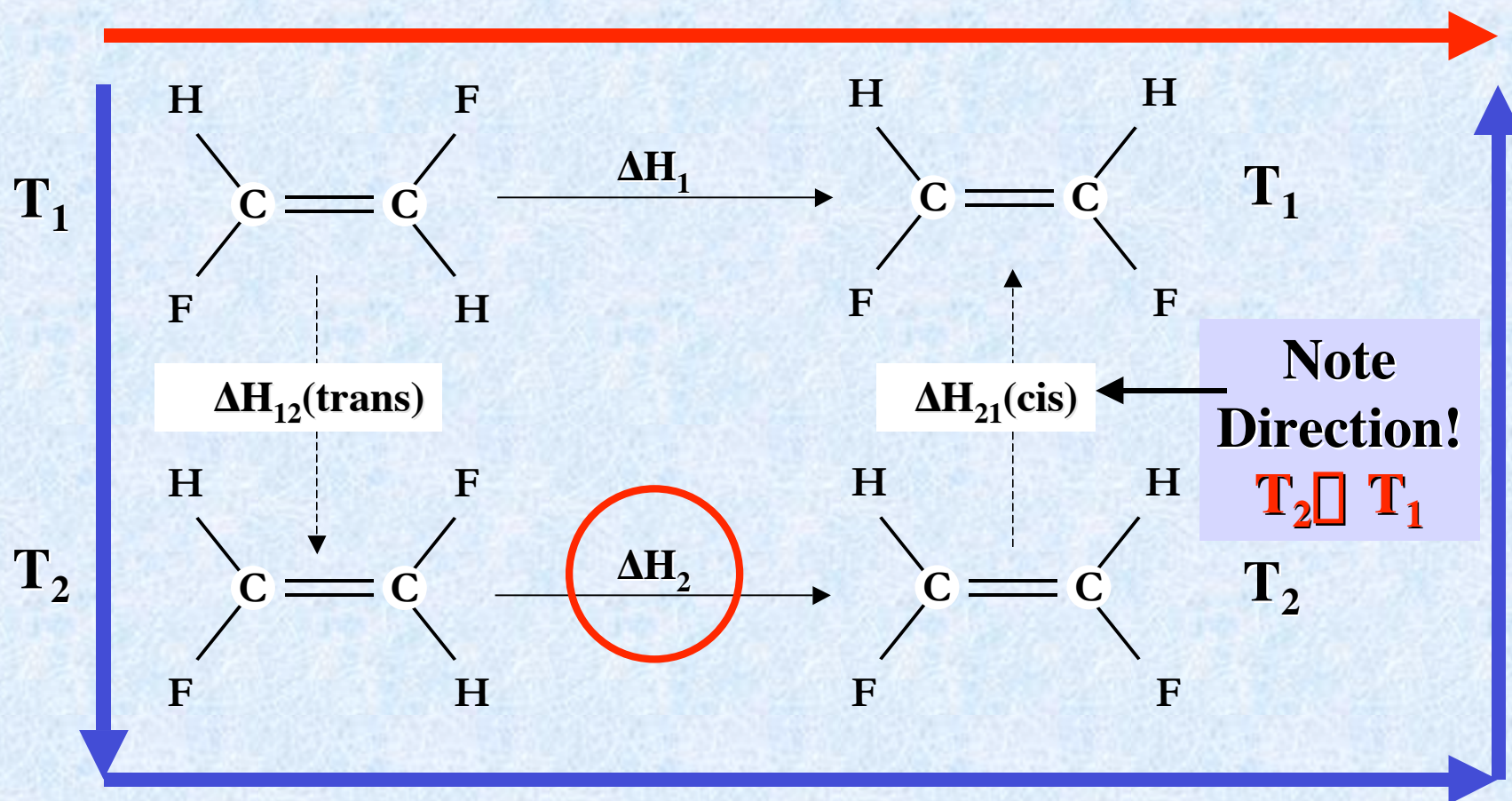
cis 1,2 difluoroethylene

Know $\Delta H = q_p$:

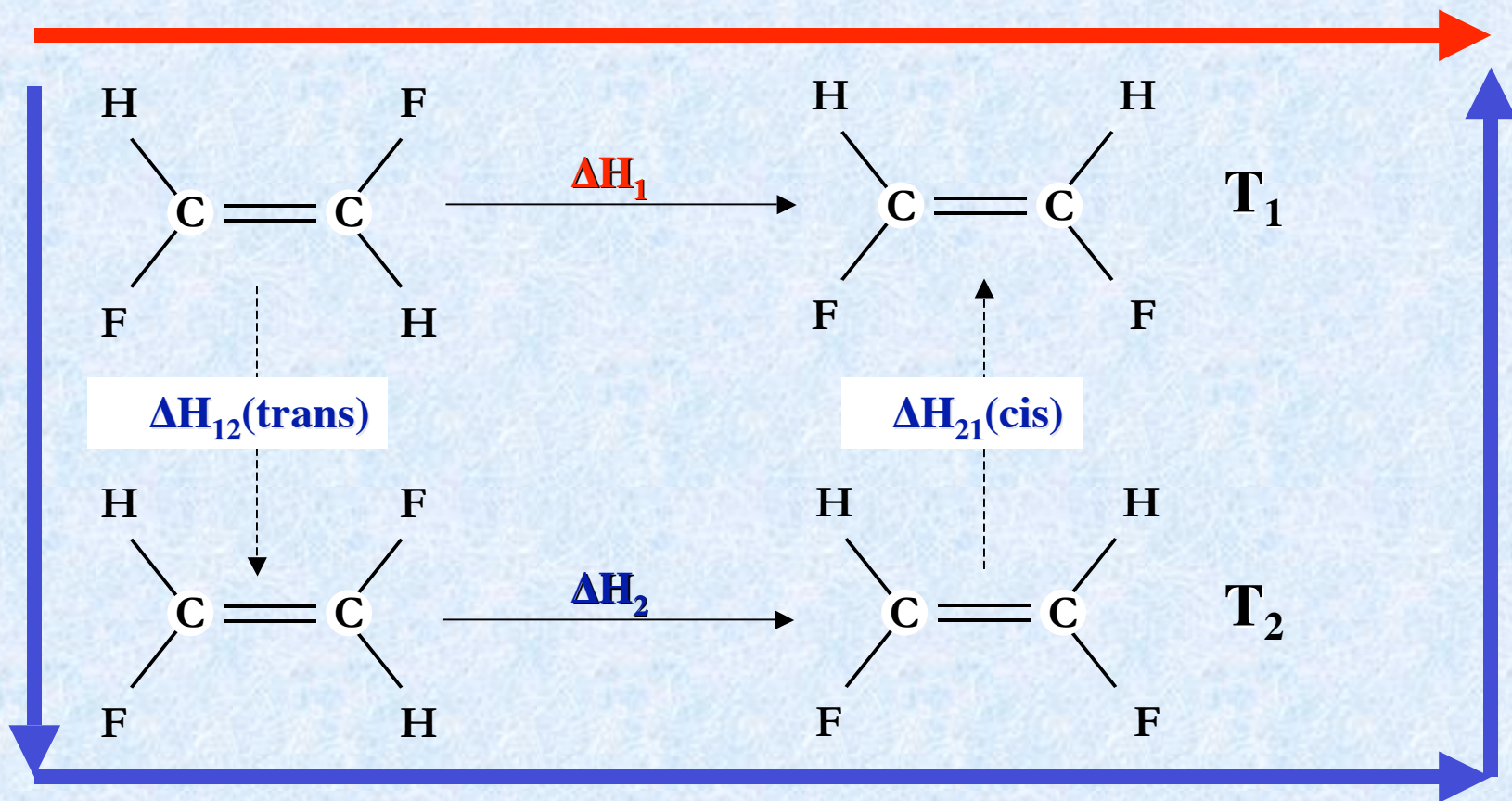
Two paths:

1) **Trans (T₁) \rightarrow Cis (T₁)**

2) **Trans (T₁) \rightarrow Trans (T₂) \rightarrow Cis (T₂) \rightarrow Cis (T₁)**



$$\Delta H_1 = \Delta H_{12} (\text{Trans}) + \Delta H_2 + \Delta H_{21} (\text{Cis})$$



