
Entropy Changes & Processes

Chapter 4 of Atkins: The Second Law: The Concepts

Section 4.3, 7th edition; 3.3, 8th and 9th editions

*Entropy of Phase Transition
at the Transition Temperature*

Expansion of the Perfect Gas

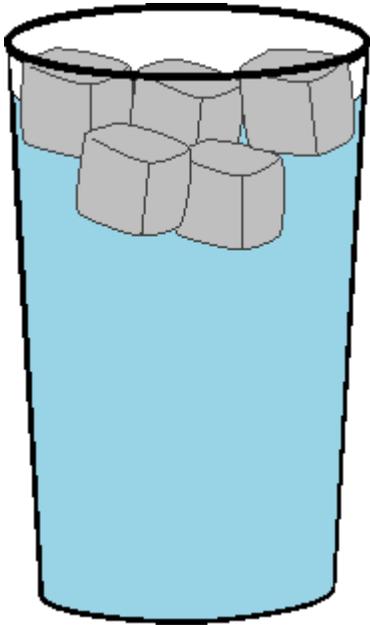
Variation of Entropy with Temperature

Measurement of Entropy

Entropy at a Phase Transition

Changes in molecular order occur when a substance freezes or boils

Consider the phase transitions of water, at transition temperatures T_{trs} . For ice water, $T_{\text{trs}} = 273 \text{ K}$, ice in equilibrium with liquid water at 1 atm and boiling water, $T_{\text{trs}} = 373 \text{ K}$, liquid water in equilibrium with vapour at 1 atm



The external pressure is constant for a glass of ice water, and in order to match attractive forces between ice molecules, energy must come from kinetic energy of the water molecules or the surroundings

At T_{trs} , any **transfer of heat between the system and surroundings is reversible since the two phases in the system are in equilibrium** (the forces pushing the ice towards melting are equal to those pushing the water towards freezing) - so a **phase transition is reversible**

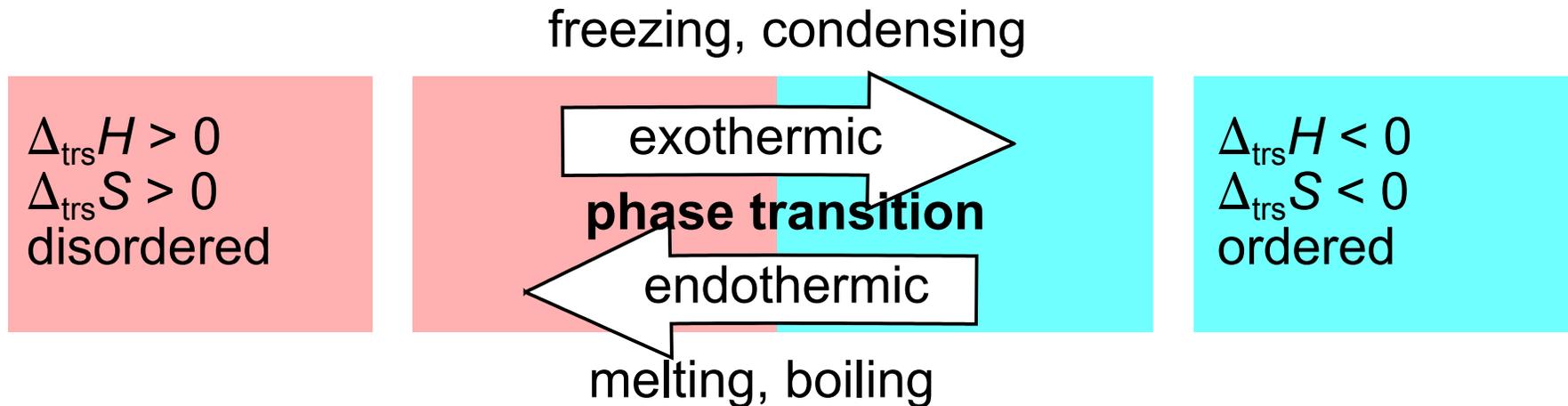
It does not matter how the ice melts (what path it takes) since entropy is a state function. What does matter for this particular expression is that the system be **isothermal**. If it was not isothermal, one would have a problem examining the process in steps – as we shall see.

