

S_{298}° Have tables of these in books.

Relationship between absolute entropies and entropies of formation:

Example $(1/2)N_2 + (1/2)O_2 \rightleftharpoons NO$ $T = 298, P = 1 \text{ atm}$

$S_{298}^{\circ}(N_2), S_{298}^{\circ}(O_2) \neq 0$

N.B. !!

By definition, however, $\Delta S \equiv \Delta S_f^{\circ} (NO)$

**(C_p different for each
Substance and not
Independent of T)**

Also by definition

$$\Delta S_f^\circ (\text{NO}) = \Delta S_f^\circ (\text{NO}) - (1/2) [\Delta S_f^\circ (\text{N}_2) + \Delta S_f^\circ (\text{O}_2)]$$

ΔS_f° is entropy change in forming a compound from its elements in their standard state.

S_{298}° is entropy change for any substance going from $T = 0$ \square $T = 298$

So for a reaction:

Special case for a substance which has a phase transition between T of interest and $T = 0$.



$C_p = \text{heat cap H}_2\text{O (s)}$ □

Step 1

$$[dq_{\text{rev}} = C_p dT]$$

$C_p' = \text{heat cap H}_2\text{O (l)}$ □

Step 3

Step 2, $q_{\text{rev}} = \Delta H_{\text{fus}}$ (heat of fusion or melting at constant $T = T_m$)

$$\Delta S(0 \rightarrow T_f) = \int_0^{T_m} \frac{C_p dT}{T} + \frac{\Delta H_{\text{fus}}}{T_m} + \int_{T_m}^{T_f} \frac{C_p' dT}{T}$$

All solid

↑
 ΔS_1

↑
 ΔS_2

Solid
□
liquid

↑
 ΔS_3

All
liquid

Free Energy

$\Delta S = 0$ for reversible process

But ΔS is for system and surroundings (i.e. the universe)

Would like a function which tells us if a process is spontaneous or not without referring to surroundings.

Define new State Function

Most common conditions under which chemical changes occur are P, T = consts □

$$\Delta G = \Delta H - \Delta(TS) = \Delta H - T\Delta S$$

$$\Delta G = q - T\Delta S$$

$$\Delta G = q - q_{\text{rev}}$$

If a process is reversible $q = q_{\text{rev}}$, $\Delta G = 0$

All at const T, P

Thus, at constant T, P compute ΔG for system alone to determine if a process is spontaneous/irreversible.

$\Delta G > 0$ \square not spontaneous but reverse is!

Bonus * Bonus * Bonus *
Bonus * Bonus * Bonus



$\Delta G > 0$ for $T (31.5) < 5012$

$T < 159^\circ\text{K}$

$\Delta G < 0$ for $T (31.5) > 5012$

$T > 159^\circ\text{K}$

$T = 159^\circ\text{K}$ is melting pt!

Get **ir**reversible conversion of s \rightleftharpoons l above T_m .

Get **ir**reversible conversion to solid:



Consider freezing of water:



$$\Delta H = -6007 \text{ joules/mole} \quad \Delta S = -21.99 \text{ joules/mole-deg}$$

$$\Delta G = \Delta H - T\Delta S = -6007 \text{ joules} - T (-21.99 \text{ joules/deg})$$

273

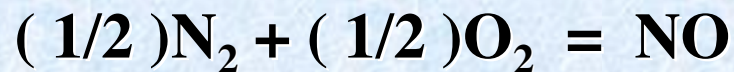
$\Delta G > 0$ for
 $T (21.99) > 6007$
or $T > 273^\circ\text{K}$
Water won't
freeze Spontaneously!

$\Delta G < 0$ for
 $T (21.99) < 6007$
or $T < 273^\circ\text{K}$
Water Freezes
Spontaneously

Water/Ice
Equilibrium
Point
at $P=1 \text{ atm}$
 $T=273$

Free energy and Equilibrium Constants

Standard free energy of formation, 298°K, 1 atm.



