Experimental Determination of Reaction Rate Constants and Enthalpies of Reaction

Computer Project

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I. Introduction

In this project, we investigate how reaction rate constants, activation energies, and enthalpies of reaction are obtained from experimental data. We derive the mass and energy balance equations on which we will perform the regression. We show how the reaction rate constants, activation energies, and enthalpies of reaction are fitted from the equations.

This project requires the ability to

- perform linear least squares regression and
- perform numerical integration of data.

II. Objective:

The objective of this project is to obtain the reaction rate constant, energy of activation, and heat of reaction for the homogeneous liquid-phase reaction

$$\upsilon_A A + \upsilon_B B \rightarrow \upsilon_C C + \upsilon_D D \tag{A.1}$$

given typical experimental data, namely (i) concentration of one species as a function of time and temperature and (ii) the inlet and outlet temperatures of the reactor coolant fluid.

III. Project Description

In order to determine the reaction rate constant, energy of activation, and heat of reaction for the homogeneous liquid-phase reaction, we choose the simplest reactor system possible. The values we obtain for the reaction parameters from this simple system will hold for more complicated systems. Therefore we choose to obtain the reaction rate constant, energy of activation, and heat of reaction for the homogeneous liquid-phase reaction

$$\upsilon_A A + \upsilon_B B \rightarrow \upsilon_C C + \upsilon_D D \tag{A.1}$$

taking place in an isothermal, jacketed, batch reactor. The rate of reaction, $r(t)$, is of the form:

$$r(t) = A^{|\upsilon_A|} B^{|\upsilon_B|} k_o e^{\frac{-E_a}{RT}} \tag{A.2}$$

where A is the concentration of species A in moles/liter, B is the concentration of species B in moles/liter, k_o is the reaction rate prefactor constant, E_a is the activation energy, R is the gas constant, 8.314 J/mol/K, and T is the temperature in K.

The rate of production or consumption of an individual species is, for example for species A,

$$\frac{dA}{dt} = \upsilon_A r(t) = \upsilon_A A^{|\upsilon_A|} B^{|\upsilon_B|} k_o e^{\frac{-E_a}{RT}} \tag{A.3}$$

where the stoichiometric coefficient, υ_A, is negative for reactants and positive for products. The units of equation (A.3) are moles/liter/time. We can write equation (A.3) for all components of interest. The rate of heat production/consumption is given by

$$\frac{dH}{dt} = -\Delta H_r A^{|\upsilon_A|} B^{|\upsilon_B|} k_o e^{\frac{-E_a}{RT}} \tag{A.4}$$

where ΔH_r is the heat of reaction. An exothermic reaction has a negative ΔH_r so we include a negative sign in (A.4) to ensure that an exothermic reaction generates heat, a positive $\frac{dH}{dt}$.

Therefore, we need to determine 3 constants:

- k_o, the reaction rate constant prefactor (units of $\left(\frac{mol}{\ell}\right)^{1-|\upsilon_A|-|\upsilon_B|} s^{-1}$)
- E_a, the activation energy (units of J/mol), and
- ΔH_r, the heat of reaction, (units of J/mol), and

The physical meaning of E_a and ΔH_r are shown in Figure One.

