


Irrespective of being a “State Function” or “Path Function” Internal energy (U), heat (q), and work (w) are all measured in the same units [recommended in joule (J)].

 $1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$

Question: A sample of 3.0 mol of a gas at 200 K and 2.0 atm is compressed reversibly and adiabatically until the temperature reaches 250 K. Given that its molar constant volume heat capacity is $27.5 \text{ J K}^{-1} \text{ mol}^{-1}$, calculate q , w , ΔT , ΔU , ΔH , and the final pressure and volume.

Adiabatic process, $q = 0$

$$\Delta U = q + w = w \quad C_V = \left(\frac{\partial U}{\partial T} \right)_V$$

$$w = \Delta U = nC_{V,m}(T_f - T_i) = 3 \text{ mol} \times 27.5 \text{ J K}^{-1} \text{ mol}^{-1} \times (250 - 200) \text{ K} = +4.1 \text{ kJ}$$

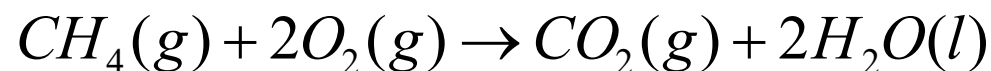
$$V_f = \left(\frac{T_f}{T_i} \right)^{C_{V,m}/R} \times V_i = \left(\frac{T_i}{T_f} \right)^{C_{V,m}/R} \times \frac{nRT_i}{p_i} = \left(\frac{250}{200} \right)^{27.6/8.3145} \times \frac{3 \text{ mol} \times 0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 200 \text{ K}}{2 \text{ atm}} = 11.8 \text{ L}$$

$$p_f = \frac{nRT_f}{V_f} = 5.2 \text{ bar}$$

$$\Delta H = \Delta U + nR\Delta T = 4.1 \text{ kJ} + \frac{3 \text{ mol} \times 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \times 50 \text{ K}}{1000} = +5.4 \text{ kJ}$$

Question 1: Calculate the maximum non-expansion work per mole that may be obtained from a fuel cell in which the chemical reaction is the combustion of methane at 298 K.

Solution:



$$\Delta_r G^\circ = \Delta_f G^\circ(CO_2, g) + 2\Delta_f G^\circ(H_2O, l) - \Delta_f G^\circ(CH_4, g)$$

$$\Delta_r G^\circ = \{-394.36 + (2 \times -237.13) - (-50.72)\} \text{ kJ mol}^{-1} = -817.90 \text{ kJ mol}^{-1}$$