$$= \Delta S_f^\circ (\text{NO}) - \left(\frac{1}{2} \right) \Delta S_f^\circ (\text{N}_2) - \left(\frac{1}{2} \right) \Delta S_f^\circ (\text{O}_2) = \Delta S_f^\circ (\text{NO})$$

$$\Delta S_f^\circ (\text{N}_2, \text{O}_2) = 0$$



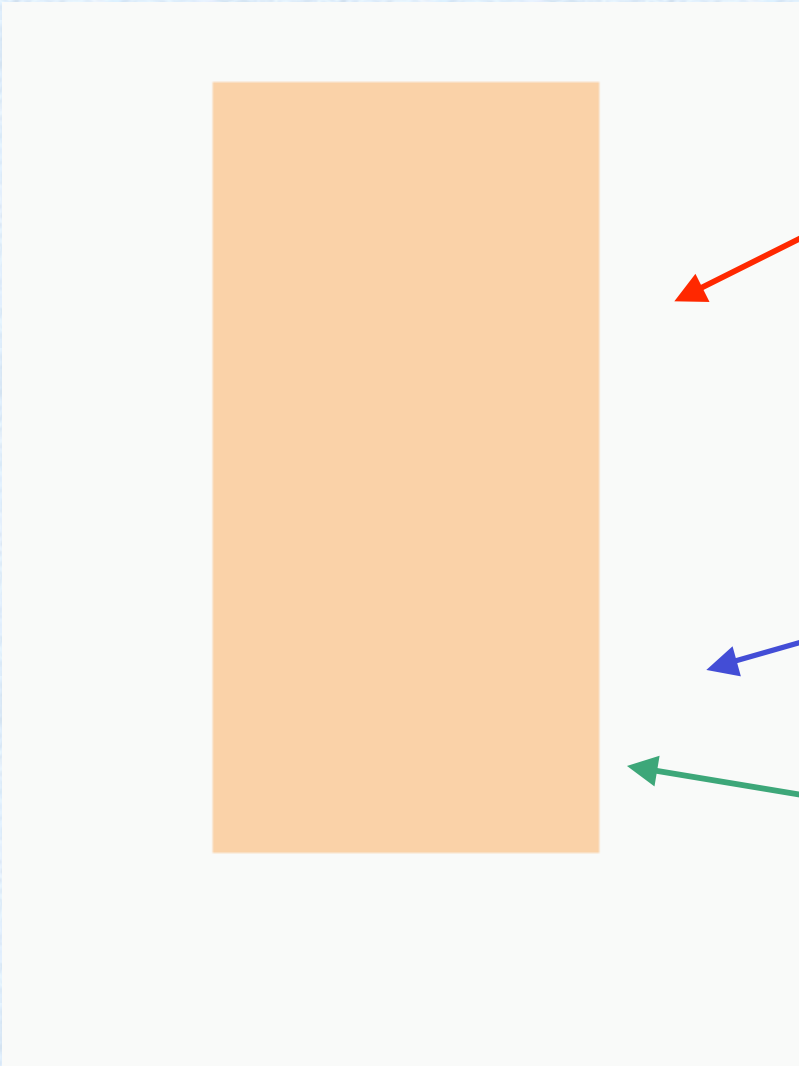
0



0

ΔG , ΔH , ΔS changes for the reaction: $3\text{NO}(\text{g}) \rightleftharpoons \text{N}_2\text{O}(\text{g}) + \text{NO}_2(\text{g})$

However, ΔG varies by $> 100\%$ over this range because the S term is multiplied by T with
$$\Delta G = \Delta H - T\Delta S$$