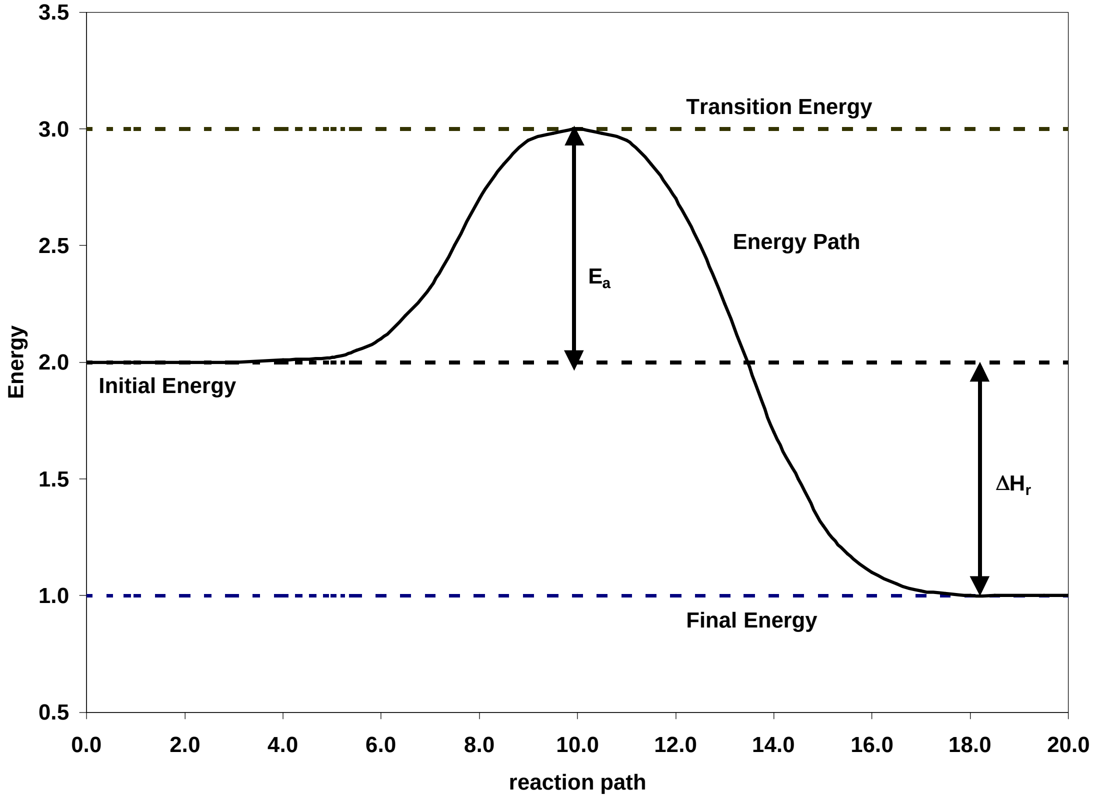

Figure One. The Reaction Path

IV. Experimental Method

We cannot directly measure the rate of the reaction. We can only sample the concentration and temperature in the reactor as a function of time. We measure the concentration by taking a small sample at each sample time and submitting it to some sort of analysis to determine the composition of the fluid. The analysis can be as simple as a refractive index or as complicated as a liquid chromatography or mass spectrometry analysis.

The reactor has a jacket around it through which coolant fluid flows to maintain a constant temperature within the reactor. In the experiment we keep the flow-rate of coolant constant. We also keep the inlet coolant temperature, T_{in}, constant. The other property we can directly measure is the outlet temperature of the coolant fluid, T_{out}. The amount of heat removed by the coolant fluid is determined by examining the difference in temperature of the coolant fluid used to keep the reactor isothermal. If we write a simple energy balance on the coolant fluid we have

$$\text{accumulation} = \text{in} - \text{out} + \text{generation}$$

$$V_j \frac{d\left(\rho C_p \left(T_{jacket} - T_{ref}\right)\right)}{dt} = F_{X,in}\rho C_p \left(T_{in} - T_{ref}\right) - F_{X,out}\rho C_p \left(T_{out} - T_{ref}\right) + \text{generation} \quad \text{(A.5)}$$

Each term in this equation has units of energy per time. Whatever coolant flows in must flow out so $F_{X,in} = F_{X,out} = F_X$. The generation term is heat transferred to the coolant fluid from the reactor and is equal to the heat generated by the reaction.

This entire procedure is repeated for several different reactor temperatures.

V. Obtaining k_o and E_a

Since Equation (A.3) is in terms of the rate of disappearance of species A, rather than the concentration of A itself, we must integrate equation (A.3) into a form where we can obtain the rate constants from the experimental data. First, let us show that we can write all of the other concentration as a function of the concentration of species A.

$$\frac{dB}{dt} = \upsilon_B r(t) = \upsilon_B A^{|\upsilon_A|} B^{|\upsilon_B|} k_o e^{\frac{-E_a}{RT}} = \frac{\upsilon_B}{\upsilon_A} \frac{dA}{dt} \quad \text{(A.6)}$$

Integrating, we obtain:

$$\int_{B(t_o)}^{B(t)} dB = \frac{\upsilon_B}{\upsilon_A} \int_{A(t_o)}^{A(t)} dA \quad \text{(A.7)}$$

$$B(t) - B(t_o) = \frac{\upsilon_B}{\upsilon_A}\left[A(t) - A(t_o)\right] \quad \text{(A.8)}$$

$$B(t) = B(t_o) + \frac{\upsilon_B}{\upsilon_A}\left[A(t) - A(t_o)\right] \quad \text{(A.9)}$$