Therefore, the maximum non-expansion work is 817.90 kJ mol⁻¹

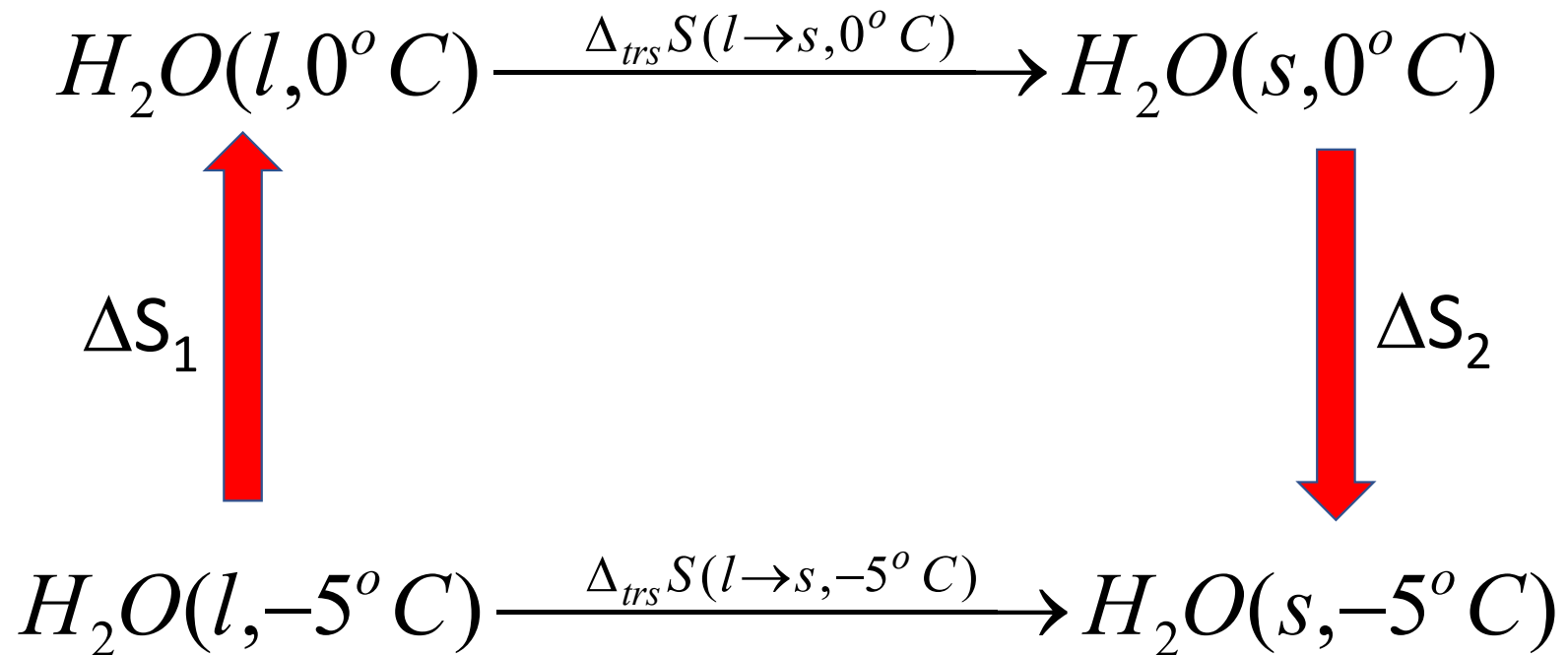
Question 2: Calculate the difference in molar entropy

- (a) Between liquid water and ice at -5°C ,
- (b) Between liquid water and its vapour at 95°C and 1.00 atm

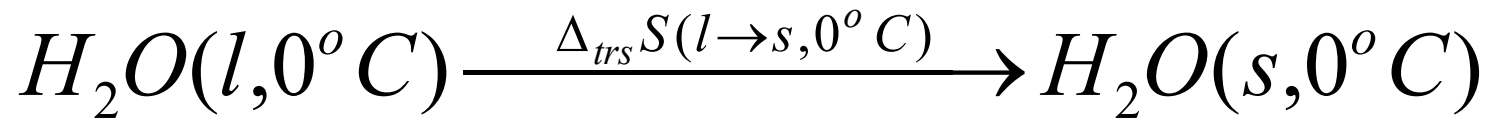
The differences in heat capacities on melting and on vaporization are $37.3\text{ J K}^{-1}\text{ mol}^{-1}$ and $-41.9\text{ J K}^{-1}\text{ mol}^{-1}$, respectively.

Distinguish between the entropy changes of the sample, the surroundings, and the total system, and discuss the spontaneity of the transitions at the two temperatures.

Solution:



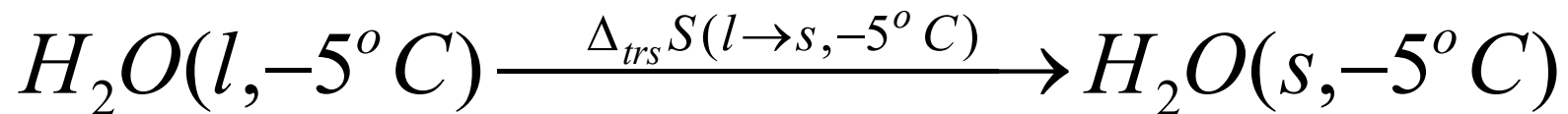
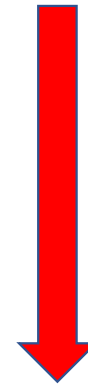
$$\Delta_{trs} S(l \rightarrow s, -5^\circ C) = \Delta S_1 + \Delta_{trs} S(l \rightarrow s, 0^\circ C) + \Delta S_2$$



