University of Washington
Department of Chemistry
Chemistry 452
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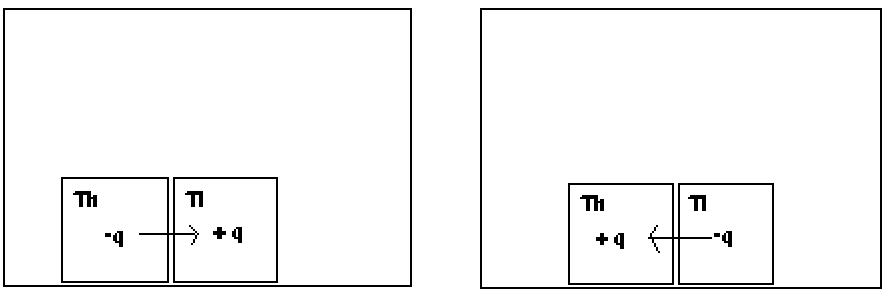
Lecture 7 7/09/14
ERD: 5.1, 5.2-5.6
DeVoe: 4.1, 4.2, 4.4

A. The Second Law of Thermodynamics: Introduction

The idea of reversibility is crucial for constructing a state function whose changes are dictated by another Law of Thermodynamcs. The necessity for restrictions beyond energy conservation is shown in the following example. Consider the two systems, shown below.



Each system consists of a ”hot” block of a solid material at a temperature T_h, in thermal contact with a second “cold” block of solid material which is at a temperature T_l. Note that $T_h>T_l$. These two “systems” are isolated from the rest of the universe (i.e. the surroundings) by thermally and mechanically isolating barriers. Because the temperatures of the blocks are unequal, heat will flow from one block to the other. The two systems above show two possible outcomes when heat flows. In the system at the above left a quantity of heat q moves from the hot block and an equivalent quantity of heat moves into the cold block. As a result the hot block gets cooler and the cold block gets warmer. In the system at the above, right, heat q moves from the cold block into the hot block and as a result, the hot block gets warmer and the cold block gets cooler.

In each case energy is conserved in accordance with the First Law because the amount of heat that moves out of one block is always equal to the amount of heat that appears in the other block. Despite this fact, the outcome shown in the system at the above right, has never been observed and is considered impossible.

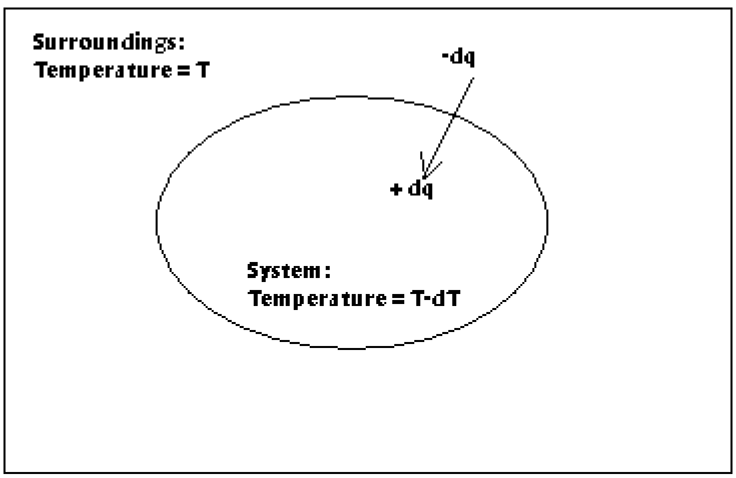
B. The Second Law of Thermodynamics and the Direction of Heat Transfer

Let’s go back to the two blocks (see figure in Lecture 8), held at different temperatures T_H and T_L where $T_H>T_L$.If these two blocks are enclosed in a thermally and mechanically isolating container, and if these blocks are placed in thermal contact with each other, experience shows heat will flow from the hotter block to the cooler block..