ΔH varies less than 5% over the range $0\text{-}300^\circ\text{C}$

ΔS varies only about 5% over the range $0\text{-}300^\circ\text{C}$

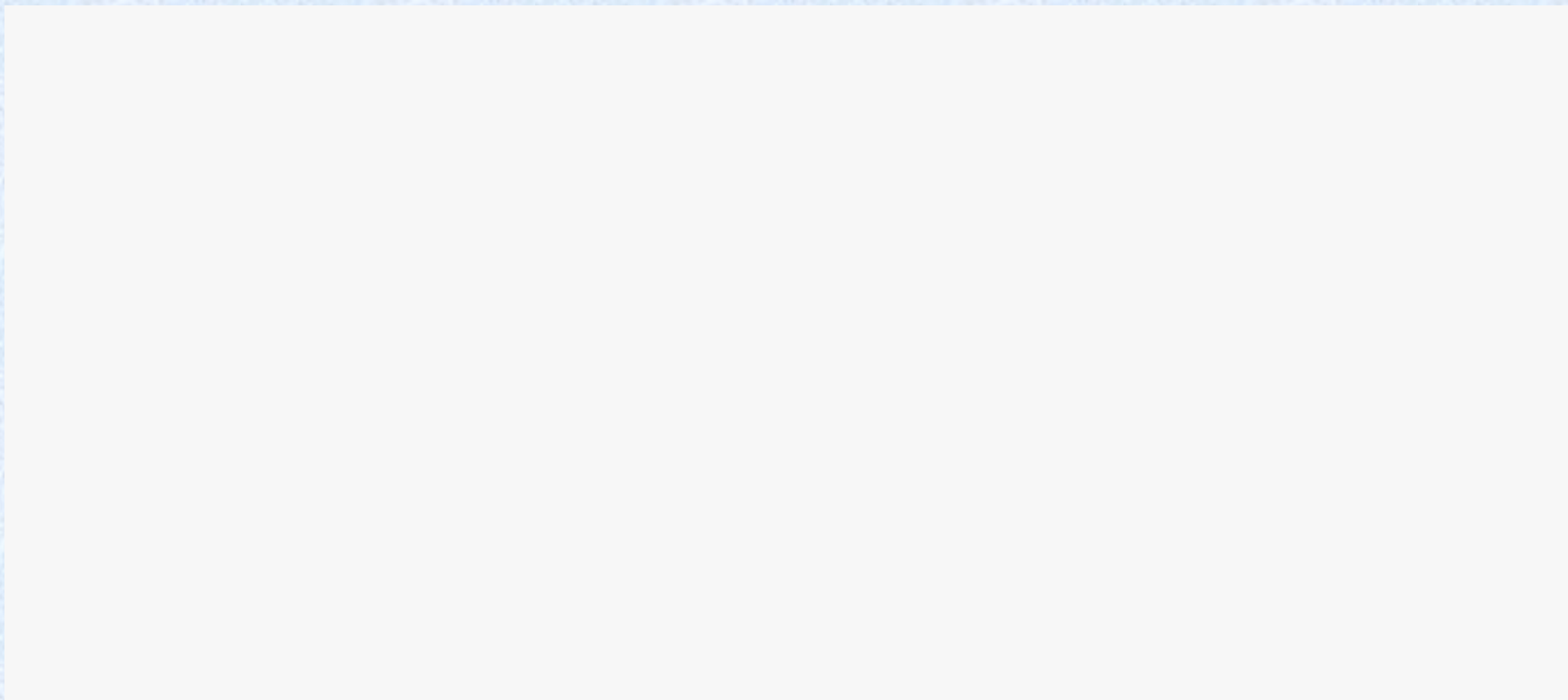
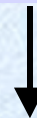
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Competition between ΔH° and ΔS°
determines sign of ΔG° .

Define T^* by setting $\Delta G^\circ = \Delta H^\circ - T^*\Delta S^\circ = 0$ \square $T^* = \Delta H^\circ / \Delta S^\circ$

Both $\Delta H^\circ, \Delta S^\circ < 0$, \square
 $\Delta G^\circ < 0$ when $T < T^*$

Both $\Delta H^\circ, \Delta S^\circ > 0$, \square
 $\Delta G^\circ < 0$ when $T > T^*$



Standard free energy change for a reaction:



$$\Delta G^\circ = c\Delta G_f^\circ(C) + d\Delta G_f^\circ(D) - a\Delta G_f^\circ(A) - b\Delta G_f^\circ(B)$$

[i.e. mixture of **a** of A, **b** of B, etc, goes spontaneously to right]

Must be careful. Does not imply complete conversion from reactants to products.

Need to know how ΔG depends on **concentration**.

Concentration Dependence for Simplest Case :

1 mole , ideal gas, constant T, but not const P. (Note: P defines concentration)

but $\Delta E = 0$ since T = constant and $\Delta(PV) = \Delta(RT) = 0$

$$\Delta S = \frac{q_{\text{rev}}}{T} \text{ so}$$

$$\Delta G = - q_{\text{rev}}$$

However since $\Delta E = q + w = 0$, $q = -w$

$$\Delta G = w_{\text{rev}} \quad (\text{Free energy related to reversible work})$$

$$\Delta G = - \int_{v_i}^{v_f} p \, dV \quad p_{\text{ext}} = p = \frac{RT}{V} \quad \Delta G = G_f - G_i$$

Because work is reversible

If we define $G_i = G^\circ (P_i = 1 \text{ atm})$ then

where P_f must be expressed in atmospheres.

In general for 1 mole ideal gas

Shows how G depends on P at fixed T if know $G^\circ(T)$.

To distinguish G for 1 mole, call it $\square (T, P) = \square^\circ (T) + RT \ln P$