ΔS_1



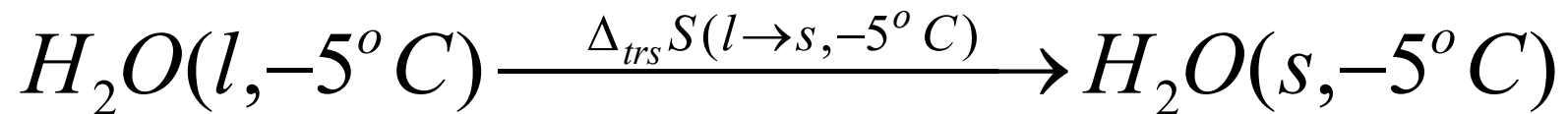
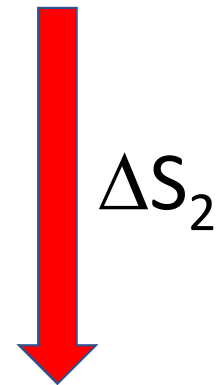
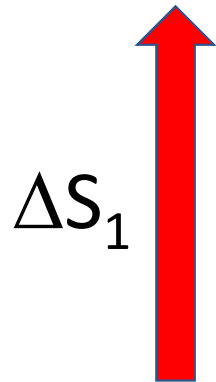
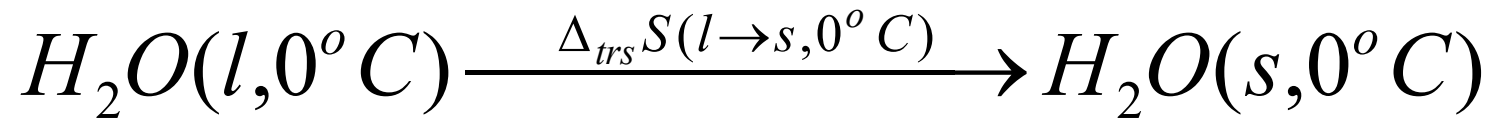
ΔS_2



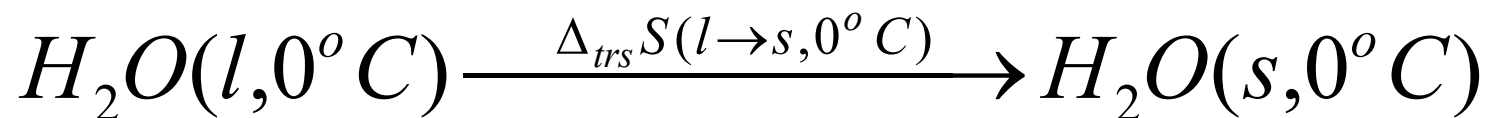
$$\Delta S_1 = C_{p,m}(l) \ln \frac{T_f}{T_i}$$

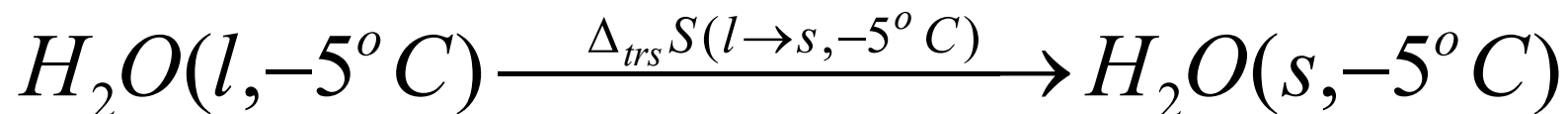
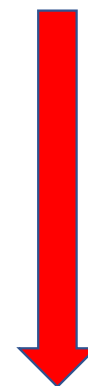
$$\Delta S_2 = C_{p,m}(s) \ln \frac{T_i}{T_f}$$

$$\Delta S_1 + \Delta S_2 = \{C_{p,m}(l) - C_{p,m}(s)\} \ln \frac{T_f}{T_i}$$



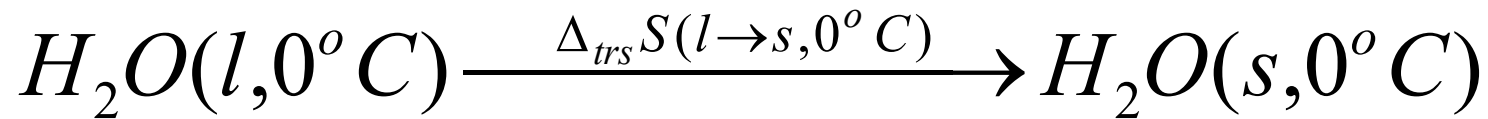
$$\Delta_{trs} S(l \rightarrow s, T_f) = -\frac{\Delta_{fus} H}{T_f}$$