Heat will continue to flow in this way until the two blocks reach thermal equilibrium (i.e. when their temperatures are equal). The First Law requires that the heat transferred be conserved (i.e. the heat that appears in the cooler block must be exactly balanced by heat that is removed from the warmer block). However, the First Law does not specify the *direction* of the heat flow (i.e. hot-to-cold). We only know from our experience that the direction of heat flow will be from hot-to-cold or from the higher temperature to the lower temperature. The rule of direction of heat flow comes from another Law…the Second Law of Thermodynamics.

Reversible Heat Transfer:

- Suppose the temperature of the surroundings is T and the temperature of the system is lower by a small amount dT…that is the temperature of the sustem is T-dT (see figure, below)



- Because of this small temperature difference dT, a small amount of heat –dq leaves the surroundings, and a small amount of heat +dq enters the system.
- Because the heat transfer occurs between a system and a surrounding that differ in temperature by an infinitesimally small amount dT, the heat transfer is reversible and the heat transferred reversibly is designated dq_{rev}.
- For this situation :

$$\frac{heat\ transferred\ reversibly\ from\ surroundings}{temperature\ of\ surroundings} + \frac{heat\ transferred\ reversibly\ to\ system}{temperature\ of\ system} = \frac{-dq}{T} + \frac{+dq}{T - dT}$$

$$= dq_{rev}\left(\frac{1}{T - dT} - \frac{1}{T}\right) \approx 0$$

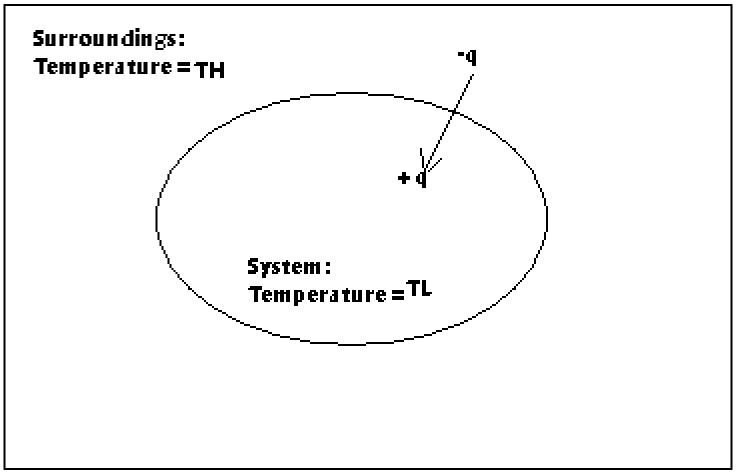
i.e. because dT is so small.

Comments:

- Reversible Heat Flow: $\frac{-dq_{rev}}{T_H} + \frac{+dq_{rev}}{T_L} = dq_{rev}\left(\frac{1}{T-dT} - \frac{1}{T}\right) \approx 0$
- Let $T=T_H$ *and* $T_L=T-dT$
- Define the state function entropy as $\Delta S = \int_i^f dS = \int_i^f \frac{dq_{rev}}{T}$
- For reversible heat flow
  $dS_{surroundings} + dS_{system} = \frac{-dq_{rev}}{T_H} + \frac{+dq_{rev}}{T_L} = dq_{rev}\left(\frac{1}{T-dT} - \frac{1}{T}\right) \approx 0$
- For reversible heat flow $\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} = 0$

B. Irreversible Heat Transfer

- For irreversible heat flow…ΔU must be the same as for reversible heat flow…because ΔU is a state function… $\Delta U = q_{rev} + w_{rev} = q_{irrev} + w_{irrev}$
  - As discussed earlier work performed reversibly is greater than work performed irreversibly i.e. $-w_{rev} > -w_{irrev} \Rightarrow w_{irrev} > w_{rev}$
  - Then because $q_{rev} + w_{rev} = q_{irrev} + w_{irrev}$ it follows that $q_{rev} > q_{irrev}$ and more heat is absorbed by the system when it is absorbed reversibly than irreversibly.
  - It follows that $\Delta S = \int_i^f \frac{dq_{rev}}{T} = \frac{q_{rev}}{T} > \frac{q_{irrev}}{T}$.
  - Assume heat flows irreversibly into a system at temperature T_L from the surroundings at temperature T_H. From experience we that heat will flow in this direction only if $T_H>T_L$.