Entropy at a Phase Transition, 2

At constant pressure, $q = \Delta_{\text{trs}}H$, and the change in **molar entropy** is

$$\Delta_{\text{trs}}S = \frac{\Delta_{\text{trs}}H}{T_{\text{trs}}}$$

For exothermic and endothermic phase transitions:



Consistent with decreasing disorder: gases > liquids > solids

Example: when compact condense phase vapourizes into a widely dispersed gas, one can expect an increase in the disorder of the molecules

Trouton's Rule

Trouton's Rule: This empirical observation (see Table 4.2) states that most liquids have approximately the same **standard entropy of vaporization**, $\Delta_{\text{vap}}S^{\circ} \approx 85 \text{ J K}^{-1} \text{ mol}^{-1}$: So, $\Delta_{\text{vap}}H^{\circ} = T_b \times 85 \text{ J K}^{-1} \text{ mol}^{-1}$

Some Standard Entropies of Vaporization

	$\Delta_{\text{vap}}H^{\circ}$ (kJ mol ⁻¹)	θ_{boil} (°C)	$\Delta_{\text{vap}}S^{\circ}$ (J K ⁻¹ mol ⁻¹)
Benzene	+30.8	80.1	+87.2
CCl ₄	+30.00	76.7	+85.8
Cyclohexane	+30.1	80.7	+85.1
H ₂ S	+18.7	-60.4	+87.9
Methane	+8.18	-161.5	+73.2
Water	+40.7	100.0	+109.1

Exceptions:

- In **water**, molecules are more organized in the liquid phase (due to hydrogen bonding), so a greater change of disorder occurs upon vapourization
- In **methane**, the entropy of the gas is slightly low (186 J K⁻¹ mol⁻¹ at 298 K) and in light molecules very few rotational states are accessible at room temperature - associated disorder is low

Expansion of a Perfect Gas

The ΔS for an isothermally expanding perfect gas can be written as

$$\Delta S = nR \ln \left(\frac{V_f}{V_i} \right) \quad (\text{see lecture 10 notes})$$

(equation applies for reversible or irreversible change, S = state function)

N.B.: Atkins uses ΔS instead of ΔS_{sys} - they are equivalent!

Reversible change:

$$\Delta S_{\text{tot}} = 0$$

The surroundings are in thermal and mechanical equilibrium with system, so $\Delta S_{\text{sur}} = -\Delta S = -nR \ln (V_f / V_i)$

Free irreversible expansion:

$$w = 0$$

If isothermal, $\Delta U = 0$, and therefore $q = 0$.

Thus, $\Delta S_{\text{sur}} = 0$ and $\Delta S_{\text{tot}} = \Delta S = nR \ln (V_f / V_i)$

Variation of Entropy with Temperature

The entropy of a system at temperature T_f can be calculated from knowledge of initial temperature and heat supplied to make ΔT :

$$\Delta S = \int_i^f \frac{dq_{\text{rev}}}{T}$$

When the system is subjected to constant pressure (i.e., the atmosphere) during heating, from the definition of constant pressure heat capacity, if the system is not doing expansion work ($w = 0$), then

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

Then, at constant pressure (or constant volume, replace with C_v):

$$S(T_f) = S(T_i) + \int_i^f \frac{C_p dT}{T}$$

If C_p is invariant to temperature change

$$S(T_f) = S(T_i) + C_p \int_i^f \frac{dT}{T} = S(T_i) + C_p \ln \left(\frac{T_f}{T_i} \right)$$

Calculating the Entropy Change

Calculate ΔS when argon at 25°C and 1.00 atm in a container of volume 500 cm³ expands to 1000 cm³ and is simultaneously heated to 100°C

Methodology: Since S is a state function, we can choose a convenient path from initial to final state: (1) **isothermal expansion** to final volume, then (2) **reversible heating at constant volume** to final temperature