We substitute equation (A.9) into equation (A.3)

$$\frac{dA}{dt} = \upsilon_A A^{|\upsilon_A|}\left\{B(t_o) + \frac{\upsilon_B}{\upsilon_A}\left[A(t) - A(t_o)\right]\right\}^{|\upsilon_B|} k_o e^{\frac{-E_a}{RT}} \quad \text{(A.10)}$$

Now equation (A.10) is only a function of the concentration of species A. We rearrange equation (A.10)

$$\frac{dA}{\upsilon_A A^{|\upsilon_A|}\left\{B(t_o) + \frac{\upsilon_B}{\upsilon_A}\left[A(t) - A(t_o)\right]\right\}^{|\upsilon_B|}} = k_o e^{\frac{-E_a}{RT}} dt \quad \text{(A.11)}$$

and integrate

$$\int_{A(t_o)}^{A(t)} \frac{dA}{\upsilon_A A^{|\upsilon_A|}\left\{B(t_o) + \frac{\upsilon_B}{\upsilon_A}\left[A(t) - A(t_o)\right]\right\}^{|\upsilon_B|}} = \int_{t_o}^{t} k_o e^{\frac{-E_a}{RT}} dt \quad \text{(A.12)}$$

The integral on the right hand side of equation (A.12) is

$$\int_{t_o}^{t} k_o \exp^{\frac{-E_a}{RT}} dt = k_o e^{\frac{-E_a}{RT}}\left(t - t_o\right) \quad \text{(A.13)}$$

The integral on the left hand side is somewhat trickier. Let's massage it into shape. Let $a = \frac{\upsilon_B}{\upsilon_A}$, $b = B(t_o) - \frac{\upsilon_B}{\upsilon_A}A(t_o)$, $n = |\upsilon_A|$, $m = |\upsilon_B|$, $x = A$. With these substitutions we have

$$\int_{A(t_o)}^{A(t)} \frac{dA}{\upsilon_A A^{|\upsilon_A|}\left\{B(t_o) + \frac{\upsilon_B}{\upsilon_A}\left[A(t) - A(t_o)\right]\right\}^{|\upsilon_B|}} = -\frac{1}{n}\int_{x_o}^{x} \frac{dx}{x^n (ax + b)^m} = I_{n,m}(A) - I_{n,m}(A_o) \quad \text{(A.14)}$$

where

$$I_{n,m} = -\frac{1}{n}\int_{x_o}^{x}\frac{dx}{x^n(ax+b)^m} \tag{A.15}$$

Regardless of the particular form of the left-hand-side integral, the analytical function can be obtained. Check the Appendix for some examples of the analytical evaluation of this integral for realistic values of n and m.

After the integration, equation (A.12) becomes

$$I_{n,m}(A) - I_{n,m}(A_o) = k_o e^{\frac{-E_a}{RT}}(t - t_o) \tag{A.16}$$

We linearize this so that we can perform a linear least squares regression to obtain k_o and E_a:

$$\ln\left[I_{n,m}(A) - I_{n,m}(A_o)\right] = \ln\left[k_o e^{\frac{-E_a}{RT}}(t - t_o)\right] \tag{A.17}$$

$$\ln\left[I_{n,m}(A) - I_{n,m}(A_o)\right] = \ln[k_o] + \ln\left[e^{\frac{-E_a}{RT}}\right] + \ln[t - t_o] \tag{A.18}$$

$$\ln\left[I_{n,m}(A) - I_{n,m}(A_o)\right] = \ln[k_o] + \frac{-E_a}{RT} + \ln[t - t_o] \tag{A.19}$$

$$\ln\left[\frac{I_{n,m}(A) - I_{n,m}(A_o)}{t - t_o}\right] = \ln[k_o] + \frac{-E_a}{RT} \tag{A.20}$$

Let $y = \ln\left[\frac{I_{n,m}(A) - I_{n,m}(A_o)}{t - t_o}\right]$, $x = -\frac{1}{RT}$, $m = E_a$, $b = \ln[k_o]$. With these substitutions, we see that our equation is in the form

$$y = mx + b \tag{A.21}$$

We can perform a linear least-squares regression to obtain the parameters of best fit for the slope and the intercept. From these we can obtain k_o and E_a.