Rearrange this to get:

$$\Delta H_2 + \Delta H_{12} (\text{Trans}) = \Delta H_1 - \Delta H_{21} (\text{Cis})$$

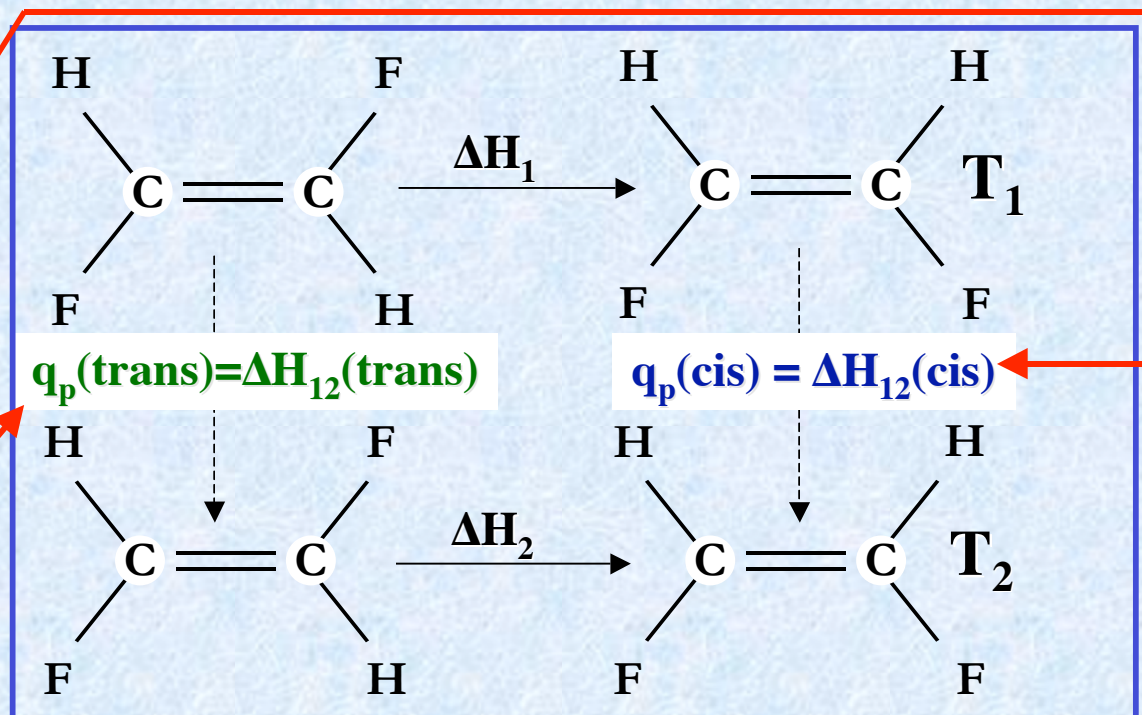
Note: $\Delta H_{21} (\text{Cis}) = -\Delta H_{12} (\text{Cis})$

$$\Delta H_2 + \Delta H_{12} (\text{Trans}) = \Delta H_1 + \Delta H_{12} (\text{Cis})$$

$$\Delta H_2 (T_2) = \Delta H_1 (T_1) + \Delta H_{12}(\text{cis}) - \Delta H_{12}(\text{trans})$$