Amount of Ar present is $n = pV/RT = 0.0204$ mol

$$C_{p,m}(\text{Ar}) = 20.786 \text{ J K}^{-1} \text{ mol}^{-1}$$

(1) **Expansion** from 500 cm³ to 1000 cm³ at **constant T**:

$$\Delta S = nR \ln 2.00 = +0.118 \text{ J K}^{-1}$$

(2) **Reversible heating** from 25°C to 100°C at **constant V**:

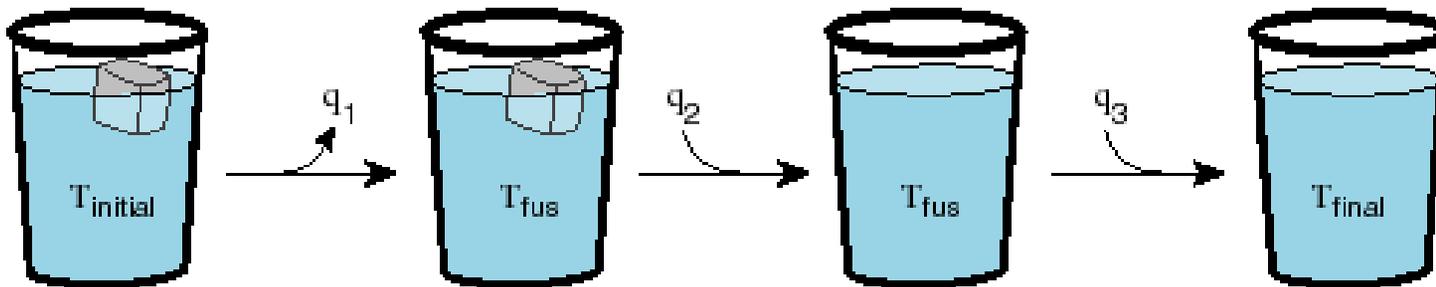
$$\begin{aligned} \Delta S &= (0.0204 \text{ mol}) \times (12.48 \text{ J K}^{-1}) \times \ln (373 \text{ K} / 298 \text{ K}) \\ &= +0.057 \text{ J K}^{-1} \end{aligned}$$

Overall entropy change:

$$\Delta S = +0.118 \text{ J K}^{-1} + 0.057 \text{ J K}^{-1} = +0.175 \text{ J K}^{-1}$$

Entropy Change of Melting Ice

Consider the entropy changes for putting an ice cube in a glass of warm water and letting it melt (**adiabatic container**)



Start at T_i

- (1) Calculate ΔS to cool the water to 0°C by reversibly removing heat, q_1 , from the system
- (2) At T_{fus} , calculate the amount of heat, q_2 , to be added to the system to melt the ice cube
- (3) Calculate the difference between the two amounts of heat and add back remaining heat so that the total heat lost or gained is zero (adiabatic system) - determine the entropy change in this process

At each step, the infinitesimal entropy change for the system, dS , is just dq divided by the T . For the cooling and heating of water, integrate over the temperature range, since the temperature is not constant.

Entropy Change of Melting Ice, 2

Step 1: Entropy decrease for the system as the water is cooled

$$\Delta S_1 = \int_{T_i}^{T_{\text{fus}}} \frac{dq}{T} = C_p \int_{T_i}^{T_{\text{fus}}} \frac{dT}{T} = C_p \ln \left(\frac{T_{\text{fus}}}{T_i} \right)$$

Step 2: Melt the ice at the temperature of $T_{\text{fus}} = 0^\circ\text{C}$ ($q_{\text{fus}} = q_2$)

$$\Delta S_2 = \frac{q_{\text{fus}}}{T} = \frac{\Delta H_{\text{fus}}}{T}$$

Step 3: Balance the heat by (in this example) adding an amount of heat $-(q_1 + q_2)$ back into the glass (ice cube melted completely), remove more heat to cool the glass to 0°C than you would have to add in order to melt the ice -- increase in entropy:

$$\Delta S_3 = C_p \ln \left(\frac{T_f}{T_{\text{fus}}} \right)$$

Entropy Change of Melting Ice, 3

How do we know T_f ? System is adiabatic so the total heat must be zero, or $q_3 = -(q_1 + q_2)$, giving $T_f = T_{\text{fus}} + q_3/C_p$

Is the process spontaneous? (We know intuitively that it is - sticking an ice cube into warm water melts the ice cube!!) How do we prove this?

