

# Physical Chemistry Crib Sheet

## The First Law of Thermodynamics

The First Law may be written:

$$\Delta U = q + w$$

where  $\Delta U$  is the change in internal energy of the system,  $q$  is the heat *given to* the system, and  $w$  is the work *done on* the system. We adopt the convention that quantities with primes refer to the *surroundings*, so that, for example,  $q' = -q$  is the heat given to the surroundings (lost by the system).

## Expansion work

The work done in expansion by a volume  $dV$  against an external pressure  $p_{\text{ex}}$  is given by

$$dw = -p_{\text{ex}}dV$$

For *irreversible* expansion,  $p_{\text{ex}}$  is constant (as when a gas expands into the atmosphere) and by integration,

$$w = -p_{\text{ex}}\Delta V$$

In particular, when the system expands into a vacuum,  $w = 0$ .

For *reversible* expansion, the external pressure is controlled to be only infinitesimally smaller than the pressure of the system. For an ideal gas ( $pV = nRT$ ), work done as the system expands from volume  $V_i$  to  $V_f$  is:

$$w = -nRT \ln \left( \frac{V_f}{V_i} \right)$$

## Heating at constant volume

At constant volume,  $dV = 0$  and the First Law gives:

$$\Delta U = q_V$$

The *heat capacity at constant volume* is defined by:

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V \quad \text{so } dU = C_V dT$$

## Heating at constant pressure

The *enthalpy*,  $H$ , is defined by:

$$H = U + pV$$

so that the enthalpy change is equal to the heat transferred at constant pressure:

$$\Delta H = q_p$$

For an ideal gas, since  $pV = nRT$ , and gases have a much larger volume than solids and liquids,

$$\Delta H = \Delta U + \Delta n_g RT$$

Where  $\Delta n_g$  is the change in amount (number of moles) of gas in the process. The *heat capacity at constant pressure* is defined by:

$$\boxed{C_p = \left(\frac{\partial H}{\partial T}\right)_p} \quad \text{so } dH = C_p dT$$

For an ideal gas, it can be shown that:

$$C_p - C_V = nR$$

### Reaction enthalpies

From Hess's law (since  $H$  is a *state function*), any reaction enthalpy change,  $\Delta_r H^\ominus$ , may be expressed in terms of the enthalpies of formation of the products and reactants,  $\Delta_f H^\ominus$ :

$$\Delta_r H^\ominus = \sum_{\text{products}} \nu \Delta_f H^\ominus - \sum_{\text{reactants}} \nu \Delta_f H^\ominus$$

where  $\nu$  are the stoichiometric coefficients.

The temperature dependence of the enthalpy of reaction is given by *Kirchoff's Law*:

$$\Delta_r H^\ominus(T_2) = \Delta_r H^\ominus(T_1) + \int_{T_1}^{T_2} \Delta_r C_p^\ominus dT$$

where

$$\Delta_r C_p^\ominus = \sum_{\text{products}} \nu C_p^\ominus - \sum_{\text{reactants}} \nu C_p^\ominus$$

### Entropy and The Second Law

The entropy of the universe never decreases in the course of all observed changes:

$$\boxed{\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \geq 0}$$

A thermodynamic definition of entropy in terms of the heat given reversibly to the system:

$$\boxed{dS = \frac{dq_{\text{rev}}}{T}}$$

The entropy change of a transition (*e.g.* vaporisation) at the transition temperature is:

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

since the transition is an isothermal reversible process.

The entropy change associated with the isothermal expansion of an ideal gas can be shown to be:

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

The variation of entropy with temperature at constant pressure is:

$$\Delta S = \int_{T_i}^{T_f} \frac{C_p}{T} dT$$

a similar equation holding at constant volume (replace  $C_p$  with  $C_V$ ).

### The Third Law of Thermodynamics

The *Nernst heat theorem*:  $\Delta S \rightarrow 0$  as  $T \rightarrow 0$ .

The *Third Law Entropy* is the entropy based on the convention that  $S(0) = 0$ . Calculations based on third law entropies fail to agree with measured entropies if there is some disorder in the substance at 0 K (*residual entropy*), so that  $S(0) > 0$ .

As  $S$  is a state function, the Third Law allows  $\Delta_r S_m^\ominus$  for a reaction may be calculated from tables of standard molar entropies:

$$\Delta_r S_m^\ominus = \sum_{\text{products}} \nu S_m^\ominus - \sum_{\text{reactants}} \nu S_m^\ominus$$

### The Gibbs and Helmholtz Free Energies

The Helmholtz Free Energy,

$$A = U - TS$$

and the Gibbs Free Energy,

$$\boxed{G = H - TS}$$

are useful because they provide a signpost indicating the direction of spontaneous change in terms of state functions of the *system* only:

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

In particular, they define a condition for equilibrium at constant temperature and volume ( $dA_{T,V} = 0$ ) and constant temperature and pressure ( $dG_{p,T} = 0$ ). Changes in the Helmholtz and Gibbs free energies in a process are equal to the maximum work and the maximum non-expansion work respectively that a system can do:

$$\Delta A = w_{\max} \quad \Delta G = w_{\text{other},\max}$$

As state functions, the changes in Gibbs and Helmholtz free energies can be calculated for (isothermal) processes by:

$$\Delta_r A^\ominus = \Delta_r U^\ominus - T \Delta_r S^\ominus$$

$$\boxed{\Delta_r G^\ominus = \Delta_r H^\ominus - T \Delta_r S^\ominus}$$

A general change in Gibbs free energy (for a pure substance) may be written:

$$\boxed{dG = V dp - S dT}$$

so that

$$\left(\frac{\partial G}{\partial p}\right)_T = V \quad \left(\frac{\partial G}{\partial T}\right)_p = -S$$

The pressure dependence of  $G$  for a perfect gas may be derived as:

$$G(p_f) = G(p_i) = nRT \ln \left( \frac{p_f}{p_i} \right)$$

The temperature-dependence of  $G$ , and hence for  $\Delta G$ , is given by the *Gibbs-Helmholtz equation*:

$$\left( \frac{\partial(\Delta G/T)}{\partial T} \right)_p = -\frac{\Delta H}{T^2}$$

### Chemical Potential and Phase Changes

The chemical potential of a substance,  $i$ , in a system is defined by:

$$\mu_i = \left( \frac{\partial G}{\partial n_i} \right)_{p,T,n_{j \neq i}}$$

where the subscript indicates that pressure, temperature, and the amounts of all other substances present are treated as constant. In words,  $\mu_i$  is the change in Gibbs free energy (at constant  $p, T$ ) when one mole of substance  $i$  is added to such a large mixture that the concentrations of the other substances are unaffected.

The chemical potential provides the driving force towards chemical equilibrium, when  $\mu$  is the same for all species present.

For a pure substance,  $\mu = G_m$ , the molar Gibbs free energy, and hence for an ideal gas:

$$\mu = \mu^\ominus + RT \ln \frac{p}{p^\ominus}$$

where  $\mu^\ominus$  is the *standard chemical potential*, that of the pure gas at  $p^\ominus = 1$  bar. A *phase diagram* is a plot of the phase boundaries (where  $\mu_\alpha = \mu_\beta$  for phases  $\alpha$  and  $\beta$  in equilibrium) as they vary with  $p$  and  $T$ . The slope of these boundaries is given by the *Clapeyron equation*:

$$\frac{dp}{dT} = \frac{\Delta_{\text{trs}} S_m}{\Delta_{\text{trs}} V_m}$$

The *Clausius-Clapeyron equation* gives the temperature dependence of the vapour pressure of a substance:

$$\frac{d \ln p}{dT} = \frac{\Delta_{\text{vap}} H}{RT^2}$$

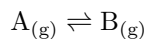
When  $p = p_{\text{ex}}$  (e.g. the surrounding atmospheric pressure), the substance is at its boiling point.

### Equilibrium

In general, the Gibbs free energy is a function of pressure, temperature, and the amounts of all substances present:

$$dG = Vdp - SdT + \mu_A dn_A + \mu_B dn_B + \dots$$

Considering the simplest possible chemical process:



The *extent of reaction*,  $\xi$ , may be defined as a differential in terms of infinitesimal changes in the amounts of reactant or product:

$$d\xi = dn_B = -dn_A$$

Therefore, at constant pressure and temperature, the reaction Gibbs free energy is defined as the slope of  $G$  plotted against  $\xi$ :

$$\Delta_r G = \left( \frac{\partial G}{\partial \xi} \right)_{p,T}$$

Relating  $\Delta_r G$  to the chemical potentials of A and B:

$$\Delta_r G = \mu_B - \mu_A, \quad \text{so at equilibrium } \Delta_r G = 0$$

and from the pressure-dependence of  $\mu$ :

$$\begin{aligned} 0 &= \mu_B^\ominus - RT \ln \left( \frac{p_B}{p^\ominus} \right) - \mu_A^\ominus + RT \ln \left( \frac{p_A}{p^\ominus} \right) \\ \mu_B^\ominus - \mu_A^\ominus &= RT \ln \left( \frac{p_A}{p_B} \right) \quad \text{at equilibrium.} \end{aligned}$$

Therefore, in terms of the equilibrium constant,  $K = p_B/p_A$ :

$$\Delta_r G^\ominus = -RT \ln K$$

This derivation generalises for reactions involving more than two species. If a species is in solution, replace  $p_i/p^\ominus$  with the *activity*,  $a_i$ .

$K$  is unaffected by changes in pressure (although, of course, the equilibrium *composition*) may change.

The *van't Hoff equation* relates the effect of temperature on  $K$ :

$$\frac{d \ln K}{dT} = \frac{\Delta_r H^\ominus}{RT^2}$$

$$\Rightarrow \ln K_2 - \ln K_1 = -\frac{\Delta_r H^\ominus}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$