VI. Obtaining ΔH_r

We start with equation (A.5). We assume that the density and heat capacity of the coolant fluid are constant with respect to temperature. We take the thermodynamic reference temperature to be 0 K. We equate the generation term in equation (A.5) to the heat generated by the reaction in equation (A.4). With these assumptions, we have

$$V_j\rho C_p \frac{dT_{jacket}}{dt} = F_X\rho C_p T_{in} - F_X\rho C_p T_{out} - V_r\Delta H_r A^{|\upsilon_A|}B^{|\upsilon_B|}k_o e^{\frac{-E_a}{RT}} \qquad \text{(A.22)}$$

The unknowns in this equation are ΔH_r and T_{jacket}, the temperature of the coolant in the jacket. If we assume that the jacket temperature is spatially uniform and heat transfer from the reactor is much faster than the residence time of the coolant in the jacket, then we have $T_{jacket} = T_{out}$, which we measured. (Remember, we measured the outlet temperature of the coolant. Of course, we also assume we measured the inlet temperature of the coolant which remains constant during the experiment.) We have two different volumes, the volume of the jacket, V_j, and the volume of the reactor, V_r.

$$\frac{dT_{out}}{dt} = \frac{F_X}{V_j}T_{in} - \frac{F_X}{V_j}T_{out} - \frac{V_r}{V_j}\frac{\Delta H_r A^{|\upsilon_A|}B^{|\upsilon_B|}k_o e^{\frac{-E_a}{RT}}}{\rho C_p} \qquad \text{(A.23)}$$

$$\frac{F_X}{V_j}T_{out} + \frac{dT_{out}}{dt} = \frac{F_X}{V_j}T_{in} - \frac{V_r}{V_j}\frac{\Delta H_r A^{|\upsilon_A|}B^{|\upsilon_B|}k_o e^{\frac{-E_a}{RT}}}{\rho C_p} \qquad \text{(A.24)}$$

Use the method of the integrating factor:

$$e^{\frac{F_X}{V_j}t}\left(\frac{F_X}{V_j}T_{out} + \frac{dT_{out}}{dt}\right) = e^{\frac{F_X}{V_j}t}\left[\frac{F_X}{V_j}T_{in} - \frac{V_r}{V_j}\frac{\Delta H_r A^{|\upsilon_A|}B^{|\upsilon_B|}k_o e^{\frac{-E_a}{RT}}}{\rho C_p}\right] \qquad \text{(A.25)}$$

$$\frac{d\left(e^{\frac{F_X}{V_j}t}T_{out}\right)}{dt} = e^{\frac{F_X}{V_j}t}\left[\frac{F_X}{V_j}T_{in} - \frac{V_r}{V_j}\frac{\Delta H_r A^{|\upsilon_A|}B^{|\upsilon_B|}k_o \exp^{\frac{-E_a}{RT}}}{\rho C_p}\right] \qquad \text{(A.26)}$$

$$\int_{t_o}^{t} d\left(e^{\frac{F_X}{V_j}t}T_{out}\right) = \int_{t_o}^{t} e^{\frac{F_X}{V_j}t}\left[\frac{F_X}{V_j}T_{in} - \frac{V_r}{V_j}\frac{\Delta H_r A^{|\upsilon_A|}B^{|\upsilon_B|}k_o \exp^{\frac{-E_a}{RT}}}{\rho C_p}\right]dt \qquad \text{(A.27)}$$

$$e^{\frac{F_X}{V_j}t}T_{out}(t) - e^{\frac{F_X}{V_j}t_o}T_{out}(t_o) = \frac{F_X}{V_j}\int_{t_o}^{t} e^{\frac{F_X}{V_j}t}T_{in}dt - \int_{t_o}^{t} e^{\frac{F_X}{V_j}t}\frac{V_r}{V_j}\frac{\Delta H_r A^{|\upsilon_A|}B^{|\upsilon_B|}k_o \exp^{\frac{-E_a}{RT}}}{\rho C_p}dt \qquad \text{(A.28)}$$

$$T_{out}(t) = e^{-\frac{F_X}{V_j}(t-t_o)} T_{out}(t_o) + T_{in}\left(1 - e^{-\frac{F_X}{V_j}(t-t_o)}\right) - e^{-\frac{F_X}{V_j}t} \int_{t_o}^{t} e^{\frac{F_X}{V_j}t} \frac{V_r}{V_j} \frac{\Delta H_r A^{|\upsilon_A|} B^{|\upsilon_B|} k_o \exp^{\frac{-E_a}{RT}}}{\rho C_p} dt \tag{A.29}$$

$$T_{out}(t) = e^{-\frac{F_X}{V_j}(t-t_o)} T_{out}(t_o) + T_{in}\left(1 - e^{-\frac{F_X}{V_j}(t-t_o)}\right) - \Delta H_r e^{-\frac{F_X}{V_j}t} \frac{V_r}{V_j} \frac{k_o \exp^{\frac{-E_a}{RT}}}{\rho C_p} \int_{t_o}^{t} e^{\frac{F_X}{V_j}t} A^{|\upsilon_A|} B^{|\upsilon_B|} dt \tag{A.30}$$