Show that the total entropy change (the system plus the surroundings) is positive. The entropy change of the system we know is:

$$\Delta S_1 + \Delta S_2 + \Delta S_3$$

Homework problem 1:

Try the above steps for 5 g of ice at 60°C in 100 mL of water

With $C_{p,m}$ of water of $75.6 \text{ J K}^{-1} \text{ mol}^{-1}$ and $\Delta_{\text{fus}}H = 6.01 \text{ kJ mol}^{-1}$, T_f should be around 53.4 °C with $\Delta S = 1.39 \text{ J K}^{-1}$ for the system.

Note that since the system is adiabatic, $\Delta S_{\text{sur}} = 0$

Homework problem 2:

Use the same conditions as above, except try the calculation for an isothermal system

Useful Entropy Equations

Some changes in state and associated entropy changes for the system, for an infinitesimal change in entropy, $dS = dq/T$:

Vary the temperature at **constant volume** (C_V independent of T):

$$\Delta S = \int_{T_i}^{T_f} \frac{dq}{T} = \int_{T_i}^{T_f} \frac{C_V dT}{T} = C_V \ln \left(\frac{T_f}{T_i} \right)$$

Vary the temperature at **constant pressure** (C_p independent of T):

$$\Delta S = \int_{T_i}^{T_f} \frac{dq}{T} = \int_{T_i}^{T_f} \frac{C_p dT}{T} = C_p \ln \left(\frac{T_f}{T_i} \right)$$

For **isothermal expansion** of a perfect gas

$$\Delta S = nR \ln \left(\frac{V_f}{V_i} \right) = nR \ln \left(\frac{P_i}{P_f} \right)$$

What if both T and P or T and V change? **Simple, use two steps!** First change the T holding either V or P constant, then change V or P at constant T (depending on what you are given).

Measurement of Entropy

Entropy of a system at temperature T can be related to entropy at $T = 0$ by measuring heat capacities at different temperatures, and evaluating

$$S(T_f) = S(T_i) + \int_i^f \frac{C_p dT}{T}$$

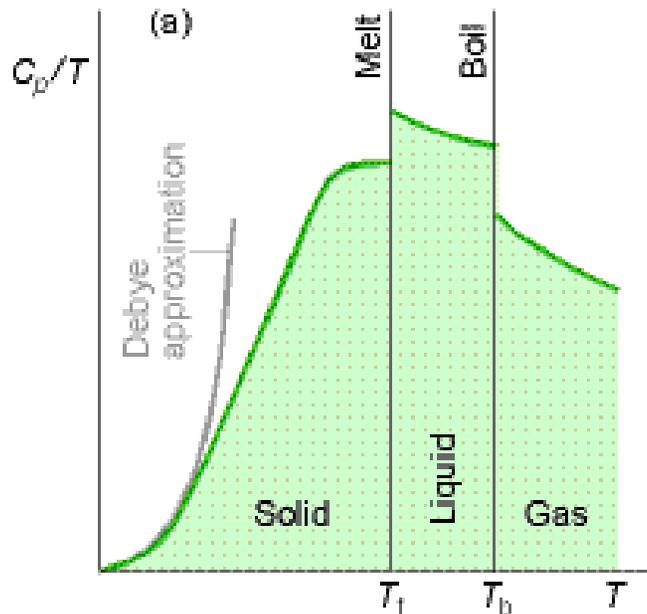
The entropy of transition, $\Delta_{\text{trs}} S = \Delta_{\text{trs}} H / T_{\text{trs}}$, is added for each phase transition between $T = 0$ and T (temperature of interest)