 ΔS_1

 ΔS_2


$$\Delta_{trs} S(l \rightarrow s, -5^\circ C) = \{C_{p,m}(l) - C_{p,m}(s)\} \ln \frac{T_f}{T_i} - \frac{\Delta_{fus} H}{T_f}$$

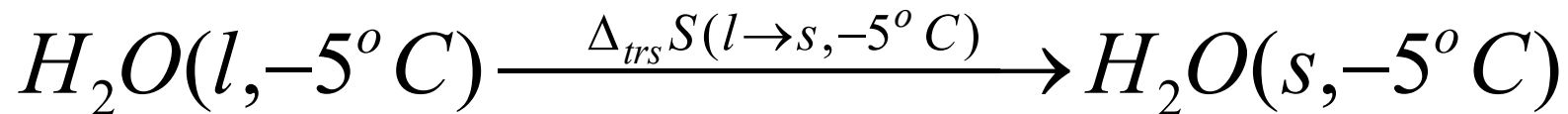
$$\Delta_{trs} S(l \rightarrow s, -5^\circ C) = (37.3 \text{ J K}^{-1} \text{ mol}^{-1}) \ln \frac{273}{268} - \frac{6.01 \times 10^3 \text{ J mol}^{-1}}{273 \text{ K}} = -21.3 \text{ J K}^{-1} \text{ mol}^{-1}$$