Since $\Delta H = q_p$ □

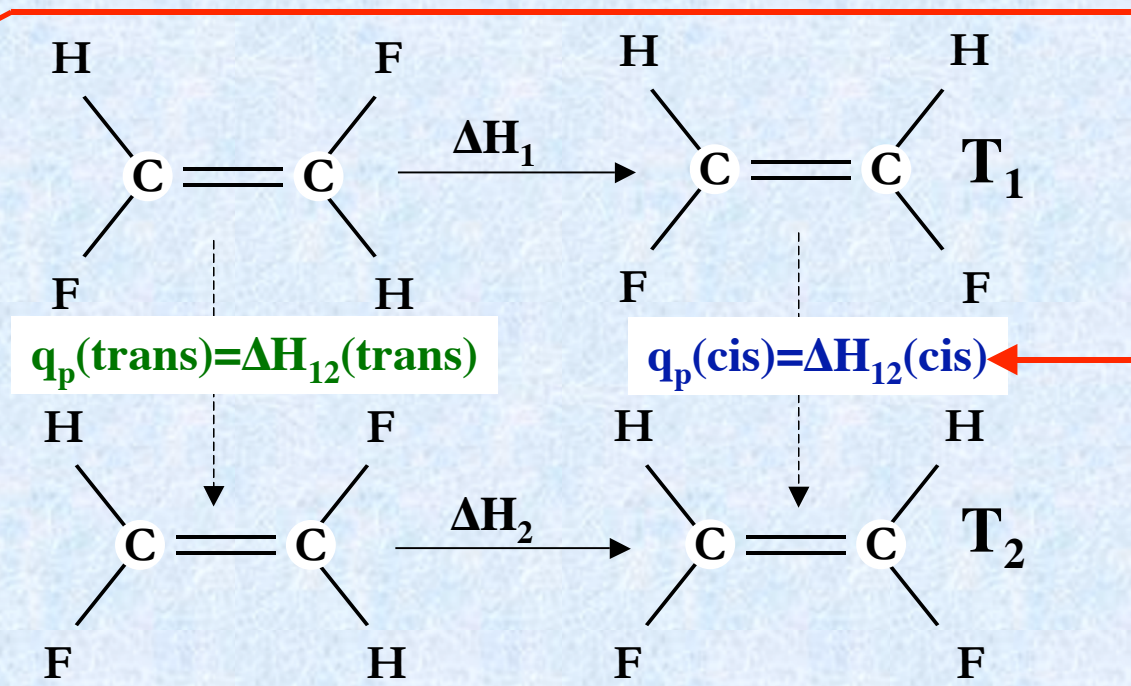
$q_p(\text{cis})$ is heat needed to increase temperature of cis 1,2 from T_1 □ T_2



However, $q_p(\text{cis})$ and $q_p(\text{trans})$ correspond to **physical** changes not chemical changes, so □

$$q_p(\text{cis}) = C_p(\text{cis}) \Delta T$$

with $\Delta T = T_2 - T_1$

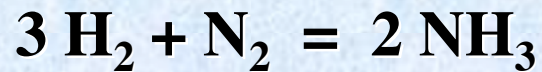


$$\Delta H_2 = \Delta H_1 + \Delta C_p \Delta T \text{ where } \Delta C_p = [C_p(\text{cis}) - C_p(\text{trans})]$$

Or, in the general case:

$$\Delta C_p = \sum C_p(\text{products}) - \sum C_p(\text{reactants})$$

Numerical Example of $\Delta H (T_2) = \Delta H (T_1) + \Delta C_p \Delta T$



$$\begin{aligned} 3 \text{ H}_2 + \text{ N}_2 = 2 \text{ NH}_3 \quad \Delta H_{298}^\circ &= 2 \Delta H_f^\circ (\text{NH}_3) \\ &= 2 (-46.19 \text{ kJoules/mole }) = -92.38 \text{ kJoule} \end{aligned}$$

Simplest picture: $C_p (\text{ H}_2) = C_p (\text{ N}_2) = (5/2)R + R = (7/2)R$

$$C_p (\text{NH}_3) = (6/2) R + R = 4R$$

$$\Delta H_{398}^\circ = -92.38 \text{ kJoules} + (-6 (8.314) \text{ joule)/deg) } 100 \text{ deg}$$