The remaining integral probably is not analytically integrable. Let's rewrite this as

$$T_{out}(t) = e^{-\frac{F_X}{V}(t-t_o)} T_{out}(t_o) + T_{in}\left(1 - e^{-\frac{F_X}{V_j}(t-t_o)}\right) + \Delta H_r f(t,T) \tag{A.31}$$

We can determine $f(t,T)$ for each data point using a numerical integration technique, where

$$f(t,T) = -e^{-\frac{F_X}{V_j}t} \frac{V_r}{V_j} \frac{k_o \exp^{\frac{-E_a}{RT}}}{\rho C_p} \int_{t_o}^{t} e^{\frac{F_X}{V_j}t} A^{|\upsilon_A|} B^{|\upsilon_B|} dt \tag{A.32}$$

This numerical integration must be done for every data point.

If we assign the substitutions $y = T_{out}(t) - e^{-\frac{F_X}{V_j}(t-t_o)} T_{out}(t_o) - T_{in}\left(1 - e^{-\frac{F_X}{V_j}(t-t_o)}\right)$, $x = f(t,T)$, $m = \Delta H_r$, $b = 0$, our equation is in the form

$$y = mx + b \tag{A.33}$$

We can perform a linear least-squares regression to obtain the parameters of best fit for the slope and the intercept. From these we can obtain ΔH_r.

VII. Report Requirements

This project requires a written report. In this report, you must present a description of what you have done so that a chemical engineer studying the system after you can easily determine what you were studying, what your results were, how you obtained those results, what assumptions you made in obtaining those results, and what conclusions you made based upon those results.

To write a technical report takes practice. I suggest that you follow the instructions given in "Writing Guidelines for ChE 310 & 410" by Dr. Fred E. Weber & Dr. Duane D. Bruns, a copy of which can be found on the course website at http://clausius.engr.utk.edu/che301/text/cp.html .

In presenting technical information, you will need to reply on plots and other graphical aids. These plots should present your results as clearly and objectively as possible. Guidelines for technical plots can be found at "Plot Formatting Guidelines for Research Reports" by Dr. David Keffer, a copy of which can be found on the course website at http://clausius.engr.utk.edu/che301/text/cp.html .

A collection of computer codes, print-outs, and hand-written notes is totally unacceptable and will not be accepted.

There are a few mandatory elements of the report:

- values of k_o, E_a, and ΔH_r obtained from linear least-squares regression
- the standard deviations for k_o, E_a, and ΔH_r
- expressions of the two equations upon which linear least-squares regression was performed
- the form of the integrand which you numerically integrated
- a few sample values of the numerical integration

Do **not** include in the report:

- pages and pages of program output, (not even 1 page)
- MATLAB code, unless you made significant changes worth pointing out. In that case, include your code as an appendix.

VIII. Experimental Specifications

The experimental data can be obtained from the course website once you have obtained your team identification number from the instructor. This data is unique to your team.

Other parameters are common to all teams. Use the following values in your evaluation of the reaction rate parameters. The coolant fluid is water.

- coolant heat capacity: $C_p = 4.184 \frac{J}{g \cdot K} = 4184 \frac{J}{kg \cdot K}$
- coolant flow rate: $F_X = 0.5 \frac{\ell}{s}$
- coolant inlet temperature: $T_{in} = 50^\circ F = 10^\circ C$
- jacket volume: $V_j = 100.0 \ell$
- reactor volume: $V_r = 100.0 \ell$
- coolant density: $\rho = 1.0 \frac{g}{cm^3}$

We have the following initial conditions at time $t_o = 0$

- concentration of A in reactor: $A(t_o) = 2.0 \frac{mol}{\ell}$
- concentration of B in reactor: $B(t_o) = 2.5 \frac{mol}{\ell}$
- outlet temperature of coolant: $T_{out}(t_o) = T_{in}$