ΔS_1



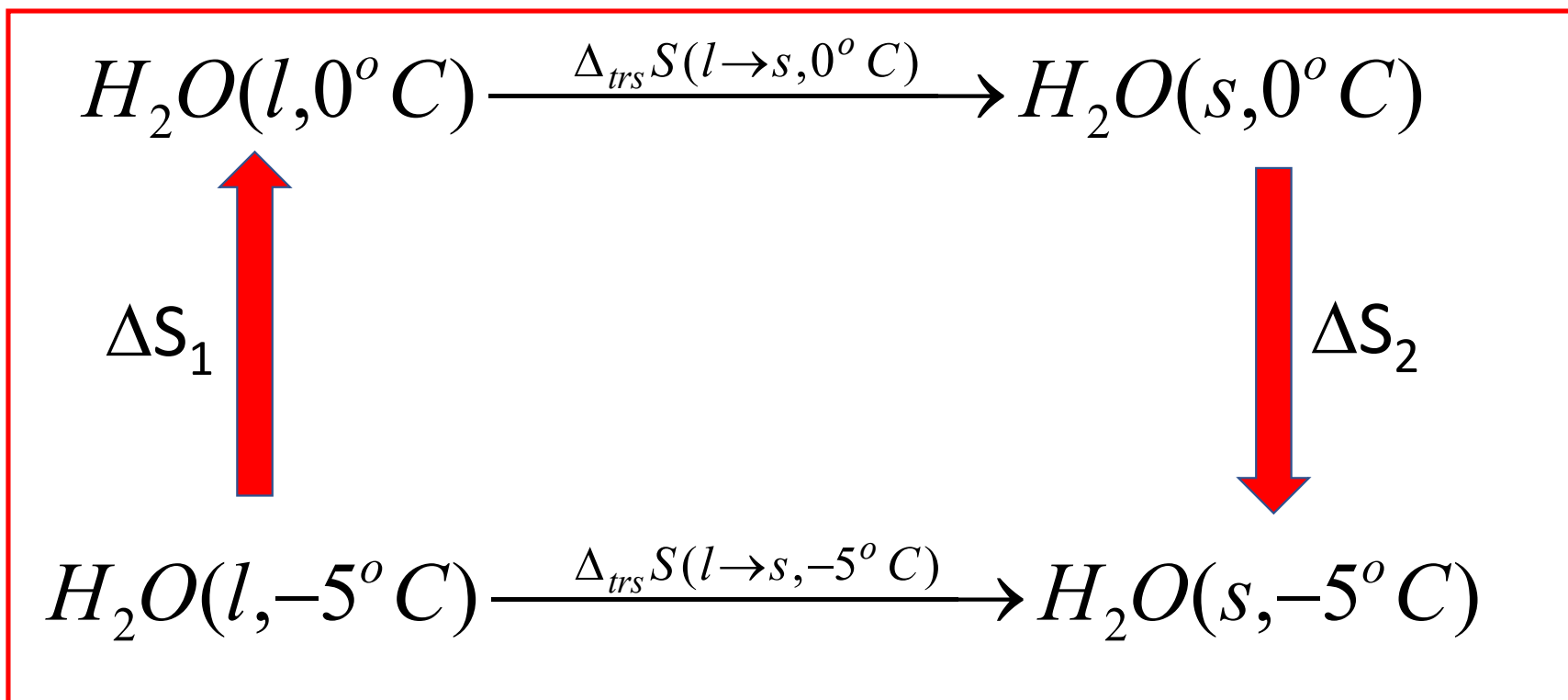
ΔS_2



$$\Delta S(\text{surroundings}) = \frac{\Delta_{fus} H(T_i)}{T_i} = \frac{-\Delta H_1 + \Delta_{fus} H(T_f) - \Delta H_2}{T_i}$$

$$\Delta S(\text{surroundings}) = \frac{C_{p,m}(l)\{T_i - T_f\} + C_{p,m}(s)\{T_f - T_i\}}{T_i} + \frac{\Delta_{fus} H}{T_i} = \frac{\{C_{p,m}(s) - C_{p,m}(l)\}\{T_f - T_i\}}{T_i} + \frac{\Delta_{fus} H}{T_i}$$

$$\Delta S(\text{surroundings}) = \frac{6.01 \text{ kJ mol}^{-1}}{268 \text{ K}} + (-37.3 \text{ J K}^{-1} \text{ mol}^{-1}) \times \frac{273 - 268}{268} = +21.7 \text{ J K}^{-1} \text{ mol}^{-1}$$



$$\Delta S(\text{total}) = (21.7 - 21.3) \text{ J K}^{-1} \text{ mol}^{-1} = 0.4 \text{ J K}^{-1} \text{ mol}^{-1}$$

Note that since $\Delta S(\text{total}) > 0$, the transition $l \rightarrow s$ is spontaneous

Question 3: Calculate the change in entropy when 200g of

(a) water at 0° C

(b) Ice at 0° C is added to 200g of water at 90° C in an insulated container

Solution:

$$T_f = \frac{n_1 T_{i,1} + n_2 T_{i,2}}{n_1 + n_2} = \frac{T_{i,1} + T_{i,2}}{2} \text{ (if } n_1 = n_2) = 318 \text{ K}$$

$$\Delta S = n_1 C_{p,m} \ln \frac{T_f}{T_{i,1}} + n_2 C_{p,m} \ln \frac{T_f}{T_{i,2}} = n_1 C_{p,m} \ln \frac{T_f^2}{T_{i,1} T_{i,2}} \text{ (because } n_1 = n_2)$$

$$\Delta S = \left(\frac{200 \text{ g}}{18.02 \text{ g mol}^{-1}} \right) \times 75.3 \text{ J K}^{-1} \text{ mol}^{-1} \times \ln \left(\frac{318^2}{273 \times 363} \right) = +16.9 \text{ J K}^{-1}$$

Heat required for melting: $n\Delta_{fus}H = (11.1 \text{ mol}) \times (6.01 \text{ kJ mol}^{-1}) = 66.7 \text{ kJ}$

The decrease in temperature of hot water as a result of melting :

$$\Delta T = \frac{q}{C_{p,m}} = \frac{66.7 \text{ kJ}}{(11.1 \text{ mol}) \times (75.3 \text{ J K}^{-1} \text{ mol}^{-1})} = 79.8 \text{ K}$$

At this stage, the system has 200 g water at 0°C and 200 g water at (90-79.8)°C = 10°C

$$\Delta S = \frac{n\Delta_{fus}H}{T_f} + nC_{p,m} \ln \frac{283}{363}$$

$$\Delta S = \frac{11.1 \text{ mol} \times 6.01 \text{ kJ mol}^{-1}}{273 \text{ K}} + 11.1 \text{ mol} \times 75.3 \text{ J K}^{-1} \text{ mol}^{-1} \times \ln \frac{283}{363} = +35.3 \text{ J K}^{-1}$$