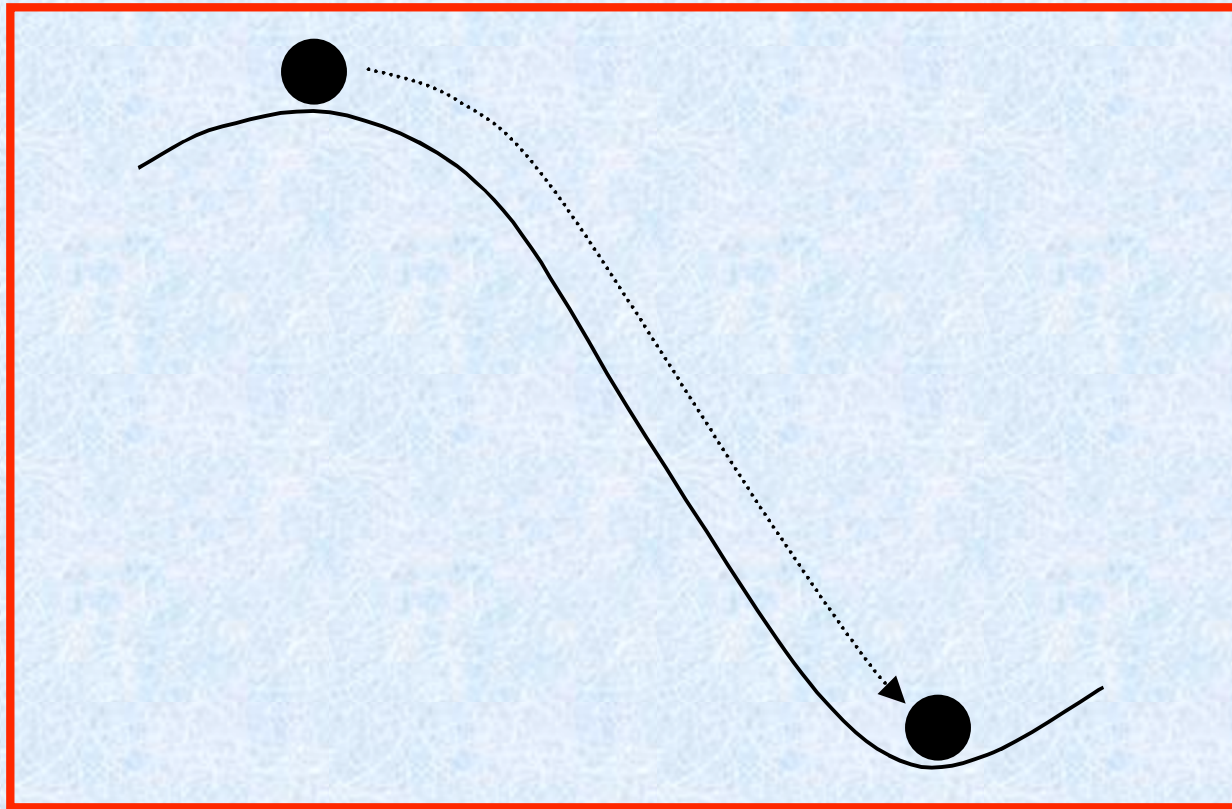
$$= -92.38 - 4.9884 \text{ kJoules} = -97.37 \text{ kJoules}$$

$$\Delta H_{398}^\circ = -97.37 \text{ kJoules using simplest heat capacity}$$

Small, but not negligible change with temperature (5-6%)

The Second Law and the Definition of Entropy

We know that a ball will roll down hill in a gravitational field to arrive at a lower potential energy :



Occurs spontaneously. Don't need to do work to get ball to roll down hill.

**Opposite process of ball rolling up hill requires work be done!
Uphill process is up in energy -- does not occur spontaneously.**

i.e. are all energy down hill processes spontaneous and all energy up hill processes not spontaneous?

Look at some chemical systems that undergo spontaneous reaction:

These spontaneous processes are exothermic or energy downhill! Maybe E is all that counts!