IX. Nomenclature and Units

A	concentration of component A	mol/liter
B	concentration of component B	mol/liter
C	concentration of component C	mol/liter
C_p	coolant heat capacity	J/kg/K
D	concentration of component D	mol/liter
E_a	activation energy	J/mol
F_X	flowrate of coolant	liter/sec
$F_{X,in}$	inlet flowrate of coolant	liter/sec
$F_{X,out}$	outlet flowrate of coolant	liter/sec
k_o	reaction rate prefactor constant	$\left(\frac{\mathrm{mol}}{\ell}\right)^{1-\lvert\upsilon_A\rvert-\lvert\upsilon_B\rvert}\mathrm{s}^{-1}$
r	reaction rate	mol/liter/sec
R	gas constant	J/mol/K
t	time	sec
T	reactor temperature	K
T_{in}	inlet coolant temperature	K
T_{jacket}	coolant temperature while in jacket	K
T_{out}	outlet coolant temperature	K
T_{ref}	thermodynamic reference temperature	K
V_j	jacket volume	liters
V_r	reactor volume	liters
ΔH_r	heat of reaction	J/mol
υ_i	stoichiometric coefficient of species i	dimensionless
ρ	coolant density	kg/liter

X. References

1. Keffer, D., Course Lecture Notes, ChE 301, 1998, University of Tennessee, Department of Chemical Engineering, http://clausius.engr.utk.edu/che301

2. Weber, F., Bruns, D., “Writing Guidelines for ChE 310 & 410”, University of Tennessee, Department of Chemical Engineering, http://clausius.engr.utk.edu/che301/text/cp.html

3. Keffer, D., "Plot Formatting Guidelines for Research Reports", University of Tennessee, Department of Chemical Engineering, http://clausius.engr.utk.edu/che301/text/cp.html

4. Spiegel, M.R., “Mathematical handbook of Formulas and Tables”, McGraw Hill, Inc. New York, 1992, pp. 60-61.

Appendix I. Table of Relevant Integrals

Examples of analytical evaluations of integrals of the form: $\int \frac{dx}{x^n(ax+b)^m}$. These can be evaluated using the technique of partial fraction expansions.

n=1, m=1
$$\int \frac{dx}{x^n(ax+b)^m} = \frac{1}{b}\ln\left(\frac{x}{ax+b}\right) \tag{I.1}$$

n=2, m=1
$$\int \frac{dx}{x^n(ax+b)^m} = -\frac{1}{bx} + \frac{a}{b^2}\ln\left(\frac{ax+b}{x}\right) \tag{I.2}$$

n=3, m=1
$$\int \frac{dx}{x^n(ax+b)^m} = \frac{2ax-b}{2b^2x^2} + \frac{a^2}{b^3}\ln\left(\frac{x}{ax+b}\right) \tag{I.3}$$

n=1, m=2
$$\int \frac{dx}{x^n(ax+b)^m} = \frac{1}{b(ax+b)} + \frac{1}{b^2}\ln\left(\frac{x}{ax+b}\right) \tag{I.4}$$

n=2, m=2
$$\int \frac{dx}{x^n(ax+b)^m} = \frac{-a}{b^2(ax+b)} + -\frac{1}{b^2x} + \frac{2a}{b^3}\ln\left(\frac{ax+b}{x}\right) \tag{I.5}$$

n=3, m=1
$$\int \frac{dx}{x^n(ax+b)^m} = -\frac{(ax+b)^2}{2b^4x^2} + \frac{3a(ax+b)}{b^4x} - \frac{a^3x}{b^4(ax+b)} - \frac{3a^2}{b^4}\ln\left(\frac{ax+b}{x}\right) \tag{I.6}$$

n=1, m=3
$$\int \frac{dx}{x^n(ax+b)^m} = \frac{a^2x^2}{2b^3(ax+b)^2} - \frac{2ax}{b^3(ax+b)} - \frac{1}{b^3}\ln\left(\frac{ax+b}{x}\right) \tag{I.7}$$

n=2, m=3
$$\int \frac{dx}{x^n(ax+b)^m} = \frac{-a}{2b^2(ax+b)^2} - \frac{2a}{b^3(ax+b)} - \frac{1}{b^3x} + \frac{3a}{b^4}\ln\left(\frac{ax+b}{x}\right) \tag{I.8}$$

n=3, m=3
$$\int \frac{dx}{x^n(ax+b)^m} = \frac{a^4x^2}{2b^5(ax+b)^2} - \frac{4a^3x}{b^5(ax+b)} - \frac{(ax+b)^2}{2b^5x^2} - \frac{6a^2}{b^5}\ln\left(\frac{ax+b}{x}\right) \tag{I.9}$$