- For irreversible heat transfer

$$\frac{heat\ transferred\ irreversibly\ from\ surroundings}{temperature\ of\ surroundings} + \frac{heat\ transferred\ irreversibly\ to\ system}{temperature\ of\ system} = \frac{-q_{irrev}}{T_H} + \frac{+q_{irrev}}{T_L}$$

$$= q_{irrev}\left(\frac{1}{T_L} - \frac{1}{T_H}\right) > 0$$

Conclusion:

- There is a state function called the entropy S: $\Delta S = \frac{q_{rev}}{T} > \frac{q_{irrev}}{T}$ *or* $\Delta S \geq \frac{q}{T}$
- Reversible Processes: $\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} = 0$
- Irreversible Processes: $\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} > 0$

This conclusion is a statement of the Second Law of Thermodynamics.

C. Entropy Expressions

- From the remarks above the entropy expression $dS = \frac{\delta q_{rev}}{T}$ can be incorporated into the internal energy equation

$$dU = \delta q_{rev} + \delta w_{rev} = TdS - PdV \qquad (7.1)$$

where only pressure volume work is considered. We can rearrange equation 7.1 and use the fact that entropy is an exact differential:

$$dS = \frac{dU}{T} + \frac{P}{T}dV = \left(\frac{\partial S}{\partial U}\right)_V dU + \left(\frac{\partial S}{\partial V}\right)_U dV \qquad (7.2)$$

- Equating the coefficients of dU and dV...

$$\left(\frac{\partial S}{\partial U}\right)_V = \frac{1}{T}; \quad \left(\frac{\partial S}{\partial V}\right)_U = \frac{P}{T} \qquad (7.3)$$

- Let’s consider the change of entropy with U at constant V using an ideal gas as an example...

$$dS_V = \frac{dU}{T} = \frac{nC_V dT}{T} \qquad (7.4)$$

- We similarly consider the change of S with volume v at constant U...

$$dS_U = \frac{P}{T}dV = \frac{nR}{V}dV \qquad (7.5)$$

- Combining 7.4 and 7.5:

$$dS = \frac{nC_V}{T}dT + \frac{nR}{V}dV$$
$$\therefore \Delta S = nC_V \ln\left(\frac{T_2}{T_1}\right) + nR\ln\left(\frac{V_2}{V_1}\right) \qquad (7.6)$$

- Equation 7.6 can be converted into the effect on entropy of pressure changes:

$$\Delta S = nC_V \ln\left(\frac{T_2}{T_1}\right) + nR\ln\left(\frac{V_2}{V_1}\right)$$
$$= nC_V \ln\left(\frac{T_2}{T_1}\right) + nR\ln\left(\frac{T_2 P_1}{T_1 P_2}\right) = n\left(C_V + R\right)\ln\left(\frac{T_2}{T_1}\right) + nR\ln\left(\frac{P_1}{P_2}\right) \qquad (7.7)$$
$$= nC_P \ln\left(\frac{T_2}{T_1}\right) + nR\ln\left(\frac{P_1}{P_2}\right)$$

D. Examples of Calculations of Entropy Changes

Example 1: Entropy changes for Phase Transitions

Phase transitions including fusion (i.e. melting), freezing, vaporization, condensation, etc. may be treated as reversible heat transfers occuring at constant temperature and pressure. Therefore…

$$\Delta S = \int_i^f \frac{dq_{rev}}{T} = \frac{1}{T}\int_i^f dq_{rev} = \frac{\Delta H}{T}$$

- Calculate the entropy change when 2 moles of liquid water vaporize at T=373K. Assume for $\Delta H_{vap} = 40{,}66 kJ / mole$ water
- Solution: $\Delta S = \frac{\Delta H_{vap}}{T} = \left(2\, moles\right)\frac{40{,}660 J / mole}{373K} = 218.0 J / K$

Example 2: Entropy Change for a Reversible, Isothermal Expansion/Compression

- For an ideal gas, an isothermal expansion (i.e. ΔT=0) means $\Delta U = nC_{V,m}\Delta T = q_{rev} + w_{rev} = 0 \Rightarrow q_{rev} = -w_{rev}$
- $q_{rev} = -w_{rev} = \int_{V_1}^{V_2} PdV = nRT\int_{V_1}^{V_2}\frac{dV}{V} = nRT\ln\left(\frac{V_2}{V_1}\right)$
- $\Delta S = \frac{q_{rev}}{T} = nR\ln\left(\frac{V_2}{V_1}\right)$
- Calculate the entropy change when 5 moles of an ideal gas expand isothermally and reversibly from a volume of 10L to a volume of 50L.