All evaporations:



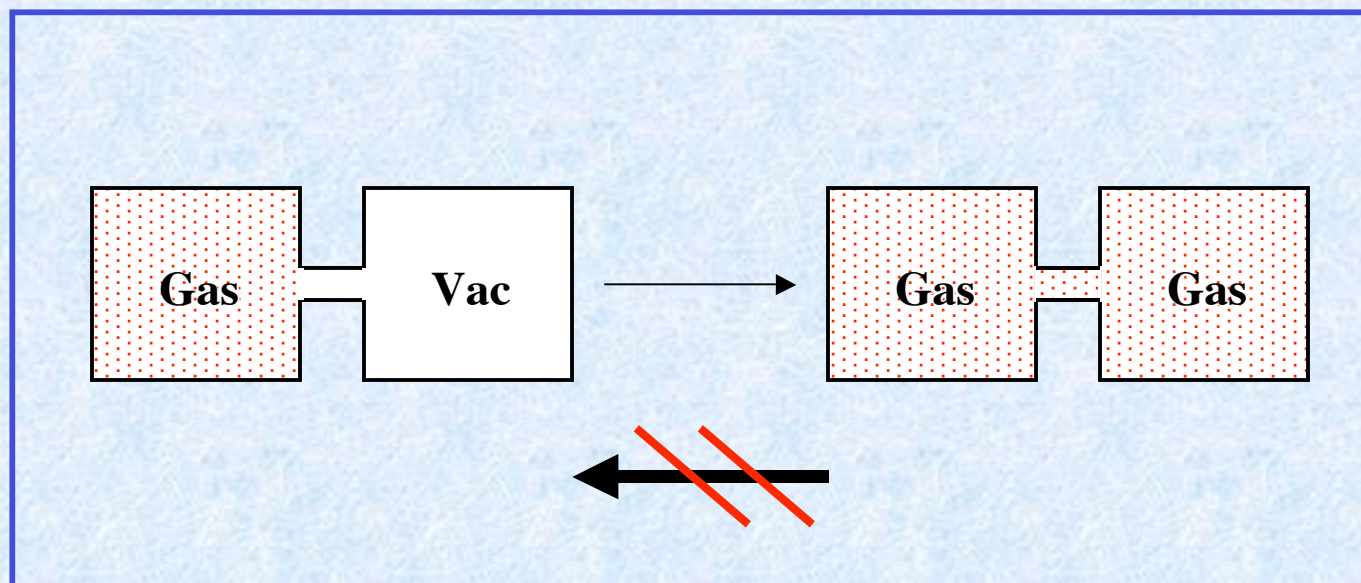
$$\Delta H_{\text{vap}}^\circ = + 44.0 \text{ kJ}$$

endothermic

ΔH alone (its sign) does not seem to predict which way a reaction will proceed spontaneously.

Two other observations:

**$\Delta E = 0$ at
const T so
have no
energy gain
or loss**



Entropy in Action

Probability for a molecule to be on left is $(1/2)$. Probability to be on right is also $(1/2)$

Each configuration has a probability of $(1/2)(1/2)$ □
 $(1/2)(1/2)=(1/16)$



Configurations with equal number of molecules on left and right occur 6 times! Total probability for these configurations is $6/16$.