The final temperature is :

$$T_f = \frac{273 + 283}{2} = 278 \text{ K}$$

$$\Delta S = n_1 C_{p,m} \ln \frac{T_f}{T_{i,1}} + n_2 C_{p,m} \ln \frac{T_f}{T_{i,2}} = n_1 C_{p,m} \ln \frac{T_f^2}{T_{i,1} T_{i,2}} \quad (\text{because } n_1 = n_2)$$

$$\Delta S = 11.1 \text{ mol} \times 75.3 \text{ J K}^{-1} \text{ mol}^{-1} \times \ln \left(\frac{278^2}{273 \times 283} \right) = +0.27 \text{ J K}^{-1}$$

$$\text{Total } \Delta S = (35.3 + 0.27) \text{ J K}^{-1} = +36 \text{ J K}^{-1}$$

Question 4: Calculate (a) the maximum work and (b) the maximum non-expansion work that can be obtained from the freezing of super cooled water at -5°C and 1.0 atm. The densities of water and ice are 0.999 and 0.917 g cm^{-3} , respectively at -5°C .

Solution:

$$W_{\text{max}, \text{non-pV}} = \Delta G(T) = \Delta H(T) - T\Delta S(T)$$

$$\Delta G(T) = \left(\frac{T}{T_f} - 1 \right) \Delta_{\text{fus}} H(T_f) - \Delta C_{p,m} \left(T - T_f - T \ln \frac{T}{T_f} \right)$$

$$\Delta G(268\text{K}) = \left(\frac{268}{273} - 1 \right) \times (6.01 \text{ kJ mol}^{-1}) - (37.3 \text{ J K}^{-1} \text{ mol}^{-1}) \times \left(268 - 273 - 268 \ln \frac{268}{273} \right) = -0.11 \text{ kJ mol}^{-1}$$

Maximum non-expansion work = $\Delta G = -0.11 \text{ kJ mol}^{-1}$

$$\Delta A = \Delta G - p\Delta V = \Delta G - pM\Delta\left(\frac{1}{\rho}\right)$$

$$\Delta A = (-0.11 \text{ kJ mol}^{-1}) - (1.013 \times 10^5 \text{ Pa}) \times 18.02 \times 10^{-3} \text{ kg mol}^{-1} \times \left(\frac{1}{917 \text{ kg m}^{-3}} - \frac{1}{999 \text{ kg m}^{-3}} \right) = -0.11 \text{ kJ mol}^{-1}$$

Thus both maximum work (ΔA) and maximum non-expansion work are about 0.11 kJ mol⁻¹ each.

.....getting some qualitative answers

Comment on the entropy changes in

- (i) Adiabatic irreversible expansion of a gas
- (ii) Adiabatic reversible expansion of a gas

- ▶ Show that gas expansion into a vacuum is spontaneous
- ▶ Show that cooling (transfer of heat from hot to cold) is spontaneous
- ▶ Procedure to be used:
- ➔ Need to show that $dS(\text{system}) + dS(\text{surroundings}) > 0$

The molar heat capacity of a certain solid at 10 K is $0.43 \text{ J K}^{-1} \text{ mol}^{-1}$. What is its molar entropy at that temperature?

Solution:

$$S(T) = S(0) + \int_0^T \frac{C_p}{T} dT$$

$$S_m(10K) = S_m(0) + \int_0^{10} \frac{aT^3}{T} dT = S_m(0) + a \int_0^{10} T^2 dT = S_m(0) + \frac{aT^3}{3}$$

At low temperature, $C_p = aT^3$;

$$S_m(10K) = S_m(0) + \frac{C_p}{3} = S_m(0) + 0.14 \text{ J K}^{-1} \text{ mol}^{-1}$$

Note that heat capacity is very small at low temperatures, therefore only small errors arise from Debye extrapolation

Question: 200 g of tin (at wt. = 118.7, $C_p = 6.1 \text{ cal K}^{-1} \text{ mol}^{-1}$) initially at 100°C and 100g of water ($C_p = 18 \text{ cal K}^{-1} \text{ mol}^{-1}$) initially at 25°C are mixed together in a calorimeter. Assuming that the heat capacities are constant and that no heat is lost or gained by the surroundings or by the calorimeter, calculate the entropy change for (i) tin, (ii) water, and (iii) the universe.