- Solution:
$$\Delta S = \frac{q_{rev}}{T} = nR\ln\left(\frac{V_2}{V_1}\right) = \left(5 moles\right)\left(8.31 J / mole\cdot K\right)\ln\left(\frac{50L}{10L}\right) = (41.55 J / K)\ln(5) = 66.87 J / K$$

Example 3: Entropy Change for a temperature change at constant pressure/volume

- Constant Pressure: $\Delta H = nC_{P,m}\Delta T$
- $$\Delta S = \int_{T_1}^{T_2} \frac{dq_{rev}}{T} = \int_{T_1}^{T_2} \frac{nC_{P,m}dT}{T} = nC_{P,m}\int_{T_1}^{T_2} \frac{dT}{T} = nC_{P,m}\ln\left(\frac{T_2}{T_1}\right)$$

- Constant Volume: $dq_V = dU = nC_{V,m}dT$

$$\Delta S = \int_{T_1}^{T_2} \frac{dq_{rev}}{T} = \int_{T_1}^{T_2} \frac{nC_{V,m}dT}{T} = nC_{V,m}\int_{T_1}^{T_2} \frac{dT}{T} = nC_{V,m}\ln\left(\frac{T_2}{T_1}\right)$$

- Calculate the entropy change when 18 grams of water are heated from 300K to 350Kat constant pressure. Assume $\overline{C}_P = 75.30J/mole \cdot K$.

Solution: $$\Delta S = nC_{P,m}\ln\left(\frac{T_2}{T_1}\right) = (18g)\left(\frac{1mole}{18g}\right)(75.30J/mole \cdot K)\ln\left(\frac{350K}{300K}\right)$$
$$= (75.30J/K)\ln(1.17) = 11.82J/K$$

Example 4; Calculation of Entropy Changes for the System, Surroundings, and Universe

An insulated water bath maintained at 273K contains 20 grams of ice. The pressure is constant at 1 atm. A piece of nickel weighing 73 g at a temperature of 373K is dropped into a very large ice-water bath. The temperature of the bath does not change, but when the nickel cools to 273K, 10 grams of ice have melted. Calculate the entropy change of the nickel, the entropy change of the bath+ice (i.e. surroundings) and the entropy change of the universe. For nickel $\overline{C}_P = 0.46J/g \cdot K$, for ice $\overline{C}_P = 2.09J/g \cdot K$, and for ice $\Delta H_{fusion} = 334Jg^{-1}$.

Solution:

- First calculate entropy change in lowering the temperature of 73g of nickel from 373K to 273K at constant pressure.

$$\Delta S = gC_{P,g}\ln\left(\frac{T_2}{T_1}\right) = (73g)(0.46JK^{-1}g^{-1})\ln\left(\frac{273}{373}\right) = -10JK^{-1}$$

- Now calculate the entropy change of the surroundings=ice+bath. This is the entropy change for melting 10g of ice…

$$\Delta S_{bath+ice} = (10g)\frac{\Delta H_{fusion}}{T_{fusion}} = (10g)\frac{334Jg^{-1}}{273K} = 12JK^{-1}$$

- The entropy change for the universe is the sum of the entropy change for the nickel (i.e. the system) and the entropy change for the bath+ice (i.e. the surroundings)
$$\Delta S_{universe} = \Delta S_{Ni} + \Delta S_{bath+ice} = (-10+12)J/K = 2J/K$$

  - Note the entropy change for the system is negative, but no Second law violation results because the overall entropy change of the universe is positive.