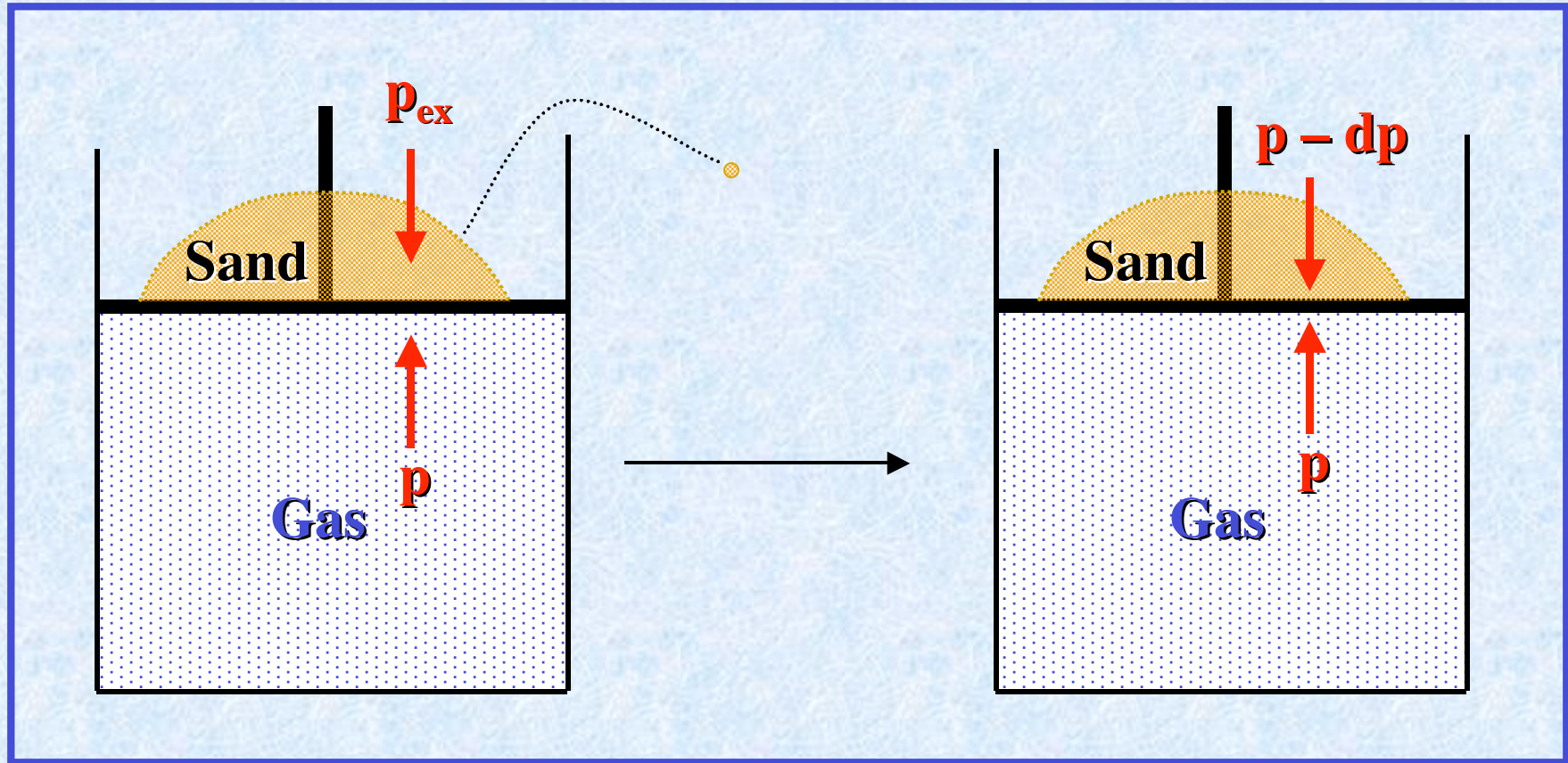
Imagine the situation with 10^{23} molecules!

For an ideal gas, all configurations are of equal energy

Reversible and Irreversible Processes

Reversible processes: A reversible process is one in which the value of all thermodynamic state functions can be determined throughout the process of change. (T, p for system and surroundings (bath) differ only by dT , dp)

(This is analogous to having well defined functions in mathematics -- continuous etc.) must be able to define T, p, V, E throughout process.



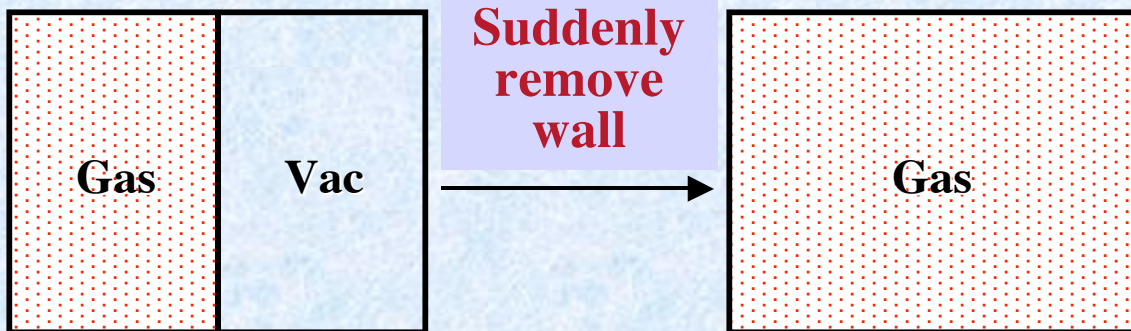
Assume at start that force due to weight of sand is sufficient to just balance pressure of gas:

$p = p_{\text{ex}}$ once again (except now p, p_{ex} are smaller than their initial value and V is larger by an infinitesimal amount).