Let T be the final temperature of mixing

Heat lost by tin + heat gained by water = 0

$$n_{tin} \times C_{p,tin} \times (T - 373) + n_{water} \times C_{p,water} \times (298 - T) = 0$$

$$\left(\frac{200}{118.7}\right) \text{mol} \times 6.1 \text{ cal K}^{-1} \text{ mol}^{-1} \times (T - 373) \text{ K} + \left(\frac{100}{18}\right) \text{mol} \times 18 \text{ cal K}^{-1} \text{ mol}^{-1} \times (298 - T) \text{ K} = 0$$

$$T = 305 \text{ K}$$

$$\Delta S_{tin} = n C_{p,m,tin} \ln \frac{305}{373} = \left(\frac{200}{118.7}\right) \times 6.1 \text{ cal K}^{-1} \text{ mol}^{-1} \times \ln \frac{305}{373} = -2 \text{ cal K}^{-1}$$

$$\Delta S_{water} = n C_{p,m,water} \ln \frac{305}{298} = \left(\frac{100}{18}\right) \times 18 \text{ cal K}^{-1} \text{ mol}^{-1} \times \ln \frac{305}{298} = +2.3 \text{ cal K}^{-1}$$

$$\Delta S_{total} = (-2.0 + 2.3) \text{ cal K}^{-1} = +0.3 \text{ cal K}^{-1}; (\Delta S_{surroundings}) = 0$$

Question: Calculate the change in entropy when a perfect gas is compressed to half its volume and simultaneously heated to twice its initial temperature.

$$dU = dq + dw$$

$$nC_{v,m}dT = TdS - pdV = TdS - \frac{nRT}{V}dV$$

$$dS = \frac{nC_{v,m}dT}{T} + \frac{nR}{V}dV$$

$$\Delta S = nC_{v,m} \ln \frac{T_f}{T_i} + nR \ln \frac{V_f}{V_i}$$

For monatomic perfect gas :

$$\Delta S = \frac{3}{2}R \ln 2 + R \ln 0.5 = 2.88 J K^{-1} mol^{-1}$$

Criterion of spontaneity
in terms of properties of system alone

$$dS_{U,V} \geq 0; \quad dU_{S,V} \leq 0$$

$$dS_{H,p} \geq 0; \quad dH_{S,p} \leq 0$$

$$dA_{T,V} \leq 0; \quad dG_{T,p} \leq 0$$

**These inequalities are the most important conclusions from
thermodynamics for chemistry**

Significance of Helmholtz Energy (A)

(A is sometimes called the Maximum work function or work function)

(*Arbeit* is the German word for work; hence the symbol A)