For example, if substance melts at T_f and boils at T_b , entropy above T_b is

$$S(T) = S(0) + \int_0^{T_f} \frac{C_p(\text{s}) dT}{T} + \frac{\Delta_{\text{fus}} H}{T_f} + \int_{T_f}^{T_b} \frac{C_p(\text{l}) dT}{T} + \frac{\Delta_{\text{vap}} H}{T_b} + \int_{T_b}^T \frac{C_p(\text{g}) dT}{T}$$

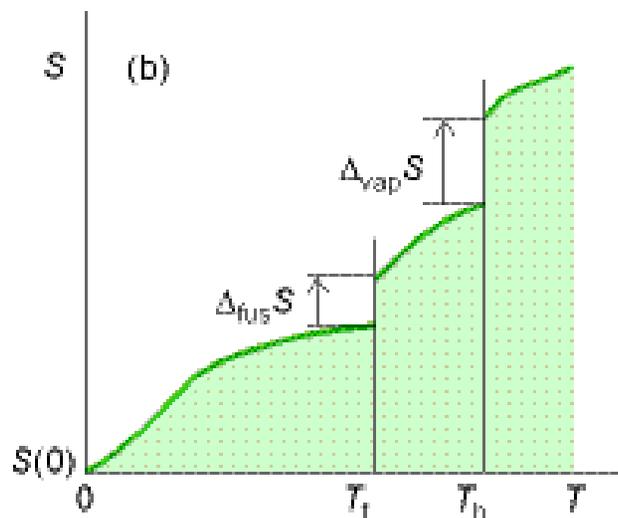
All of the quantities can be determined from calorimetry excepting $S(0)$, and integrals can be evaluated analytically (see next page)

Measurement of Entropy, 2



Plot (a) shows the variation of C_p/T with sample temperature. The area under the curve of C_p/T as a function of T is required - since $dT/T = d \ln T$, we can also evaluate area under a plot of C_p vs. $\ln T$

Plot (b) shows the entropy of the system varying with temperature, which is equal to the area under the curve up to the corresponding temperature, plus entropy of each phase transition passes



One problem with measuring ΔS is measuring C_p at low T near $T = 0$:

Debye extrapolation: It has been shown that at temperatures near $T = 0$, the heat capacity is approximately equal to T^3 (i.e., $C_p = aT^3$ as $T \rightarrow 0$)

Example: Calculating Entropy

Consider standard molar **entropy** of N_2 (g) at 25°C , calculated from the following data:

	S_m° (J K ⁻¹ mol ⁻¹)
Debye extrapolation	1.92
Integration from 10 - 35.61 K	25.25
Phase transition at 35.61 K	6.43
Integration from 35.61 - 63.14 K	23.38
Fusion at 63.14 K	11.42
Integration from 63.14 - 77.32 K	25.25
Vapourization at 77.32 K	72.13
Integration from 77.32 - 298.15 K	39.20
Correction for Gas Imperfection*	0.92
Total	192.06

$$S_m^\circ(298.15 \text{ K}) = S_m^\circ(0) + 192.1 \text{ J K}^{-1} \text{ mol}^{-1}$$

*** look up: failure of hard sphere approximation in Atkins

Calculating Entropy at Low Temperature

The molar constant-pressure heat capacity of some solid material at 10 K is $0.43 \text{ J K}^{-1} \text{ mol}^{-1}$. What is the molar entropy at that temperature?

Because temperature is low, we can assume that heat capacity varies with temperature as aT^3 :

$$\begin{aligned} S(T) &= S(0) + \int_0^{T_f} \frac{aT^3 dT}{T} = S(0) + a \int_0^{T_f} T^2 dT \\ &= S(0) + \frac{1}{3}aT^3 = S(0) + \frac{1}{3}C_p(T) \\ &= S_m(10\text{K}) = S_m(0) + 0.14 \text{ JK}^{-1} \text{ mol}^{-1} \end{aligned}$$

aT^3 is the heat capacity at temperature T

It turns out that the final result can be expressed in terms of heat capacity a constant pressure...