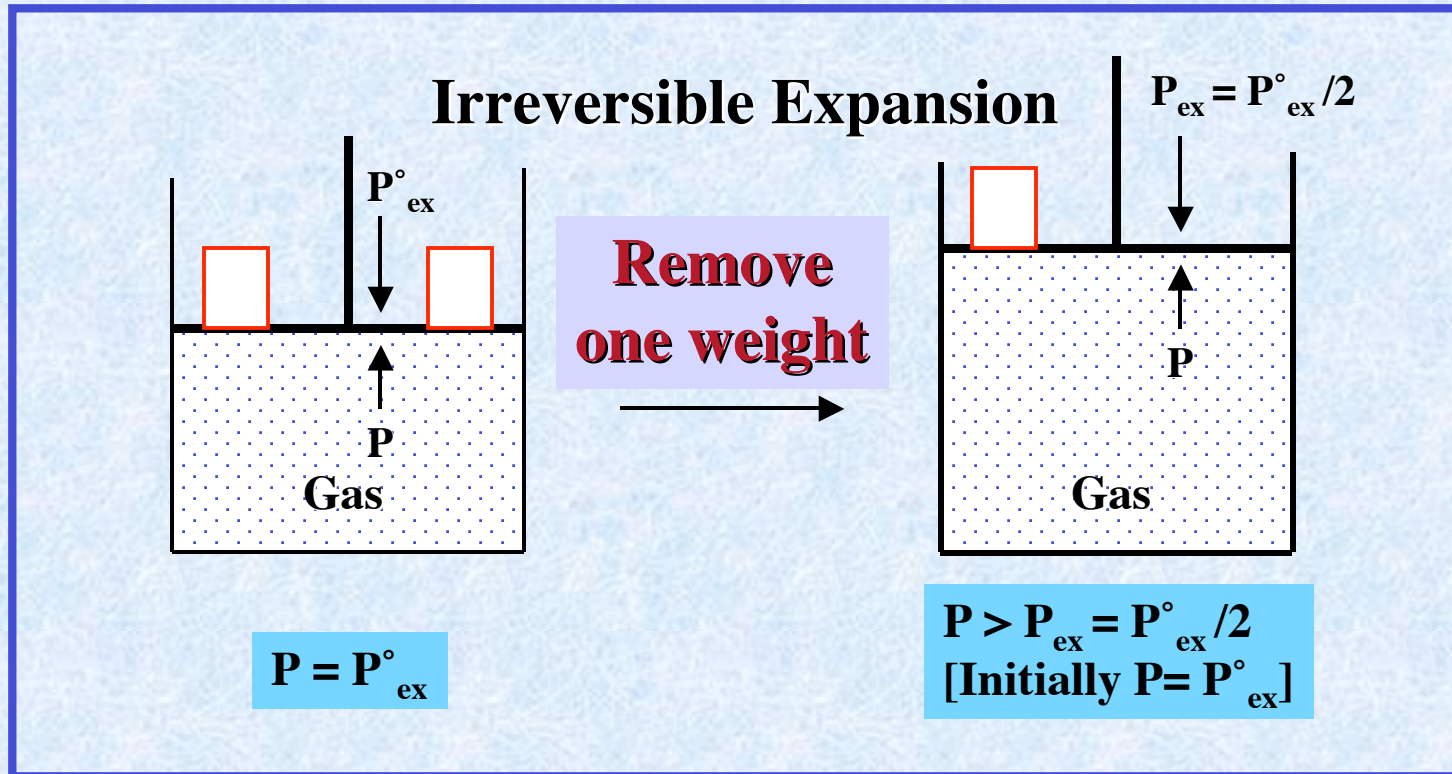
Two examples of irreversible expansions:

A)

Irreversible Expansion



B)



Since p_{ex} , p_{gas} differ only by an infinitesimal amount can reverse any change by going backward an infinitesimal amount.