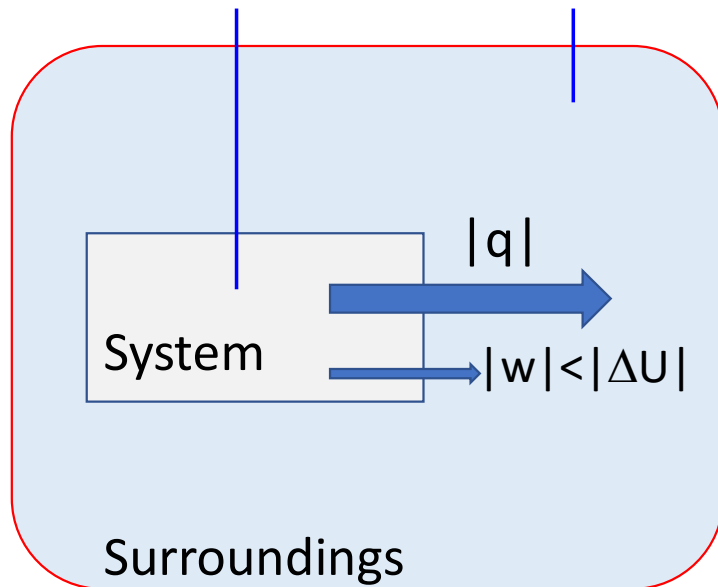
$$w_{\max} = \Delta A$$

$$w_{\max} = \Delta U - T\Delta S$$

The change in Helmholtz energy is equal to the maximum work the system can do

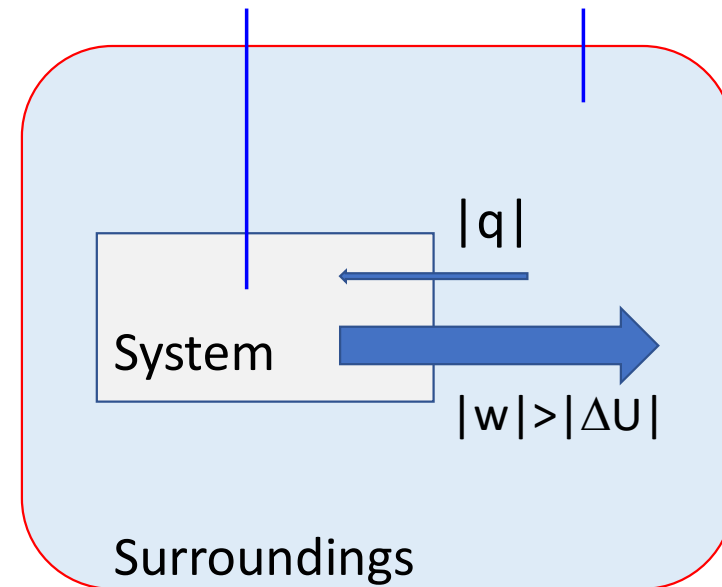
$$w_{\max} = \Delta U - T\Delta S$$

$\Delta U < 0$; $\Delta S < 0$ $\Delta S(\text{surroundings}) > 0$



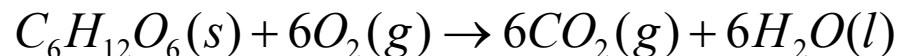
Maximum work is less than ΔU

$\Delta U < 0$; $\Delta S > 0$ $\Delta S(\text{surroundings}) < 0$



Maximum work is more than ΔU

Example: When 1.0 mol glucose is oxidized to carbon dioxide and water at 25°C according to the equation.



Calorimetric measurements give $\Delta U = -2808$ kJ and $\Delta S = +182.4$ J K⁻¹ at 25°C and standard conditions. How much of this energy change can be extracted at (a) heat at constant pressure, and (b) work?

Solution: Since $\Delta n_g = 0$; $q_p = \Delta H = \Delta U = -2808$ kJ

$$\Delta A = \Delta U - T\Delta S = -2808 \text{ kJ} - (298 \text{ K})(0.1824 \text{ kJ K}^{-1}) = -2862 \text{ kJ}$$

Note that

- ▶ Maximum work available is greater than the change in internal energy
- ▶ Positive entropy of the reaction accounts for it
- ▶ System can draw in energy from surroundings and make it available for doing work

Maximum non-expansion work (non p-V work)

$$dw_{\text{max, non p-V}} = dG \quad (T, p \text{ constant})$$

$$w_{\text{max, non p-V}} = \Delta G \quad (T, p \text{ constant})$$

ΔG (which is equal to $\Delta H - T\Delta S$) at constant temperature and pressure is the maximum non-expansion work we can obtain from a process

Question: How much energy is available for sustaining muscular and nervous activity from the combustion of 1.0 mol of glucose molecules under standard conditions at 37°C (blood temperature)? The standard entropy of the reaction is +182.4 J K⁻¹. The standard enthalpy of reaction is -2808 kJ.

Solution:

We need to calculate non-expansion work given by $\Delta G = \Delta H - T\Delta S$

$$\Delta G = \Delta H - T\Delta S = -2808 \text{ kJ} - (310 \text{ K}) \times (0.1824 \text{ kJ K}^{-1}) = -2864 \text{ kJ}$$

Combustion of 1 mol glucose molecules can be used up to 2864 kJ of non-expansion work

Calculations suggest that a 70-kg person would need to do 2.1 kJ of work to climb vertically through 3 m. At least 0.13 g of glucose is needed to complete the task (and in practice significantly more is required).

How to determine the values of Gibbs energies?

- ▶ **Calorimetry: For ΔH directly and for S via heat capacities**
- ▶ **From equilibrium constants**
- ▶ **From electrochemical measurements**
- ▶ **From data obtained from spectroscopic observations**

The Maxwell relations

df = gdx + hdy is exact if

$$\left(\frac{\partial g}{\partial y}\right)_x = \left(\frac{\partial h}{\partial x}\right)_y$$

Power of thermodynamics
for establishing relations

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$$

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$$

$$\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$$

$$\left(\frac{\partial p}{\partial T}\right)_V = -\left(\frac{\partial S}{\partial P}\right)_T$$